

## A01.能量转换与存储材料

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### A01-01

#### LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> as cathode material for Li-ion Batteries

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Electrical vehicles represent one approach to reduce undesirable emissions from conventional internal combustion engines in heavily populated areas. Li-ion battery is becoming the key enabling technology for EVs. Presently, Li-ion batteries with LiMn<sub>2</sub>O<sub>4</sub>, NCM/NCA, LiFePO<sub>4</sub> as cathode active material are widely used in EVs. High-voltage spinel LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathode material has specific energy (~640 mAh/g due to the high operation voltage of ~4.7 V. The relatively inexpensive Ni and Mn in LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> make this cathode material particularly desirable for large-scale applications. A detailed investigations of its local atomic-level structure with lithium extraction/insertion is observed via an aberration-corrected scanning transmission electron microscopy (STEM). The surface regions (~ 2nm) show an irreversible migration of TM ions into lithium tetrahedral sites to form a Mn<sub>3</sub>O<sub>4</sub>-like structure. It contributes to the dissolution of TM ions as well as the rocksalt-like structures with heavy TM ions on the lithium pathways blocks the migration of lithium ions, resulting in building-up of charge transfer impedance and degradation of capacity. When the surface LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> was modified by Ti<sup>4+</sup> and Ta<sup>5+</sup> superficial doping, the cycling performance of the material at elevated temperatures has been much improved and the coulombic efficiency of discharge/charge is also obviously increased. Theoretical calculations analyses reveal that the stability of O at surface layer is enhanced by those surface modifications and detailed analyses will be reported.

### A01-02

#### 层状富锂锰基征集材料的研究进展

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### A01-03

#### Development of separators for high safety lithium-ion batteries

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The lithium-ion batteries (LIBs) are regarded as the one of the most competitive candidates of the power source for electric vehicles (EVs), but its safety performance should be greatly improved. As a safety device inside the cell, separator acts as a last line of defense to ensure the battery safety. However, the currently used polyolefin-based separator usually fails its function at elevated temperature due to its intrinsic low melting point. Coating with ceramic particles has been proved to be a practical approach to minimize the risk of thermal damage of polyolefin-based separators. Based on the study of the effect of the thickness and the morphology of the ceramic layer, we have further developed several functional ceramic-coated separators, including the core-shell structured functional ceramic coated separator, and a stereocomplex structured separator which can maintain its dimensional stability up to 230 °C. Another clue is to alter the substrates for the separator. We developed functional separator based on nonwoven. By coating PE particle layer onto the surface of the PI nonwoven fabric, a composite separator with shut-down function along with an excellent thermal stability was obtained. Through in situ polymerization, a modified core-shell structure greatly improves the thermal stability of PVDF-based nonwoven separator. The currently liquid electrolyte-based cell has an intrinsic safety risk. Adopting solid state electrolyte would essentially improve the safety performance. We developed a single lithium-ion conducting polymer electrolyte based on poly(hexafluoro butyl methacrylate-co-lithium allyl sulfonate). And further study on solid electrolyte is conducting. All these works will elaborate our understanding on the safety of LIBs in terms of the separator.

### A01-04

#### 三维多级孔金属集流体的储锂性能研究

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稳定高效的金属锂电极是发展可充放电金属锂电池的关键。充放电过程中锂枝晶和界面副反应是导致金属锂电池安全性差和库伦效率低的主要原因。本文采用 PS 微球为模板，在泡沫铜表面构筑具有微米和纳米尺寸的多级孔铜结构，应用于储存金属锂具有良好的性能。以预沉积锂的多级孔铜电极为负极，磷酸铁锂为正极，在 2C 倍率下循环 500 次，还保持 115 mAh g<sup>-1</sup> 的比容量（以磷酸铁锂质量计算），库伦效率保持在 99.7%。多级孔铜电极具有优异的储锂性能，原因在于其具有很高的比表面积、孔体积和均匀的多级 3 维互通的孔结构。

#### A01-05

##### **In situ formation of hierarchical electronic/ionic conducting shells for Silicon nanoparticles anode**

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Silicon (Si) based materials have been identified as the next-generation anodes to replace the low-capacity graphite anode. However, the commercial success of Si-based materials is hindered by the inert electronic conductivity and large volume changes during lithium insertion and extraction. We design a hierarchical electronic/ionic conducting shell structure by in-situ reaction of lithium source with Si nanoparticles.

Methods: A thin amorphous SiO<sub>2</sub> grows on the surface of Si nanoparticles. The as-treated Si nanoparticles were mixed with lithium source. The precursor was pressured under certain pressure to gain a pellet. Then, the pellet was placed in a closed steel container and heated in argon. After washed with deionized water and ethanol, the resultant hierarchical shells were built.

Results: The Si/LSO/C composite was synthesized simply by autoxidation and high temperature solid state reaction process. When exposed to air during storage, the native oxide layer grows uniformly on the Si surface. Many studies report that the oxide layer can be converted to a good mechanical properties lithium silicate, resulting in a stable SEI layer. Based on this consideration, we achieve the same conversion reaction by in situ solid state reaction process. The formation of the hierarchical shell structure was confirmed by TEM measurements. The fresh Si nanoparticles have an amorphous layer with a thickness of ~1 nm on the surface. After in-situ reaction, the hierarchical shell structure can be clearly observed on the surface of Si/LSO/C nanoparticles. The electrochemical performance of Si/SiO<sub>2</sub> electrodes show a capacity of 720 mAh g<sup>-1</sup> in the voltage range of 0.7-0.1 V, which is mainly caused by the decomposition of electrolyte and the reduction of SiO<sub>2</sub> layer. In contrast, the capacities for the Si/LSO, Si/LSO/C and fresh Si electrodes are 497.9, 416.0 and 151.4 mAh g<sup>-1</sup>, respectively. This result indicates much less irreversible reactions on the surface of fresh Si surface. The first irreversible capacity loss of fresh Si was mainly due to the pulverization of electrode structure. Hence, the highest initial CE of Si/LSO/C can be ascribed to the passive surface and stable structure.

Conclusion: The hierarchical structure shells were constructed successfully. The as-prepared Si-based composite delivered high reversible capacity, improved rate capacity and long-term cycling stability. Our work provides a new facile strategy to improve the electrochemical performance of commercial Si nanoparticles, which could be expanded for practical lithium ion battery applications.

#### A01-06

##### **片状氧化亚铜与石墨烯复合材料的制备及其在锂离子电池负极材料中的应用研究**

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#### A01-07

##### **Sulfide solid electrolytes based all-solid-state rechargeable batteries**

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The rapidly growing domination of lithium ion batteries in daily life has raised concerns regarding both safety and durability issues of state-of-the-art lithium ion batteries with liquid electrolytes. All-solid-state rechargeable batteries employing nonflammable inorganic solid electrolytes have been considered as the ultimate solution to combustion and leakage safety issues. Compared with

oxide electrolytes, sulfide electrolytes are considered to be promising ion conductors due to their high ionic conductivities and favorable interface compatibility with sulfide or sulfur-based electrodes. [1]

A series of sulfide solid electrolytes with room temperature ionic conductivity of  $10^{-3} \sim 10^{-2}$  S/cm are successfully synthesized, including lithium and sodium superionic conductors. The electrochemical stability and compatibility with lithium can be improved with oxide or halogen doping.[1] The effect of ionic conductivity as well as particle size of sulfide electrolytes on the electrochemical performances will be discussed. Meanwhile, a battery construction containing a solid electrolyte bilayer, *i.e.*  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  and 70% $\text{Li}_2\text{S}$ -29% $\text{P}_2\text{S}_5$ -1% $\text{P}_2\text{O}_5$ , have been designed, well addressing the compatibility between electrolyte and metallic lithium.[2]

Furthermore, different type transition metal sulfides or sulfur-based materials are employing as electrodes for all-solid-state rechargeable batteries.[3-5] The intimate contact interface can be realized by coating sulfide electrolytes evenly on the surface of active materials, which enables the battery to withstand the large stresses/strains during repeated charging/discharging, leading to significant improvements in energy density and cycle life.[4,5]

References:

- [1] S. J. Chen, D. J. Xie, G. Z. Liu et al., *Energy Storage Materials*, 2018, **14**: 58-74.
- [2] H. L. Wan, G. Peng, X. Y. Yao et al., *Energy Storage Materials*, 2016, **4**: 59-65.
- [3] X.Y. Yao, N. Huang, F. D. Han et al., *Adv Energy Mater* 2017, **7**, 1602923.
- [4] X. Y. Yao, D. Liu, C. S. Wang et al., *Nano Letters*, 2016, **16**: 7148-7154.
- [5] H. L. Wan, J. P. Mwizerwa, X. G. Qi et al., *ACS Nano*, 2018, **12**, 2809-2817.

#### A01-08

##### 基于“造孔工程”的层次孔碳材料及其在超级电容器中的应用

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为了增加碳材料中电解液可接触比表面积、改善电解液离子传输特性, 从而增强碳基超级电容器的超电容性能、提升倍率性能。基于 KOH 在高温下对碳材料的化学刻蚀作用, 在一定温度下对 PVDF、GO/PTFE 复合物进行活化处理, 获得具有超高比表面积、大孔容和层次孔结构(微-介-大孔)的碳材料。利用固-气界面控制的镁热还原反应, 在柔性基底上将温室气体  $\text{CO}_2$  转变为以微孔和介孔为主的层次孔管状纳米碳。进一步地, 结合镁热还原反应和模板法, 构筑了孔径分布于微孔、介孔和大孔的层次孔树莓状石墨烯超级粒子。采用原位合成技术, 简单、快速地实现了层次孔碳材料的高比例多重异质原子掺杂。

基于一步 KOH 化学刻蚀制备的层次孔碳所组装的超级电容器在 1 M  $\text{Na}_2\text{SO}_4$  电解液中, 获得最高 21.2 Wh  $\text{kg}^{-1}$  的能量密度和 16 kW  $\text{kg}^{-1}$  的功率密度。在高粘度、低离子电导率和大离子尺寸的 EMIMBF<sub>4</sub> 电解液中, 同时表现出 35 kW  $\text{kg}^{-1}$  的高功率密度和 51.7 Wh  $\text{kg}^{-1}$  的高能量密度, 且拥有了很好的循环稳定性。直接转化  $\text{CO}_2$  所获得的层次孔管状纳米碳呈现出优异的面电容, 达到 320 mF  $\text{cm}^{-2}$ , 并拥有优异的倍率性能。树莓状石墨烯超级粒子, 在电流密度增加 250 倍后, 依然能够实现 88.3% 的电容保持率。原位合成的氮、氯共掺杂碳化物衍生碳在 6 M KOH 电解液下, 获得了目前同类型材料最高的质量比电容值 (270 F  $\text{g}^{-1}$ )。直接热处理碱性生物质转化而来的氮、氧、硫三元异质原子共掺杂的层次孔碳, 在离子液体中表现出优异的比电容和倍率性能。

基于伏安分析法, 对表面电容效应的贡献和赝电容贡献进行了区分, 明确了异质原子掺杂对电容性能提升的机制。为可控设计具有优异超电容性能的层次孔碳材料打下了一定的理论基础。

参考文献:

- [1] Zhang Haitao, Yang Weiqing\*, et al. *Journal of Power Sources*, 2016, 315, 120-126.
- [2] Su Hai, Yang Weiqing\*, et al. *Chemical Engineering Journal*, 2017, 322, 73-81.
- [3] Zhang Haitao, Yang Weiqing\*, et al. *Journal of Power Sources*, 2016, 331, 332-339.

#### A01-09

##### 钠离子电池正负极材料的研究

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发展大规模储能的二次电池不仅需要具有适宜的电化学性能，更需考虑资源成本和环境效益等应用要求。而锂离子电池用于大规模储能可能受到锂资源的制约，因此，从资源与环境方面考虑，具有与锂离子电池相似电化学性能的钠离子电池体系作为储能电池更具应用优势。然而，从目前的技术现状来看，几类不同的嵌钠正负极材料虽显现出可观的容量与较好的循环性，但能量密度与功率密度尚待提高。过渡金属氧化物和氧基正极材料，以及硬碳和合金负极材料最有希望用于钠离子电池体系，但这类材料的初始充放电效率和循环稳定性仍有待改善。本报告简要分析嵌钠正负极材料的一些问题，讨论适合嵌钠反应的一些思路，并结合本课题组的研究工作讨论钠离子电池及其关键材料的发展方向。

#### A01-10

##### 固体氧化物电池燃料极的表面反应过程

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固体氧化物电池 (Solid Oxide Cells, SOCs) 是一种高效能量转化装置，能够以两种模式运行，一种是燃料电池模式，即固体氧化物燃料电池(SOFC)，直接将燃料气中的化学能转化为电能；另一种是电解模式，即固体氧化物电解池(SOEC)，利用太阳能、风能等清洁能源，将水和二氧化碳高温电解，产生一氧化碳和氢气。原理上，SOEC 与 SOFC 互为逆过程，两种模式都具有能量转换率高、环境友好、可使用含碳燃料等优点。在 SOFC 燃料极即阳极，燃料气与氧离子发生电化学氧化反应。当燃料是碳氢化合物如甲烷、乙醇等时，通常认为燃料分子先发生重整反应，内重整或外重整，生成 CO 和 H<sub>2</sub> 混合气，然后在燃料极发生电化学氧化反应。SOFC 的燃料多样性，主要依赖于电催化剂催化氧化 CO 和 H<sub>2</sub> 的活性。在 SOEC 燃料极即阴极，CO<sub>2</sub>/H<sub>2</sub>O 被还原成 CO/H<sub>2</sub>，该反应将温室气体转化为合成气，通过费托合成，能够进一步将合成气转化为碳氢化合物，便于储存和运输。但是，H<sub>2</sub>/H<sub>2</sub>O 和 CO/CO<sub>2</sub> 在燃料极表面/界面处的电化学氧化/还原反应的微观反应机制仍不明确。本工作主要研究 H<sub>2</sub>/H<sub>2</sub>O 和 CO/CO<sub>2</sub> 的电化学转化机制，主催化剂为氧化锆和氧化铈基金属陶瓷复合电极，主催化剂为 BaCO<sub>3</sub>。研究包括电化学阻抗、电化学弛豫和 DFT 计算。

#### A01-11

##### Study about supercapacitor based on printed electronic technology

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Printing electronic technology is a new type of flexible electronic device preparation technology based on the traditional printing technology, which dissolves the chemical reagents of various regulating substances to forms the specific functional ink for printing. This technology has many advantages over traditional electronic device fabricated on silicon substrates. The preparation is relatively simple and can be prepared in accordance with the designed pattern style. It can not only print the circuit pattern on the traditional hard, inflexible conductive substrate, but also print the circuit pattern on some flexible, flexible, portable and compact substrates, which can produce new electronic devices and provide more applications for advanced electronic technology. In addition, the process of making device does not require a complex process, which greatly reduces the cost and difficulty of making the device, and it is easier to process and manufacture. In the process of fabricating, no chemical etching, such as chemical etching, can be used to reduce the use of waste water and toxic chemical reagents. The pollution of the environment will be greatly reduced, and the purpose of realizing green production and protecting the environment can be achieved.

As a kind of energy storage devices with high power density, high efficiency, long life expectancy and environmental friendliness, supercapacitors have received considerable research attention for the past two decades. For the development of wearable devices, the functional unit of flexible energy storage devices has been given more and more attention nowadays. Herein, the design and fabrication of flexible supercapacitor devices by using printing electronic technology are present in this study. As one part of this work, mesoporous carbon materials were synthesized by soft template method. In this strategy, poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) block co-polymers (F127) were used as the template while fructose were employed as the carbon precursor. After hydrothermal treatment, the soft templates could be easily removed by pyrolysis of the as-prepared carbon materials in argon. The resultant mesoporous carbon materials exhibit a specific surface area of ~420 m<sup>2</sup>g<sup>-1</sup>. In addition, the as-prepared mesoporous carbon materials were incorporated together with polyaniline (PANI) as well as surfactant and additive to form the carbon-based ink. By using the screen print method, the as-prepared carbon-based ink was printed on the flexible substrate of

polyethylene glycol terephthalate (PET) with silver layer. The as-fabricated flexible micro-supercapacitor electrode was evaluated by galvanostatic charge/discharge and cyclic voltammetry (CV). It is noticed that the specific capacitance of the as-fabricated flexible micro-supercapacitor electrode can reach  $2089 \text{ Fm}^{-2}$  at the current density of  $0.2 \text{ Am}^{-2}$ . The method of carbon-based ink synthesis and flexible micro-supercapacitor fabrication could give a potential guidance for the flexible energy storage device fabrication. The other part of this work reported mechanical exfoliation and chemical deposition method to produce high quality  $\text{MnO}_2$  nanosheets and the composite of nanosheets/graphene was coated on the carbon current collectors. The PET as substrate provides supercapacitor more flexible and extensive useful in printing electronic technology. The x-ray diffraction (XRD) profiles confirm that the material is  $\text{MnO}_2$ . The field emission scan electron microscope (FESEM) demonstrates that the spherical  $\text{MnO}_2$  nanoparticle owns more thin layers structure and it can be sure that the  $\text{MnO}_2$  nanosheet has been achieved after mechanical exfoliation and chemical deposition. The supercapacitor with the uniformly nanocomposite has outstanding conductivity and superior electrochemical performance. The electrochemical test is in the 6 mol KOH solution and the voltage range is 0–1 v. All of the electrochemical analysis apply three electrode analysis method by the electrochemical work station. The measurements of cyclic voltammetry (CV) exhibits that the supercapacitor has a large current and the huge spacer between charge and discharge process means that the supercapacitor has perfect capacitive property. The curve of galvanostatic charge and discharge is closed symmetry and the process of discharge has a platform which was caused with the faradaic pseudocapacitance react. At current density of  $0.1 \text{ mA/cm}^2$ , the supercapacitor shows  $360 \text{ mF/cm}^2$  specific capacitance. These results suggest that the obtained  $\text{MnO}_2$  nanosheets are the better candidate for supercapacitor applications.

#### A01-12

##### **Self-assembled Core-shell Structured Perovskite Cathode for Intermediate and Low Temperature Solid Oxide Fuel Cells**

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Solid oxide fuel cells (SOFCs) are the most efficient devices for the energy conversion of the chemical energy stored in fuels into electricity at elevated temperature. In the past decades, considerable progress has been achieved in reducing the temperature to an intermediate and low temperature (ILT) range of 400 to 700 °C. Although the functionality of SOFC electrodes could be significantly improved by reducing the feature size to nanoscale using infiltration/impregnation method, the practical use of nanomaterials has been limited due to multi-step preparation process and instability with the testing time. Here, we demonstrate an innovative core-shell structured  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$  (SSC) cathode by freezing drying method and one step sintering process, which allows nanoscale particles control of highly active and stable catalyst at low temperature. The cathode structure is somehow similar to the infiltrated cathode structure. The single cells with the core-shell structured SSC cathode show excellent performance and stability at low temperature. Maximum power densities of 0.83 and  $1.13 \text{ W/cm}^2$  are achieved at 550 °C and 600 °C, separately. Moreover, the single cells show excellent stability over 250 h at 600 °C.

There are three benefits of the peculiar microstructure for the oxygen reduction process: (i) the well-connected SSC nanoparticles on the surface of the electrode are favor for the conduction of electrons on the electrode surface, and accelerate the surface oxygen adsorption and desorption processes; (ii) the dense SSC backbone in the inner layer has a good connection with SDC electrolyte, which could effectively provide the channel of ionic conduction between SSC-SDC and reduce the grain-boundary resistance of SSC and interfacial polarization resistance; (iii) the nanoparticles were grown by heat driving force to form the connection. The good connection between core layer and shell layer could be facilitated to reduce the resistance of oxygen ions conduction between the two interfaces.

This work provides a simple, cost-effective and reproducible way to obtain nanoscale electrode via self-assembled method through the sintering process, and expands opportunities to effectively exploit nanotechnology in a wide range of intermediate and low temperature energy devices.

#### A01-13

##### **Effect of NiO addition on oxygen reduction reaction at lanthanum strontium cobalt ferrite cathode for solid oxide fuel cell**

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Lanthanum strontium cobalt ferrite (LSCF) has gained much attention as the electrocatalyst for the oxygen reduction reaction (ORR) in intermediate temperature solid oxide fuel cells.[1] However, it still needs a strategy to improve its catalytic activity. In this work, NiO is primarily investigated as a possible synergistic catalyst for ORR on the LSCF surface. The effect of NiO particles on the effective oxygen chemical surface exchange coefficient is revealed with the electrical conductivity relaxation (ECR) technique. At 800 °C, the coefficient is increased from  $3.48 \times 10^{-5}$  to  $6.65 \times 10^{-5}$  cm s<sup>-1</sup> and  $6.9 \times 10^{-4}$  cm s<sup>-1</sup> when NiO particles are deposited using the sputter and drop coating methods, respectively. Adding 5 wt. % NiO to LSCF reduces the area specific interfacial polarization resistance, for example from 0.108 to 0.082  $\Omega$  cm<sup>2</sup> at 700 °C, as demonstrated by impedance spectroscopy on symmetric cells using samaria-doped ceria as the electrolyte. Adding NiO can also improve the performance of anode supported button cells, increasing the peak power density from 0.731 to 1.031 W cm<sup>-2</sup> at 800 °C. On the whole, the increased oxygen surface exchange rate together with the reduced electrode resistance and improved power density, exhibit that NiO is a potential additive to enhance the LSCF catalytic activity.

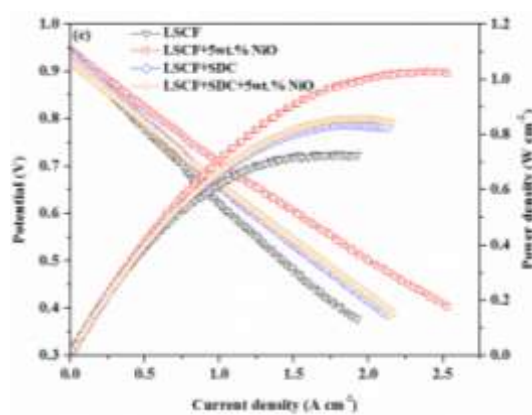


Figure 1 : Cell voltage and power density as a function of current density measured at 800 °C for single cells using LSCF, LSCF-NiO, LSCF-SDC, and LSCF-SDC-NiO cathodes

参考文献:

[1] Y. Chen, Y. Chen, M. Liu et al., *Energy Environ Sci*, 2017, 10: 964-971

#### A01-14

##### Highly conductive NiSe<sub>2</sub> nanostructures for all-solid-state battery-supercapacitor hybrid devices

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Battery-supercapacitor hybrid (BSH) comprises of a battery-type electrode offering plenty energy density and a capacitor-type electrode with ample power density. Transition metal oxides/hydroxides, as a kind of available battery-type electrode materials, whose low electronic and ionic conductivity have already become the principal restriction to the development of high-performance hybrid devices. The objective of this research is to synthesize high conductivity NiSe<sub>2</sub> nanostructures serving as electrode materials for hybrid devices, which is expected to be a potential candidate for all-solid-state energy storage devices.

The NiSe<sub>2</sub> nanostructures were synthesized by a simple hydrothermal procedure. Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and SeO<sub>2</sub> were dissolved in deionized water to form homogeneous solution. Subsequently, the solution was transferred into a Teflon-lined stainless autoclave with a piece of pretreated nickel foam immersed into, and then the autoclave was sealed and heated. Finally, the NiSe<sub>2</sub> sample was washed and dried to obtain the final products.

The NiSe<sub>2</sub> nanostructures are composed of the NiSe<sub>2</sub> films uniformly covered on the Ni foam and the NiSe<sub>2</sub> nanopyramids directly grown from the bottom films. The NiSe<sub>2</sub> nanopyramid electrode exhibits a high specific capacity of 240.83 mAh g<sup>-1</sup> at 1 Ag<sup>-1</sup>. The small values of the internal resistance (0.85  $\Omega$ ) and charge transfer resistance (0.41  $\Omega$ ) demonstrate the excellent charge transfer

rate and electrical conductivity. The hybrid device delivers a high energy density of  $0.196 \text{ mWh cm}^{-2}$  at a power density of  $1.6 \text{ mW cm}^{-2}$ . The equivalent series resistance (ESR) of the all-solid-state hybrid device is  $1.52 \Omega$ , which firmly reveals the nature of low resistance and high conductivity for BSH devices. Meanwhile, connecting two hybrid devices in series is able to drive a red LED for more than 3 minutes after charging for 9 seconds.

A facile one-step hydrothermal strategy has been carried out to synthesize pyramid-like  $\text{NiSe}_2$  nanostructures on nickel foam. The  $\text{NiSe}_2$  nanopyramid electrode exhibits a significant specific capacity, good rate capability and high conductivity. The all-solid-state hybrid device integrates the merits of high energy density at a high power density and low internal resistance. These results demonstrate the pyramid-like  $\text{NiSe}_2$  nanostructure is expected to be an ideal high-specific-capacity electrode material, representing a type of promising electrode for energy-storage hybrid devices with wide-scale applications, particularly in all-solid-state energy storage devices and portable electronic devices.

#### **A01-15**

##### **Engineering Low-Dimensional Nanostructures for Effective Energy Conversion and Storage**

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Effective energy conversion and storage play a key role in tackling the energy trilemma of security, affordability and sustainability. Carbon / graphene -based materials offer great scope for cost-efficient chemical / electrochemical / photochemical energy storage and catalysis, while the exceptional physical and mechanical properties are also utilised. Such functionalities can be effectively tuned by means of atomic doping, defect control, inter-layer spacing, porosity architecturing, and hybridisation with other nanostructures. The focus here is to demonstrate how those approaches can be effectively engineered to the development of storage materials for hydrogen, methane and  $\text{CO}_2$ , and of electrochemical catalysts for oxygen reduction and/or evolution reactions (ORR or OER), which underpins the costs and stability of rechargeable metal-air batteries and regenerative fuel cells – the energy conversion / storage technologies for portable devices, electric vehicles and the smart grid. Currently, the commercial noble metal catalysts, such as Pt/C and Ir/C, only exhibit mono-functional activity for either ORR or OER. Non-noble metal or metal-free materials are increasingly considered as cost-effective alternatives, but their catalytic activities, especially OER performance, are yet to match their metallic counterparts. Our systematic development firstly demonstrates the enrichment of N-doping and graphene / graphitic carbon-nitride intercalation are effectively for enabling rapid four-electron transfer process in ORR, and then switching of ORR and OER by single heat-treatment of a metal-organic-framework. Finally by closely coupling theory and experiment, we show the most effective catalytic sites in phosphorus-nitrogen co-doped graphene frameworks (PNGF), and then engineered the synthetic formulations to enrich such sites. The developed electrocatalysts show highly efficient bifunctionality for both ORR and OER. The ORR/OER potential gap is reduced successively from the initial  $1.252 \text{ mV}$ , to  $1.037 \text{ mV}$  with P,N co-doping, then to  $795 \text{ mV}$  after PNGF optimisation, and finally to  $705 \text{ mV}$  after purposeful enrichment of the active P-N sites. This design strategy, synthesis approach and the efficient catalysts offer great opportunities for the development of highly cost-effective energy storage technologies on a large scale.

#### **A01-16**

##### **Destabilization of light-metal borohydrides by catalysts, nanoconfinement and reactive combination**

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Light-metal borohydrides, such as  $\text{LiBH}_4$ ,  $\text{Ca}(\text{BH}_4)_2$  and  $\text{Mg}(\text{BH}_4)_2$ , possess high hydrogen capacities. However, they still suffer from unfavourable thermodynamics and kinetics. In the present study, we focus on improving the hydrogen storage properties of  $\text{LiBH}_4$  and  $\text{Ca}(\text{BH}_4)_2$  by catalysis, nanoconfinement, and reactive combination.

By in-situ introducing a nano sized niobium oxide derived from the decomposition of niobium ethoxide during dehydrogenation, which was originally introduced by ball milling, the onset dehydrogenation temperature of  $\text{LiBH}_4$  is evidently decreased to lower than  $150 \text{ }^\circ\text{C}$  and the reversibility is also favorably improved. The system shows a stepwise dehydrogenation, indicating the change of the dehydrogenation pathway by the introduction of niobium ethoxide. By optimizing the addition of niobium ethoxide, over  $10 \text{ wt}\%$

H<sub>2</sub> was released up heating to 360 °C, while only less than 2 wt% H<sub>2</sub> is released for pristine LiBH<sub>4</sub>.

A porous structured carbon nanotube/mesoporous carbon/nano TiO<sub>2</sub> multiphase composite is synthesized as the host for confining LiBH<sub>4</sub>. The loading of LiBH<sub>4</sub> in the confined system reqches *ca.* 50 wt%. The system shows a significantly low dehydrogenation peak temperature of *ca.* 320 °C, which is *ca.* 130 °C lower than that of the pristine LiBH<sub>4</sub>. 6 wt% H<sub>2</sub> is released for the confined system upon heating to 400 °C. About 5 wt% H<sub>2</sub> was reversibly released upon heating to 500 °C for the re-hydrogenated product. The nanoconfinement and the nano-sized TiO<sub>2</sub> play synergistic effect on the improved hydrogen storage property of LiBH<sub>4</sub>.

The combination of Ca(BH<sub>4</sub>)<sub>2</sub> and NH<sub>4</sub>Cl by ball milling results in an amorphous new calcium compound containing B-N-H chemical bond, which shows an extremely low dehydrogenation temperature of 60 °C, with 4.5 wt% H<sub>2</sub> releasing upon heating to 150 °C. Though the system turns to be irreversibly, the dehydrogenation property is attractive in permanent devices.

## A01-17

### The reversibility of conversion reactions in lithium stored SnO<sub>2</sub> based anode materials

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开发新型高比容量储锂电极材料是提高锂离子电池能量密度的关键技术之一。在众多可逆储锂材料中，SnO<sub>2</sub> 因其特有的容量高、安全、低温性能好等方面的优势，已成为最受重视的负极材料体系之一。SnO<sub>2</sub> 的储锂反应需两步完成：首先是原位生成 Sn 相的转化反应 (SnO<sub>2</sub> + Li+ → Sn0 + Li<sub>2</sub>O)，理论比容量为 711mAh/g；接着是合金化反应(Sn0 + xLi+ ↔ LixSn)，容量为 783mAh/g。这两个反应阶段的极大体积变化严重影响电极材料的内部和表面结构，以及电极界面反应的稳定性，导致容量的快速衰减。此外第一步转化反应的可逆性 (Sn0 + Li<sub>2</sub>O → SnO<sub>2</sub>) 极差。所以，SnO<sub>2</sub> 负极存在循环稳定性差、首次不可逆容量大和首次库仑效率低等问题。这些问题严重制约了 SnO<sub>2</sub> 负极材料的应用。

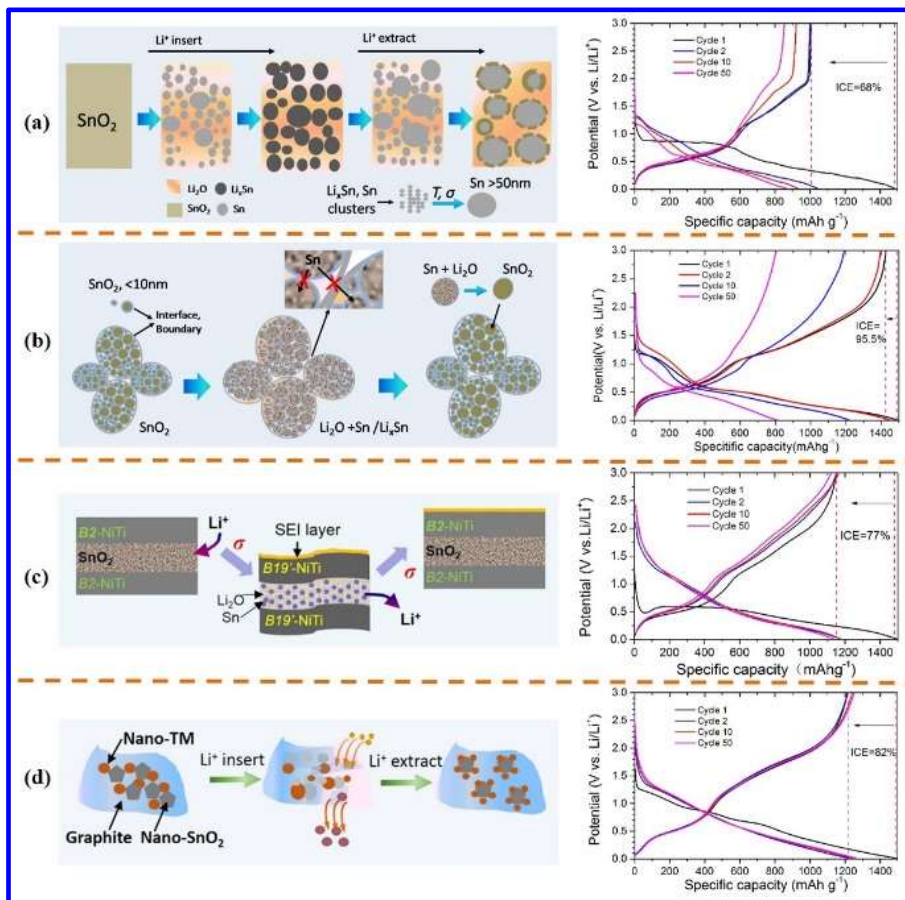


图-1(a) SnO<sub>2</sub> 嵌锂-脱锂过程结构演变示意图，热诱发和应力诱发 Sn 粗化导致 Sn/Li<sub>2</sub>O 界面减少；(b) 创制高密度晶界抑制 Sn 长程扩散；(c) NiTi 合金的超弹性效应消除 SnO<sub>2</sub> 中的应力诱发 Sn 粗化；(d) 添加过渡金属抑制 Sn 粗化。(比容量已归一化以便于比较)。

近来我们通过表面修饰、碳材料限域、形变碳基体负载等新途径，改善 SnO<sub>2</sub> 电极材料的嵌锂/脱锂表面结构稳定性。[1-5]



申请人深入研究了 SnO<sub>2</sub> 嵌锂-脱锂反应过程原位生成的 Sn/ Li<sub>2</sub>O 相的形态演变, 发现纳米 Sn 相极易热诱发粗化而降低 Sn/Li<sub>2</sub>O 界面互扩散动力学与反应活性。因此, 我们提出了 Sn 相的再结晶粗化是导致 Sn/Li<sub>2</sub>O 复合物转化反应可逆性差而首效低的主要原因(图-1a)。以此为据, 申请人通过创制多尺度界面和高密度晶界抑制嵌锂 SnO<sub>2</sub> 薄膜中的纳米 Sn 相长大, 实现最高达 95.5%的首次库伦效率(图-1b), 为迄今文献报道中的最高值。[6] 尤其是, 通过进一步电极结构设计, 我们证实 NiTi 记忆合金的超弹性约束可有效抑制嵌锂 SnO<sub>2</sub> 负极中纳米 Sn 相的应力诱发粗化(图-1c), 提高 Sn/Li<sub>2</sub>O 纳米结构稳定性, 从而改善其转化反应的可逆性; 并通过原位 Raman 光谱等方法首次直接观察到了 Li<sub>2</sub>O 相的生成与分解并伴随着 SnO<sub>2</sub> 的分解与再生。[7]

进一步研究发现嵌锂 SnO<sub>2</sub> 初始循环的容量衰减主要与 Sn 粗化导致转化反应的可逆性衰退有关, 而不是传统观点认为的嵌锂体积膨胀。此外 Sn 粗化对嵌锂 SnO<sub>2</sub> 负极的库伦效率、能量效率也产生显著影响。通过表征不同循环充电 1.0V 状态下电极的 Sn 相演化过程, 我们建立了 Sn 相尺寸、Sn/Li<sub>2</sub>O 互扩散界面与转化反应不可逆程度之间的定量线性关系, 外推确定了 Sn/Li<sub>2</sub>O 转化反应完全可逆时的 Sn 颗粒临界尺寸为 11.3nm。[8] 紧接着, 我们结合第一性原理计算发现单质 Mn 的复合降低了嵌锂 SnO<sub>2</sub> 中 Sn 相表面能而有效降低 Sn 颗粒长大趋势; 另外 Mn 在 SnO<sub>2</sub> 中掺杂会引入大量氧空位, 提高了 Sn/Li<sub>2</sub>O 转化反应的可逆性和 SnO<sub>2</sub>-Mn 复合负极材料的首效。[9] 这些研究成果为高可逆性转化反应电极材料的相尺度设计, 尤其 SnO<sub>2</sub> 基电极材料的多相复合设计策略提供了重要指导。

据此, 申请人采用高效宏量球磨法, 添加了石墨和易与 Sn 形成金属间化合物相的过渡金属抑制 Sn 颗粒粗化, 稳定 Sn/Li<sub>2</sub>O 纳米结构及其互扩散界面(图-1d), 获得了一系列同时具有高首效、长寿命和高容量的 SnO<sub>2</sub>-M (Fe, Mn, Co, Cu) -C 三相复合负极材料。其中 SnO<sub>2</sub>-Fe-C 负极的首效为~82%, 稳定容量> 800mAh/g, 寿命>1000 次, 在容量和寿命等方面性能均优于已商用的 Sn-Co-C 负极(~87%, ~500mAh/g, 300 次), 而且它在全电池测试中也具有良好的循环性能。[10] 基于相似的复合相结构设计策略, 申请人球磨制备出了也同时具有高首效和优异长循环(>1000 次)稳定性的 SiO<sub>x</sub>@FeSn<sub>2</sub> 两相复合负极材料。研究发现两种纳米相复合形成的大量界面显著改善了电子传输和离子扩散动力学, 显著提高了 FeSn<sub>2</sub> 和 SiO<sub>x</sub> 相转化反应和合金化反应的可逆性。[11] 这进一步充分验证了过渡金属复合策略提升合金化与转化反应复合储锂材料可逆性的有效性。

参考文献:

- [1] R.Z Hu, M. Zhu\*, H. Wang, et al., *Acta Materialia*, 2012, **60**:4695-4730.
- [2] R.Z. Hu, W. Sun, M.Q. Zeng, et al., *Nanoscale*, 2013, **5**: 11971-11979.
- [3] R.Z. Hu, G. Waller, Y. K. Wang, et al., *Nano Energy*, 2015,**13**: 232-244.
- [4] R.Z. Hu, H.Y. Zhang, J.W. Liu, et al., *Journal of Materials Chemistry A*, 2015, **3**: 15097-15107.
- [5] H.P. Zhang, Z. W. Chen, R.Z. Hu\*, et al., *Journal of Materials Chemistry A*, 2018, **6**: 4374-4385.
- [6] R.Z. Hu, D.C. Chen, G. Waller, et al., *Energy & Environmental Science*, 2016, **9**:595-603
- [7] R.Z. Hu, Y.P. Ouyang, D.C. Chen, et al., *Acta Materialia*, 2016, **109**: 248-258.
- [8] R.Z. Hu, H.P. Zhang, Z.C. Lu, et al., *Nano Energy*, 2018, **45**:255-265
- [9] R.Z. Hu, Y.P. Ouyang, T. Liang, et al., *Energy & Environmental Science*, 2017, **10**:2017-2029.
- [10] R.Z. Hu, Y.P. Ouyang, T. Liang, et al., *Advanced Materials*, 2017, **29**: 1605006.
- [11] H.Y. Zhang, R.Z. Hu\*, Y.X. Liu, et al., *Energy Storage Materials*, 2018, **13**:257-266

## A01-18

### Obstacles toward unity efficiency of LiNi<sub>1-2x</sub>CoxMnxO<sub>2</sub> (x=0~1/3) (NCM) cathode materials and the corresponding solutions: Insights from ab initio calculations

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Achieving the energy limit of LiNi<sub>1-2x</sub>CoxMnxO<sub>2</sub> (NCM) (x=0~1/3) cathodes has raised great research interests in recent years. In order to obtain longer cycle and calendar life, current NCM cathodes deliver far less than their theoretical energy density, even after intense modifications such as cation/anion doping, coating, core-shell structure, and concentration-gradient design. By a throughout and careful literature survey, we summarized five individual phenomena observed at the end of charge: O3-O1 phase reaction, crack propagation, Li-Ni exchange, layered-spinel phase transition, and Oxygen evolution. These five phenomena have been reported independently by different researchers using novel ex situ and in situ characteristic techniques, and which one leads to the degradation of NCM cathode is not clear.

In this study, we perform a comprehensive study of  $\text{LiNi}_{1-2x}\text{Co}_x\text{Mn}_x\text{O}_2$  (NCM) ( $x=0\sim 1/3$ ) cathodes, using first-principle calculations within the DFT+U framework and a bond model based on the effective interaction of transition metal (TM) ions. Based on our results, we have located the obstacles toward unity efficiency and revealed that the degradation strongly depends on the Ni concentration and the depth of charge (DOC). Based on our findings, the optimal composition for a good electrochemical performance of NCM cathode materials is found within the region of  $1/10 < x < 1/4$  (50-80% of Ni). We also proposed separate solutions for each Ni concentration to prevent degradation at high voltage/capacity. For  $1/4 \leq x \leq 1/3$ , a feasible way to reduce the Oxygen evolution during charge would be through doping with high valence TM ions, in order to reduce strongly covalent Co-O bonds. On the other hand, for  $0 \leq x \leq 1/4$ , the use of coating materials or novel materials design like core-shell and concentration-gradient structures could restrict the lattice distortion along the charge process. The key factors found in present work will help researchers, especially the newcomers to understand the obstacles toward unity efficiency, and also help them to rationally design NCM cathode materials with high-energy density through possible solution mechanisms, such as doping, coating or novel nanostructures, like core-shell or concentration gradient cathodes.

Related publications:

C. P. Liang, Roberto C. Longo, et al. Obstacles toward unity efficiency of  $\text{LiNi}_{1-2x}\text{Co}_x\text{Mn}_x\text{O}_2$  ( $x=0\sim 1/3$ ) (NCM) cathode materials: Insights from ab initio calculations. *Journal of Power Sources*, 2017, 340: 217-228.

C. P. Liang, F.T. Kong, et al. Unraveling the Origin of Instability in Ni-Rich  $\text{LiNi}_{1-2x}\text{Co}_x\text{Mn}_x\text{O}_2$  (NCM) Cathode Materials. *The Journal of Physical Chemistry C*, 2016, 120 (12): 6383–6393.

C. P. Liang, F.T. Kong, et al. Site Dependent Multicomponent Doping Strategy for Ni-rich  $\text{LiNi}_{1-2y}\text{Co}_y\text{Mn}_y\text{O}_2$  ( $y = 1/12$ ) Cathode Materials for Li-Ion Batteries. *Journal of Materials Chemistry A*, 2017, 5 (48): 25303-25313.

C. P. Liang, Roberto C. Longo, et al. Ab initio study on Surface Segregation and Anisotropy of Ni-rich  $\text{LiNi}_{1-2x}\text{Co}_x\text{Mn}_x\text{O}_2$  (NCM) ( $x \leq 0.1$ ) Cathodes. *ACS Applied Materials & Interfaces*, 2018, 10 (7): 6673–6680.

## A01-19

### One Dimensional Nanomaterials for Emerging Energy Storage

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由于一维纳米材料具有奇异的化学、物理效应，在能源领域的研究中发现其具有许多独特的性能。纳米线电极材料具有高的比容量等优点，但容量的快速衰减依然是电化学储能研究中的关键问题。近年来原位表征越来越多地应用于纳米技术中，为进一步研究电极材料容量衰减的本质，本工作设计并组装了可同时用于微纳系统支撑电源及原位检测微纳电池性能的单根纳米线全固态锂离子电池，通过原位表征建立了纳米线的电输运、结构与电极充放电状态的直接联系，发现电导率下降和结构劣化是导致容量衰减的关键因素。最近，我们设计了一种容易和高产量的策略，用于通过低温的热解过程从金属-有机框架（MOF）向碳纳米管（CNT）形成。应用于能量转换和存储时，封装在 N-CNT 中的金属或金属氧化物纳米颗粒组装的结构显示出优异的性能。我们利用单一  $\text{MoS}_2$  纳米片成功构筑了场调控电催化析氢器件，探索了场效应对材料导电性的影响，进而提升其催化性能。此外，我们发现  $\text{CaV}_4\text{O}_9$  纳米线具有本征的高电子电导率，应用到钠离子电池时其可逆比容量达到  $300 \text{ mAh g}^{-1}$ 。通过原位和非原位表征以及理论模拟计算，发现该材料具有一种特殊的钠离子存储机制。这些一维纳米材料的设计与合成为高性能储能器件的构筑提供了新思路和新方法。

## A01-20

### The construction of core-shell structure for SOFC cathode with enhanced performance

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To realize the commercialization and industrialization of the solid oxide fuel cell (SOFC), lowering its operation temperature to the intermediate temperature range (IT, 600-800 °C) is of great significance. However, the cathode's catalytic activity decreases with the temperature reduction. Hence, the development of high performance IT-SOFC cathode material becomes the key to the challenge. BaCo-based double perovskites have attracting ever-growing attentions due to their excellent oxygen reduction reaction (ORR) catalytic activity. Among them, (Sr,Fe) containing  $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$  (PBSCF) cathode has been widely investigated due to its

great oxygen ion conductivity. But its long-term stability is threaten by CO<sub>2</sub> gas in the air due to the existence of alkaline-earth metals Ba and Sr , which would eventually lead to the performance degradation of cathode. To circumvent this issue, we studied Ruddlesden–Popper structure layered perovskite La<sub>2</sub>NiO<sub>4+δ</sub> (LN) as functional dense film on the PBSCF scaffold as an PBSCF-LN core-shell structure cathode. In addition to the great CO<sub>2</sub> resistance, higher ORR catalytic activity can be achieved by LN coating's introduction. This study provides a potential new cathode structure for SOFC application.

#### **A01-21**

##### **Electrochemical reaction processes near the surface and interface of oxide materials**

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Perovskite-based materials have been widely studied as the electrode materials for high temperature electrochemical systems such as solid oxide fuel cells and solid state electrolysis cells, and other low-temperature electrochemical devices such as alkaline membrane fuel cells and metal–air batteries. While many perovskite-based electrodes have shown remarkable performance, cation segregation near the surface or interfaces is often observed, which greatly impacts not only electrode kinetics but also their durability and operational lifespan. The segregation of A-site alkaline earth metal oxides was reported to degrade the electrochemical performance in literature. In contrast, the segregation or exsolution of B-site transition metals and the formation of metal/oxide interface were found to significantly enhance catalyst activities and stability for the electrodes. Despite of many corresponding examples, contradicting results were reported in literature. A detail understanding of the correlation between the surface cation composition and the electrochemical reaction kinetics near the surface and interface is vital to achieving the rational design of more efficient perovskite based electrode materials with excellent durability.

In this study, we aimed to provide critical insights into the mechanisms of cation segregation and provide the guide line for how to enhance desired positive effects while suppressing negative effects associated with cation segregation under operating conditions. (La,Sr)MO<sub>3</sub> (M is the transition metal) thin films grown by pulsed laser deposition were used as model systems. The evolution of surface cation composition, morphology and local electronic structure as a function of temperature, gas environment and electric potential were systematic investigated. We observed the segregation of Sr on the surface of (La,Sr)(Fe,Co)O<sub>3</sub> (LSCF) thin films after long time operation in oxygen environment at high temperature (500 to 600° C), which lead to the degradation of oxygen reduction reaction (ORR) activity. After the deposition of Pr<sub>x</sub>Ce<sub>1-x</sub>O<sub>y</sub> (PCO, x=0, 0.2, 1) surface modification layer, both the ORR activity and stability of LSCF were greatly enhanced. Based on SEM, XPS and TEM measurements, we believe such enhancement is partly due to the suppression of A-site metal Sr segregation on LSCF surface by the top PCO layer at elevated temperature. Furthermore, the surface modification was found to change the rate limiting step of ORR on the surface, which was attributed to the change of surface electronic structure as quantified by in-situ scanning tunneling microscopy/spectroscopy. By annealing in reducing condition or applying an cathodic potential, the exsolution of B site cation was observed on the surface of (La,Sr)MO<sub>3</sub> (M=Ni,Fe,Ti) oxide. The local electronic structure changes introduced by B site exsolution were studied in details and were correlated to the catalytic activity enhancement.

#### **A01-22**

##### **Facile synthesis and superior lithium storage performance of ball-milled metal sulfides-carbon nanocomposites**

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China iron & steel research institute group

#### 1. Introduction

Lithium ion batteries (LIB), as one of the most important and widely used rechargeable power sources, are common in portable consumer electronics such as smartphones, computers, and power tools because of its high energy density, long lifespan, light weight and environment amity. However, recently, the development of electric vehicles (EVs) and hybrid electric vehicles (HEVs) has raised the higher requirement of the improved performance of the LIB. Furthermore, these applications require higher specific energy, energy power density, and long cycle life, high safety while the cost, safety, and environmental issues also must be considered. The anode is one of the major LIB components. Currently, graphite is the most popular established commercial anode material. However,

graphite-based anodes cannot satisfy the increasing demand of high energy density due to the low theoretical capacity of 372 mAh g<sup>-1</sup>. Therefore, it is essential to develop alternative anode materials with low cost, non-toxicity, high capacity and excellent cycling stability through simple method for economic consideration.

The metal sulfides (MS) are received attentions due to its low cost, environmental friendliness, and easy fabrication. It has been widely used in many fields including Na-ion battery, Mg-ion battery, supercapacitor, solar cells, hydrogen storage, catalysis, solid lubricant, optoelectronics and piezotronics.

In the present work, we take advantage of high energy ball-milling method to synthesize MS-carbon nanocomposite as a promising high-capacity anode material for reversible lithium storage. Electrochemical measurements show that the MS-C composite exhibits remarkably large capacity close to the theoretical capacity of MS, stable cyclability, high coulombic efficiency and excellent rate capability. The performance is strongly related with the carbon content and the particle size. It is the synergistic effects caused by carbon coating and ball-mill-derived nano-crystallization that greatly improve the electrochemical performance of MS.

## 2. Experimental

All of the chemicals were of analytical grade and used as received. Low-cost transition-metal dichalcogenide (MS, particle size < 10 nm, purity 98%) and graphite (C, particle size < 10 nm) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. The raw material was mechanically milled to reduce particle size on a planetary ball-mill machine (Fritsch P5, Germany) for 20 h at room temperature under argon atmosphere with a pressure of 100 kPa. Then the graphite was loaded into a stainless steel milling container and mixed with the as-prepared MS nanoparticles in different weight ratios. The MS-carbon nanocomposites were produced in the same machine for another 20 h under same condition. The MS-carbon nanocomposites powders were used as active anode materials. For comparison, the as-prepared ball-milling and raw MS powders were also studied as active anode materials. Here, it should be mentioned that the ball-milling method is easy for amplification of mass production.

The microstructure of the powders was observed by field-emission scanning electron microscope (FE-SEM, FEI NOVA-450) and transmission electron microscope (TEM, PHILIPS TECNAI F30). The phase of the synthesized samples was checked by X-ray diffraction (XRD, BRUKER D8) with Cu K $\alpha$  radiation at 40 kV and 40 mA from 10° to 90° with a step size of 0.02° and step time of 5 seconds. The surface areas of the samples were estimated by the Brunauer–Emmett–Teller (BET) method using a Quanta Autosorb-iQ2-MP-ANG-VP (surface area = 7.134 m<sup>2</sup>/g, Fig. S1). Raman scattering spectra were recorded at room temperature on a HORIBA JOBIN YVON S.A.S. system (model LabRAM HR800) with 532 nm incident wavelength radiation.

The electrodes were made from a mixture of active material, carbon black (AB) and polyvinylidene fluoride (PVDF) in weight ratio of 80:10:10. The mixture was dispersed in N-methylpyrrolidone (NMP) to form homogenous slurry. The slurry was spread onto a copper foil and dried at 110 °C for 20 h in a vacuum oven. After drying, the electrode foils were pressed and then punched into circular shape pieces. For electrochemical testing, CR2032-type coin cells were assembled in an argon-filled glove box (MBraun, Labstar (1200/780), Germany). Li metal foil was used as a counter electrode, 1 mol l<sup>-1</sup> LiPF<sub>6</sub> in mixed solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v) as the electrolyte, and Celgard 2400 as the separator. The galvanostatic charge-discharge test was conducted at cut-off voltages from 0.01 to 3 V at room temperature using an automatic Land battery measurement system (Land BT2001A, Wuhan, China). Cyclic voltammetry (CV) was carried out on VMP3 electrochemical workstation (BIO-LOGIC SA France) in a voltage range of 0.01-3.0 V at a scan rate of 0.1 mV s<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) was measured by applying a sine wave with amplitude of 5 mV in the frequency range from 1000 kHz to 1 Hz.

## 3. Results

### 3.1 MoS<sub>2</sub>-C

As anode material for lithium storage, the MoS<sub>2</sub>-C composite with 30% C shows a discharge capacity as high as 736 mAh g<sup>-1</sup> in the first cycle and retains the capacity up to 720 mAh g<sup>-1</sup> after 200 cycles at a current density of 100 mA g<sup>-1</sup>. Even at a high rate of 2000 mA g<sup>-1</sup>, the reversible capacity is still 428 mAh g<sup>-1</sup>. As carefully compared with MoS<sub>2</sub>-C composite with 20% C, raw MoS<sub>2</sub> and pure ball-milled MoS<sub>2</sub>, we ascribe the remarkably improved electrochemical performance in MoS<sub>2</sub>-C composite with 30% C to the synergistic effects caused by carbon coating and nano-crystallization derived by ball milling.

### 3.2 SnS<sub>2</sub>-C

Electrochemical analyses revealed that the SnS<sub>2</sub>-C nanocomposites as anode material in lithium ion batteries (LIBs) showed high discharge capacity and excellent cycling stability. The SnS<sub>2</sub>-C nanocomposite with 60% C showed a discharge capacity as high

as 650 mAh g<sup>-1</sup> with the coulombic efficiency of 86% in the first cycle and retained the capacity up to 700 mAh g<sup>-1</sup> after 100 cycles at a current density of 100 mA g<sup>-1</sup>. The excellent electrochemical properties of SnS<sub>2</sub>-C originated from its unique structure, which is composed of SnS<sub>2</sub> nanoparticles embedded porous carbon network, providing more lithium ion storage sites, higher electronic conductivity, and fast ion diffusion.

### 3.3 SnS<sub>2</sub>-C

The SnS-C nanocomposite with 50% C showed a discharge capacity as high as 1056 mAh g<sup>-1</sup> with the coulombic efficiency of 75% in the first cycle and retained the capacity up to 1055 mAh g<sup>-1</sup> after 100 cycles at a current density of 100 mA g<sup>-1</sup>. The excellent electrochemical properties of SnS-C originated from its unique structure with a calculated BET specific surface area of 106.26 m<sup>2</sup> g<sup>-1</sup>, providing more active sites for favorable Li-ion intercalation and large specific surface area. So, it exhibited a very high reversible capacity and high rate performances. Especially, advanced materials with hollow structures are of great interest because of its well-defined interior voids, high specific surface area, low density, accommodate volume change without pulverizing compared with that of solid counterparts of the same size. Furthermore, the unique structure can shorten ionic/electronic diffusion length and provide efficient channels for mass transport.

## 4. Conclusions

In the present work, we focus on a simple and scalable ball-milling method to synthesize MS-carbon nanocomposite as a promising high-capacity anode material for reversible lithium storage. Electrochemical measurements show that the as-obtained MS-C composite exhibits remarkably large capacity close to the theoretical capacity of MS, stable cyclability, high coulombic efficiency and excellent rate capability. The performance is strongly related with the carbon content and the particle size. It is the synergistic effects caused by carbon coating and ball-mill-derived nano-crystallization that greatly improve the electrochemical performance of MS. Our work indicates that ball milling is a facile and efficient route to prepare high-performance MS-C composite anode materials for lithium-ion batteries. It is also applicable for the synthesis of some novel nanostructured carbon-coated composite materials, especially for the large-scale synthesis.

### A01-23

#### **High-performance Mn/V-based cathode materials for Li/Na-ion batteries**

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A series of high-performance Mn/V-based cathode materials for Li/Na-ion batteries have been synthesized by co-precipitation, sol-gel and solid-state sintering methods. The microstructure and electrochemical properties of the materials are investigated by physical characterization and electrochemical measurement techniques. The cathode materials exhibit excellent electrochemical performance, including high capacity, superior rate capability, and remarkable cycling performance. Especially, O<sub>3</sub>-type Mn-based oxide as a cathode for Na-ion batteries shows a reversible capacity of 172 mAhg<sup>-1</sup> at 0.1 C and remarkable capacity retention of 70.4% after 1000 cycles at 20 C. More importantly, it offers good compatibility with pristine hard carbon as anode in the sodium-ion full cell system, delivering a high energy density of up to 215 Whkg<sup>-1</sup> at 0.1 C and good rate performance. In addition, micro-sized two-phase structured Li<sub>1.6</sub>Na<sub>0.4</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C composite is comprised of numerous primary nanocrystals. As a cathode material for Li-ion batteries, it presents a high energy density of 478.8 Whkg<sup>-1</sup> and delivers high initial discharge capacities of 121.6, 113.8 and 109.7 mAhg<sup>-1</sup> at the rate of 5 C, 10 C and 20 C in a voltage range of 3.0-4.3 V, respectively. It also exhibits an excellent high rate cycling performance, with capacity retention of 85.9 %, 81.7 % and 76.5 % after 1000 cycles at the rate of 5 C, 10 C and 20 C in a voltage range of 3.0-4.3 V. The results demonstrate that Mn/V-based materials developed in this work can be considered as the promising cathode materials for Li/Na-ion batteries.

### A01-24

#### **Bimetal Pt-Co nanoparticles supported on modified SiO<sub>2</sub> nanospheres as high-efficient catalyst for hydrogen generation from hydrolysis of ammonia borane**

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Hydrogen generation from catalytic dehydrogenation of ammonia borane is a promising way for energy. However, the design and manufacture of highly active metal catalysts is still an urgent issue.

In this work the  $\text{SiO}_2@\text{Pt}_{0.1}\text{Co}_{0.9}$  bimetallic catalyst was prepared based on chemical reduction method. In a typical procedure, 0.1 g modified  $\text{SiO}_2$  nanospheres (synthesized by Stöber method and modified by amino groups,  $-\text{NH}_2$ ) was dispersed in 50 mL DI water. Then, 0.2242 g  $\text{C}_4\text{H}_6\text{O}_4\cdot\text{Co}\cdot 4\text{H}_2\text{O}$  and 0.0518 g  $\text{H}_2\text{PtCl}_6$  were added and the solution was stirred at room temperature for 1 h to form an evenly solution. The metallic ions were reduced by freshly prepared 0.5M  $\text{NaBH}_4$  at 278 K. The product was separately washed with ethanol and water and dried under vacuum freeze drying, and the  $\text{SiO}_2@\text{Pt}_{0.1}\text{Co}_{0.9}$  catalyst was harvested.

The PtCo bimetal nanoparticles are homogeneous attached to surface of  $\text{SiO}_2$  nanospheres and the average diameter of them is about 12 nm. The catalysts perform a good dispersity under the presence of  $\text{SiO}_2$  nanospheres which were in favor of the reduction of metal nanoparticles. The XRD pattern showed that the Co and  $\text{CoPt}_3$  alloy nanoparticles generated together on the surface of  $\text{SiO}_2$  which played a synergistic role for catalytic dehydrogenation of  $\text{NH}_3\cdot\text{BH}_3$  that the plasmon excitations in the  $\text{CoPt}_3$  induce the free electrons in the Co segment to oscillate. Splendid catalytic activities were presented on hydrolysis test of AB solution, with the TOF of  $25.59 \text{ molH}_2 \text{ min}^{-1}\text{molM}^{-1}$  and  $E_a$  of  $37.05 \text{ kJ}\cdot\text{mol}^{-1}$ . Meanwhile, the catalyst showed a good cycle property, about 70 % activity remains after the fifth hydrolysis test.

#### A01-25

##### Catalytic Mechanism of Carbon Nanotubes Supported Nickel on Hydrogen Storage Properties of Magnesium Borohydride

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High-capacity hydrogen storage material is a research hotspot in the field of hydrogen storage materials at present. Light metal complex hydrides, such as  $\text{LiBH}_4$ ,  $\text{NaBH}_4$ ,  $\text{LiAlH}_4$  and  $\text{Mg}(\text{BH}_4)_2$  et al, have attracted much attention due to their high theoretical hydrogen storage capacity. However, these materials usually have problems of unduly stable thermodynamic properties, poor dehydrogenating kinetics properties and low reversible capacity, which restrict their practical application. The functionalized carbon materials with microstructure based on carbon nanotubes (CNTs), graphene (Gr) and graphite (C) can distinctly improve the hydrogen storage properties of materials. In order to improve the comprehensive properties of  $\text{Mg}(\text{BH}_4)_2$  hydrogen storage materials, CNTs, Gr and C were selected as additives combined with transition metals catalysts in this paper, which is based on present research progress of  $\text{Mg}(\text{BH}_4)_2$ . The synergistic catalytic effects of the carbon materials loaded transition metals catalysts on the hydrogen sorption-desorption thermodynamics and kinetics and cyclic stability of  $\text{Mg}(\text{BH}_4)_2$  are mainly studied. The aim of the paper is to obtain Mg-based hydrogen storage materials with a high capacity and a lower hydrogen desorption temperature to apply to fuel cells.

#### A01-26

##### 金属硼氢化物及其氨合物水解

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氢的高效制取和储存是氢能发展面临的主要问题。水解制氢因反应条件温和、氢气纯度高、对环境没有危害等优点而得到了极大的关注。金属硼氢化物由于具有高的理论水解放氢量而受到学者们的广泛重视，探索产氢量高、水解制氢性能优异的金属硼氢化物制氢材料具有十分重要的研究价值和现实意义。本文通过球磨方式制备了  $\text{NaBH}_4\text{-ZnCl}_2$  复合材料、 $\text{NaZn}(\text{BH}_4)_3$  和  $\text{Mg}(\text{BH}_4)_2$  及其氨合物并优化其水解制氢性能，实现了水解制氢性能的调控，阐明其水解反应机理，创制了了对空气稳定、产氢量高、制氢动力学性能可调的水解制氢材料。 $\text{NaBH}_4\text{-ZnCl}_2$  复合材料的水解制氢量达到 1964 mL/g，双金属硼氢化物  $\text{NaZn}(\text{BH}_4)_3$  在 5 min 的制氢量为 1740 mL/g，在  $-18^\circ\text{C}$  仍与甲醇仍然发生反应，显示了良好的醇解制氢性能， $\text{Mg}(\text{BH}_4)_2$  水解反应在 1 min 内即可产生 1700 mL/g  $\text{H}_2$ ，制氢量达到 3004 mL/g  $\text{H}_2$ ，是目前报导的制氢量最大的水解制氢材料。也通过引入氨获得了氨合硼氢化物，有效调控了  $\text{Mg}(\text{BH}_4)_2$  的水解制氢速率和制氢量并提高了  $\text{Mg}(\text{BH}_4)_2$  的对空稳定性，在移动氢源系统具有潜在的应用价值。

#### A01-27

##### Nanoconfinement of Mg by ultrathin carbon layer with enhanced hydrogen storage properties

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A facile way has been developed to fabricate ultrathin carbon layer encapsulated air-stable Mg nanoparticles (Mg@C NPs) by methane plasma metal reaction method. Compared with pure Mg NPs, the nanoconfinement of Mg by carbon layer can not only reduce particle size but also prevent Mg from oxidation. By adjust methane from 10 to 300 ml, average size of Mg@C NPs reduces from 140 to 60 nm and thickness of carbon layer increases from 1 to 4 nm. After exposure in air for 3 months, little MgO can be detected in Mg@C NPs. In these Mg@C samples, Mg@C (CH<sub>4</sub>:50ml) with size of 80 nm and ultrathin amorphous carbon shell of 3 nm shows the highest hydrogen capacity of 6.3 wt% H<sub>2</sub>. In comparison, the hydrogen capacities of Mg@C (CH<sub>4</sub>:10ml) and Mg@C (CH<sub>4</sub>:300ml) are only 5.4 wt% H<sub>2</sub> and 4.3 wt% H<sub>2</sub>, respectively. Mg@C (CH<sub>4</sub>:50ml) also displays the highest hydrogenation and dehydrogenation rates which can absorb 4.8 wt% H<sub>2</sub> within 10 min at 573 K and desorb 5.0 wt% H<sub>2</sub> within 20 min at 623 K. The apparent energies for hydrogenation and dehydrogenation of Mg@C (CH<sub>4</sub>:50ml) are 64.1 and 107.2 kJ mol<sup>-1</sup>, both smaller than Mg@C (CH<sub>4</sub>:10ml) of 66.7 and 118.9 kJ mol<sup>-1</sup> and Mg@C (CH<sub>4</sub>:300ml) of 67.7 and 137.8 kJ mol<sup>-1</sup>. The enhanced hydrogen storage properties of Mg@C (CH<sub>4</sub>:50ml) are attributed to smaller particles size and excellent antioxidant properties provided by the ultrathin carbon layer.

#### A01-28

##### **Improved hydrogen storage performance of MgH<sub>2</sub> with Ni/Co-based compounds**

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MgH<sub>2</sub> is one of the most promising hydrogen storage materials due to its high theoretical hydrogen capacity and excellent reversibility. However, high thermal stability and slow absorption/desorption kinetics restrict the practical applications of MgH<sub>2</sub>. A series of nickel/cobalt-based materials were synthesized by facile chemical method, and then ball-milled with MgH<sub>2</sub> to obtain the corresponding Mg-based hydrogen storage materials. All the nickel/cobalt-based materials can significantly improve the hydrogen storage performance of MgH<sub>2</sub>. The MgH<sub>2</sub>-10wt%Co@C composites possess the best hydrogen storage performance, which can desorb 6.1 wt% H<sub>2</sub> in 20 min at 300 °C and absorb 5.5 wt% H<sub>2</sub> within 100 s under 300 °C. Subsequently, corresponding de/rehydrogenation mechanisms have been also discussed.

#### A01-29

##### **Superior hydrogenation properties in a Mg<sub>65</sub>Ce<sub>10</sub>Ni<sub>20</sub>Cu<sub>5</sub> nanoglass processed by melt-spinning followed by high-pressure torsion**

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Jinan University

Mg-based materials are considered as promising candidates for hydrogen storage mainly owing to their high hydrogen storage capacity (7.6 wt% in the case of MgH<sub>2</sub>). However, the sluggish hydrogenation/dehydrogenation kinetics and the stable thermodynamic stability of Mg-based materials greatly hinder their practical application. Nanostructuring has been well demonstrated as an efficient strategy to tune hydrogen storage properties of Mg-based materials, especially in the kinetics aspect. However, the thermodynamics of the crystalline Mg-based materials could hardly be altered by nanostructuring even if the crystal size is reduced to a few nanometers. We recently reported a glass-to-glass transition upon hydrogenation in the Mg-based Mg-Ce-Ni amorphous alloys and reported hydrogen densities higher than those of crystalline counterpart hydrides. For these amorphous Mg-Ce-Ni alloys, the hydrogen storage properties could be well tuned by considering the mixing enthalpy of alloying elements and hydrogen. Nevertheless, hydrogenation kinetics of the amorphous Mg-Ce-Ni alloys is too sluggish, and it needs to be further improved. In this study, a novel Mg<sub>65</sub>Ce<sub>10</sub>Ni<sub>20</sub>Cu<sub>5</sub> nanoglass was fabricated by melt spinning followed by severe plastic deformation through the high-pressure torsion (HPT) method. The hydrogenation temperature of the nanoglass was greatly reduced with significant improvements on the hydrogenation kinetics upon three different HPT treatments. The 1 turn HPT-treated alloy shows the best hydrogenation properties with the highest capacity and fastest kinetics among the three samples. These superior hydrogenation properties were attributed to the HPT-induced abundant nanoglasses regions and interfaces among them, as pathways for hydrogen absorption.

### **A01-30**

#### **Hydrolysis Batteries: Generating Electrical Energy during Hydrogen Absorption**

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The hydrolysis reaction of aluminum can be decoupled into a battery by pairing an Al foil with a Pd capped yttrium dihydride (YH<sub>2</sub>-Pd) electrode. This hydrolysis battery generates a voltage around 0.45 V and leads to hydrogen absorption into the YH<sub>2</sub> layer. This represents a new hydrogen absorption mechanism featuring electrical energy generation during hydrogen absorption. The hydrolysis battery converts 8 –15% of the thermal energy of the hydrolysis reaction into usable electrical energy, leading to much higher energy efficiency compared to direct hydrolysis of Al. The hydrolysis battery could be extended to that Al could be replaced by other active meta and YH<sub>2</sub>-Pd could be replaced by other hydrogen storage metal.

### **A01-31**

#### **Numerical simulation of dendrite growth and micro segregation of Ni-Cu alloy using phase-field method**

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Ni based alloy is a key materials in the modern industrial. which has an extremely widespread application. The difficulty in the simulation of dendrite growth is how to deal with a complex shape of solid-liquid interface. Phase field method can avoid tracking the solid-liquid interface directly by introducing a phase field variables, which improves calculation efficiency, so it is a hot research topic in microstructure simulation. Dendrite growth in under-cooled melt of Ni-40.83%Cu alloy is simulated by the phase-field method in the paper. The effect of super-cooling degree and super-saturation degree and solute segregation on dendrite growth is studied systematically. The results show that: solute segregation increases initially then tends to decrease. The increase of super-saturation can promote the growth of lateral branch and destroy the constancy of the dendrite tip at the same time. The simulation result is compared with the microscopic theory, and they have a good agreement.

### **A01-32**

#### **High Energy Density Li-S Battery and its Key Materials**

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##### **Introduction**

Lithium-sulfur (Li-S) batteries are one of the most promising future generation candidates to meet the ambitious long-lasting requirements because their theoretical capacity (1672 mAh/g) and low cost. However, the shuttle effect of soluble polysulfide intermediates still poses a considerable challenge. It is clear that investigating each individual component only is insufficient to address various technological challenges associated with Li-S batteries.

##### **Methods**

##### **Synthesis of OLCM**

1g ketjen black (ECP-600JD, Changxiang, Shanghai) was first refluxed in concentrated HNO<sub>3</sub> at 130 oC for 2 h to graft carboxyl groups onto the nanoparticles. The cleaned product was dispersed in 50 mL deionized water containing 0.5 g phytic acid (J&K). After heating at 80 oC for 2 h and subsequent cooling to room temperature, 0.7587 mL ethylene glycol (phytic acid: ethylene glycol, molar ratio of 1:18) and 0.87 g ammonium persulfate were slowly added to the mixture under vigorous stirring. Subsequently, the reaction heated at 130 oC for 6 h under stirring and refluxed overnight. After washed with ethanol and de-ionized water, and dried in the vacuum oven at 60 oC, the oval-like microstructure (OLM) was obtained. The black power was then heated to 1000 oC for 10 h under nitrogen gas flow to generate oval-like carbon microstructure (OLCM).

##### **Synthesis of ECP/S, ECP-COOH/S and OLCM/S cathode**

The ECP, ECP-COOH and as-synthesized OLCM (100 mg) were transferred into separate sodium thiosulfate solution (0.025 M, 3 L), respectively. After stirring intensely for 30 min, excess hydrochloric acid solution (1 M) was added dropwise to the solution and reacted for 4 h under both ultrasonic and mechanical agitation. For both the coin cells and pouch cell, OLCM/S was mixed with



carbon black and LA-132 binder in a mass ratio of 80: 12: 8, to produce the electrode slurry. The slurry was then coated onto an aluminum foil current collector. ECP/S and ECP-COOH/S were also produced for comparison, using a mass ratio of cathode materials, carbon black and LA-132 binder, is 73: 12: 15.

## Results

Commercial ECP nanoparticles have excellent conductivity and ultrahigh BET surface, and are typically used as a conductive additive. However, they do not readily adhere to substrates even at high binder content owing to their highly polarity. Fortunately, when the interactive potential exceeds the energy of thermal vibrations of small nanoparticles, they tend to agglomerate. Inspired from this phenomenon, we first modified the surface properties of ECP nanoparticles. Concentrated nitric acid was used as an oxidant because it can react with ECP nanoparticles to generate carboxyl functional groups (termed ECP-COOH). Ethylene glycol monomers were then added to initiate polymerization and reacted with phytic acid and carboxyl functional ECP nanoparticles via double “Fischer esterification” to form polyphosphate ester and polycarbonate ester, respectively. These esters act as cantilevers that can glue carboxyl functional ECP nanoparticles together at molecular levels and reconfigure the initially scattered ECP nanoparticles into oval-like microstructures (OLMs). The obtained microstructures can be used not only to reduce the explosion risk of materials and prevent materials from being inhalation hazards, but also provide materials with good flow and handling properties.

To enhance their cathode conductivity, the OLMs were carbonized at 1000 °C under nitrogen atmosphere, which led to the formation of oval-like carbon microstructures (OLCMs). After carbonization, the constituent nanoparticles were still connected via carbon originating from the polymer in the OLMs. Scanning electron microscopy (SEM) images confirmed that the OLCMs retained their oval-like microstructures after carbonization. The average diameter of the OLCMs increased from only ~70 nm for the original ECP nanoparticles to ~2.3 μm for the OLCMs secondary particles. Additionally, each resulting OLCM particles appeared to be loosely aggregated, although they consisted of tens of thousands ECP nanoparticles. Unlike the “point-to-point” electron transport in scattered ECP nanoparticles, OLCMs exhibited “omni-directional” and isotropic electron transportation, which is benefit for efficient electron transfer. Another benefit of these modularly assembled OLCMs structure is that the double-step esterification links the nanoparticles on a molecular scale, thus affording microstructures with structural tailorability and chemical diversity. Moreover, an architecture consisting of internal pinholes affords pores and a large electrolyte/electrode interface, thus providing channels for Li-ion diffusion and reactive sites for electrochemical reaction.

The large secondary micro-sized OLCM/S particles only require 8 wt% LA-132 binder (acrylonitrile copolymer) to prepare the cathode slurry. The cathode mixture could be uniformly coated on Al foil (0.35g/100cm<sup>2</sup>) even at a high double-sided high sulfur loading of 14.0 mg/cm<sup>2</sup>. The OLCM/S cathodes were then sandwiched with Li belts to assemble pouch cells and to further investigate their performance. The capacity of assembled pouch cell is 18.6 Ah and the average voltage is 2.05 V. Typical discharge curves with two plateaus are observed. Moreover, the cells operated suitably with an electrolyte to sulfur ratio of 2.7, which further demonstrated that electrolyte could easily infiltrate the thick electrode through internal channels. The highest discharge energy of the OLCM/S pouch cell was 52748.9 mWh, corresponding to 460.08 Wh/kg, which is much higher than that of traditional lithium ions batteries (150-200 Wh/kg).

## Conclusion

Our work provides a radically different approach for tuning the performance of a variety of surfaces for energy storage materials and biological applications by reconfiguring nanoparticles into desired structures.

## A01-33

### Rational Design of Cathode Materials for Lithium-Sulfur Batteries

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Recently, lithium-sulfur batteries (LSBs) have received extensive attention due to its high energy density of 2600 Wh kg<sup>-1</sup>. At the same time, sulfur is earth-abundant, economical, and non-poisonous. Nevertheless, the poor electrochemical performance restricts its commercial application, including the inferior cycling stability caused by the significant dissolution of lithium polysulfides and the low specific capacity because of the poor electrical conductivity of sulfur. To explore the potential application of LSBs in the

emerging electric vehicle market, sulfur/tubular polypyrrole (S/T-PPy) and sulfur/alumina/polypyrrole (S/Al<sub>2</sub>O<sub>3</sub>/PPy) are prepared by cooperating on the facile ball-milling route and in-situ chemical polymerization method. In this strategy, each composition of the hybrid materials plays an essential role in cathode: alumina and PPy can provide strong adsorption for the dissolved polysulfides. Meanwhile, PPy also works as a conductive and flexible additive to improve poor conductivity of sulfur and Al<sub>2</sub>O<sub>3</sub>. Compared with sulfur, S/T-PPy and S/Al<sub>2</sub>O<sub>3</sub>/PPy manifests good electrochemical performance. S/T-PPy displays high initial discharge capacity of 1178 mAh g<sup>-1</sup>, and a discharge capacity of 675 mA h g<sup>-1</sup> after 150 cycles at a current density of 200 mA g<sup>-1</sup>. The special tubular structure of T-PPy can increase adsorption sites for polysulfides to inhibit its diffusion. In the same current density, the discharge capacity of S/Al<sub>2</sub>O<sub>3</sub>/PPy is maintained at 730 mAhg<sup>-1</sup> after 100 cycles. Besides, S/Al<sub>2</sub>O<sub>3</sub>/PPy also shows good rate capability. The synergy between alumina and PPy is the decisive factor, which gives rise to good electrochemical performance of cathode for high-performance LSBs.

#### **A01-34**

##### **The Design, Synthesis and Structure-Performance Relationship of Cathode Catalysts for Li-air Batteries**

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Recently, rechargeable Li-air batteries have attracted extensive attention due to their high energy density. However, the poor cycling stability, low rate capability, low coulombic efficiency, high charge-discharge voltage gap and some other problems hinder the practical application of Li-air battery. The sluggish kinetics of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) on the cathode is one of the biggest challenges for Li-air batteries. One effective way to solve this issue is to develop efficient cathode catalysts. Some noble metals or alloys, metal oxides and nanostructured carbon materials have been extensively studied as cathode catalysts to facilitate ORR/OER and enhance the electrochemical performances of Li-O<sub>2</sub> battery. In this talk, I will present some recent studies on the surface or interface structures modulation and the structure-performance relationship of some transition metal oxides based cathode catalysts in our group: 1) The role of oxygen vacancies in improving the performance of CoO as bifunctional cathode catalyst for rechargeable Li-O<sub>2</sub> batteries; 2) Carbon-dotted defective CoO with oxygen vacancies: A synergetic design of high performance cathode catalyst for Li-O<sub>2</sub> batteries; 3) Boosting the electrocatalytic activity of Co<sub>3</sub>O<sub>4</sub> nanosheets for Li-O<sub>2</sub> battery through modulating inner oxygen vacancy and exterior Co<sup>3+</sup>/Co<sup>2+</sup> ratio. (4) Enhancing the catalytic activity of Co<sub>3</sub>O<sub>4</sub> for Li-O<sub>2</sub> battery through the synergy of surface/interface/doping engineering.

#### **A01-35**

##### **Synthesis of TiO<sub>2</sub>-C nano-sheets by high-energy ball milling Ti<sub>2</sub>CT<sub>x</sub> for enhanced performance photocatalysts**

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Titania-carbon composite materials (TiO<sub>2</sub>-C) have aroused a great deal of interest in photocatalytic application, because carbon could effectively enhance the photocatalytic ability of TiO<sub>2</sub>. In this paper, we introduce high-energy ball milling technique and Ti<sub>2</sub>CT<sub>x</sub> precursor to produce TiO<sub>2</sub>-C composites (as shown in scheme 1). Firstly, the mechanical forces during ball milling could easily break the van der Waals force between interlayers of stacked Ti<sub>2</sub>CT<sub>x</sub>, formation of single or few layered Ti<sub>2</sub>CT<sub>x</sub> (T stands for terminated with O and OH groups) nanosheets. The decreased thickness makes the oxygen traveling through the Ti<sub>2</sub>CT<sub>x</sub> layers facile. Secondly, huge dynamic energies will be generated when the impact occurs between the high-energy balls and/or jars, which lead to instantaneous increases of the temperatures. The increased temperatures contribute to the migration of the atoms, and the occurrences of chemical reactions between Ti<sub>2</sub>CT<sub>x</sub> nanosheets and penetrated oxygen. Thirdly, structural and morphological properties of crystals could be modified by mechanical force, for example, activation of electrons in the crystal lattices; diffusion of defects; decrease of crystal size and so on.

The formation of the TiO<sub>2</sub> nano-particles and disordered graphitic carbon is identified by XRD, Raman and HRTEM. Results performed that the TiO<sub>2</sub> nanoparticles were uniformly and closely dispersed on the single or few-layered carbon nano-sheets. Many defects are also observed on TiO<sub>2</sub> nano-particles in HRTEM images. XPS results show the existence of Ti<sup>3+</sup> ions and C-Ti-O bands in TiO<sub>2</sub> lattice. And, the hybrids as photocatalysts performed higher capacity than P25 in enhancing photocatalytic degradation of

methylene blue (MB) dye in aqueous solution under UV-irradiation. The higher enhancement is attributed to the effective separation of photo-excited charge carriers by the perfect structural properties, presence of C, Ti<sup>3+</sup> ions and oxygen vacancies. Moreover, the TiO<sub>2</sub>@C catalyst possesses high photocatalytic stability.

#### A01-36

### **Insight into factors behind the different pseudocapacitance contributions of amino-contained aromatic isomers adsorbed onto graphene**

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#### 1. Aims

This study combines experiment and theory to unveil factors behind the different pseudocapacitance contributions of some aromatic isomers adsorbed onto graphene, aiming to provide a guideline for computationally screening out optimal molecules that can endow graphene with high pseudocapacitance.

#### 2. Methods

In this work, we prepared paper-like nitrogen-doped graphene (NG) films to investigate the effect of organic molecules functionalization on the capacitance enhancement. In brief, a viscous aqueous solution containing GO, NaCl, urea, and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> at a certain ratio was blade-coated to prepare hydrogel-like films. After naturally dried in air, the composite film was transferred into a Teflon-lined autoclave containing diluted ammonia solution for hydrothermal reduction at 180 °C, 3 h. After that, the paper-like NG film was obtained. Then, the NG film was immersed into the organic compound solution at 80 °C for 6 h to allow aromatic molecules to be spontaneously adsorbed onto graphene via  $\pi$ - $\pi$  interaction. After, the functionalized NG (FNG) film was repeatedly washed with DI water. The organic compounds are 4-aminophenol (AP), 2-AP, 1,5-naphthalenediamine (NAPD), 1,8-NAPD, 4,4'-oxydianiline (ODA), 3,4'-ODA, 4,4'-thiodianiline (TDA), and 2,2'-TDA.

Symmetric cells and a three-electrode system using with 1 M H<sub>2</sub>SO<sub>4</sub> electrolyte were assembled to measure the electrochemical performance of these FNG films. The organic molecules with optimized structures were computed by using the Gaussian 09 software package. The solvation model SMD and meta-GGA density functional M063 with the 6-31+G (d, p) all-electron basis set and ultrafine integration grids were used.

#### 3. Results and conclusions

In summary, we have carried out a systematic study, both experimentally and theoretically, to unveil factors behind the pseudocapacitance contribution of amino-contained aromatic molecules adsorbed onto graphene. Eight kinds of organic compounds were selected to functionalize NG films, and their efficacies in enhancing the capacitance were correlated with density functional theory calculations. The highest occupied molecular orbital level of a molecule is found to play an important role in rendering high pseudocapacitance. Also, remarkable efficacies from two kinds of molecules, 4-aminophenol and 1,5-naphthalenediamine, are newly discovered. As a result, a high specific capacitance of 877 F g<sup>-1</sup> is achieved from the functionalized graphene film. This work provides a theoretical clue for screening out optimal candidates from a large variety of redox-active organic molecules, aiming to efficiently exploit the redox of amino groups for energy storage.

#### A01-37

### **Influence of Manganese Dioxide Catalyst on Electrochemical Performances of Magnesium Air Battery**

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Magnesium air battery is a promising electrochemical energy storage and conversion device due to its high energy density, high safety, environmental benignity, and earth abundance of Mg. Low-cost, earth-abundant electrocatalysts of the oxygen reduction reaction (ORR) at the cathode is essential for magnesium air battery. Electrolytic manganese dioxide (EMD) is the most attractive for ORR due to its cheaper price.

The electrochemical properties of MnO<sub>2</sub> materials strongly depend on their crystal structure and morphology. In this study, the influences of ball-milling and thermal treatment on the structure and discharge performance of commercial EMD were studied.

It is found that the morphology of commercial EMD was obviously changed from irregular shape to spherical particles with a

significant decrease in particle size after ball-milling, and the crystal phase of commercial EMD converted from  $\gamma$ -MnO<sub>2</sub> to  $\beta$ -MnO<sub>2</sub> via thermal treatment. EMD as electrocatalyst by ball-milling or heat treatment in magnesium air battery exhibited much higher discharge performance in comparison with the commercial EMD.

Consequently, controlling the morphology and crystal structure of electrolytic manganese dioxide as cathode catalysts of magnesium air battery is important for both fundamental research and technological applications.

#### A01-38

##### **In-situ growth of MoS<sub>2</sub> on hollow carbon fibers derived from biomass for lithium and sodium storage**

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With the ever-growing demands for clean, efficient and sustainable energy, much attention has been attracted to the cutting-edge energy storage technologies.[1] Of which lithium ion batteries (LIB) and sodium ion batteries (SIB) has been accepted as the most feasible technologies, considering their high energy density, long lifespan, low discharge feature and environmental friendliness.[2-3] Even so, significant research efforts are being directed towards developing batteries with higher energy densities and better cyclic life, for that the specific capacity of the commercial graphitic anode for LIB is only 372 mAh g<sup>-1</sup>. [4-5] MoS<sub>2</sub>, a typical 2D materials, has been extensively employed as the anode materials for LIB and SIB, because of the high theoretical capacity (670 mAh g<sup>-1</sup>) and good cyclic performance, in addition the interlayer space with weak van der Waals interaction is large for the lithium and sodium ions intercalation/deintercalation.[6-10] Unfortunately, the low conductivity of sulfides, large volume variation and limited electron transfer between S-Mo-S sheets always leading to poor electrochemical reversibility, inferior rate performance and unsatisfied cyclic lifespan.[6, 11-12]

Herein, MoS<sub>2</sub> grown on hollow carbon fibers (CF) derived from palm silk via a hydrothermal method has been demonstrated for lithium and sodium storage. The hollow carbon fiber derived from palm silk was selected as the matrix to grow MoS<sub>2</sub> nanosheets. In this composite, the in-situ growth MoS<sub>2</sub> on CF results in a strong interaction between MoS<sub>2</sub> and CF, which prevents the agglomeration of MoS<sub>2</sub> nanosheets and favors the transport of electron and ion between MoS<sub>2</sub> and CF. The smaller nanosheets of MoS<sub>2</sub> on CF and abundant pores can effectively shorten the diffusion paths for ions and electrons, facilitating the electrode reaction kinetics. Finally, the hollow carbon layer can provide space for the expansion/contraction effect of MoS<sub>2</sub> during charge and discharge. Thanks to the above advantages, the prepared CF@MoS<sub>2</sub> shows good lithium storage performance (at a current density of 500 mA·g<sup>-1</sup> after 500 cycles, a high electrical capacity of 725 mAh·g<sup>-1</sup> is maintained), superior rate performance (at a current density of 3 A·g<sup>-1</sup>, the capacity is the 51.6 % of the capacity is 0.1 A·g<sup>-1</sup>) for LIB. At the same time, a tolerable performance for SIB are also obtained, typically, at a current density of 50 mA·g<sup>-1</sup> after 200 cycles, a high electrical capacity of 198 mAh·g<sup>-1</sup> is maintained; and at a current density of 2 A·g<sup>-1</sup>, the capacity is the 60 % of the capacity is 0.05 A·g<sup>-1</sup>.

References:

- [1].Hu, Y. S.; Demir-Cakan, R.; Titirici, M. M.; Muller, J. O.; Schlogl, R.; Antonietti, M.; Maier, J., Superior storage performance of a Si@SiOx/C nanocomposite as anode material for lithium-ion batteries. **Angewandte Chemie International Edition** 2008, 47 (9), 1645-1649.
- [2].Zhai, W.; Ai, Q.; Chen, L.; Wei, S.; Li, D.; Zhang, L.; Si, P.; Feng, J.; Ci, L., Walnut-inspired micro-sized porous silicon/graphene core-shell composites for high-performance lithium-ion battery anodes. **Nano Research** 2017, 10 (12), 1-10.
- [3].Xu, Z.-L.; Cao, K.; Abouali, S.; Akbari Garakani, M.; Huang, J.; Huang, J.-Q.; Kamali Heidari, E.; Wang, H.; Kim, J.-K., Study of lithiation mechanisms of high performance carbon-coated Si anodes by in-situ microscopy. **Energy Storage Materials** 2016, 3, 45-54.
- [4].Zhao, J.; Zhou, G.; Yan, K.; Xie, J.; Li, Y.; Liao, L.; Jin, Y.; Liu, K.; Hsu, P. C.; Wang, J.; Cheng, H. M.; Cui, Y., Air-stable and freestanding lithium alloy/graphene foil as an alternative to lithium metal anodes. **Nature Nanotechnology** 2017, 12 (10), 993-999.
- [5].Choi, S. H.; Kang, Y. C., Enhanced Li<sup>+</sup> storage properties of few-layered MoS<sub>2</sub>-C composite microspheres embedded with Si nanopowder. **Nano Research** 2015, 8 (8), 2492-2502.
- [6].Li, X.; Feng, Z.; Zai, J.; Ma, Z.-F.; Qian, X., Incorporation of Co into MoS<sub>2</sub>/graphene nanocomposites: One effective way to enhance the cycling stability of Li/Na storage. **Journal of Power Sources** 2018, 373, 103-109.

- [7]. Wang, G.; Zhang, J.; Yang, S.; Wang, F.; Zhuang, X.; Müllen, K.; Feng, X., Vertically Aligned MoS<sub>2</sub> Nanosheets Patterned on Electrochemically Exfoliated Graphene for High-Performance Lithium and Sodium Storage. **Advanced Energy Materials** 2018, 8 (8), 1702254.
- [8]. Wang, T.; Chen, S.; Pang, H.; Xue, H.; Yu, Y., MoS<sub>2</sub>-Based Nanocomposites for Electrochemical Energy Storage. **Advanced Science** 2017, 4 (2), 1600289.
- [9]. Wang, L.; Zhang, Q.; Zhu, J.; Duan, X.; Xu, Z.; Liu, Y.; Yang, H.; Lu, B., Nature of extra capacity in MoS<sub>2</sub> electrodes: Molybdenum atoms accommodate with lithium. **Energy Storage Materials** 2019, 16, 37-45.
- [10]. Zhang, Z.; Zhao, H.; Teng, Y.; Chang, X.; Xia, Q.; Li, Z.; Fang, J.; Du, Z.; Świerczek, K., Carbon-Sheathed MoS<sub>2</sub> Nanothorns Epitaxially Grown on CNTs: Electrochemical Application for Highly Stable and Ultrafast Lithium Storage. **Advanced Energy Materials** 2018, 8 (7), 1700174.
- [11]. Kumar, P. R.; Jung, Y. H.; Kim, D. K., High performance of MoS<sub>2</sub> microflowers with a water-based binder as an anode for Na-ion batteries. **Rsc Advances** 2015, 5 (97), 79845-79851.
- [12]. Jung, J. W.; Ryu, W. H.; Yu, S.; Kim, C.; Cho, S. H.; Kim, I. D., Dimensional Effects of MoS<sub>2</sub> Nanoplates Embedded in Carbon Nanofibers for Bifunctional Li and Na Insertion and Conversion Reactions. **Acs Applied Materials & Interfaces** 2016, 8 (40), 26758-26768.

### A01-39

#### Starfish-like Hierarchical Zn<sub>x</sub>Co<sub>1-x</sub>S@C@CNTs as high performance anode materials for lithium ion batteries

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**Aims:** Transition metal sulfides are promising anodes for lithium-ion batteries due to their high theoretical specific capacity, natural abundance and environmental friendliness. Among this, ZnS has attracted tremendous interests due to its high theoretical capacity (962 mAh g<sup>-1</sup>) and non-toxic properties. However, poor cycling stability and rate performance which result from low conductivity and large volume change during charge-discharge process hinder its application. It's of great significance to find proper solution to address this concern.

**Methods:** Doping alien metals can greatly improve the intrinsic conductivity of metal sulfides. And dedicate architectures fabrication, especially the hierarchically porous structure can greatly shorten the diffusion lengths of Li-ions and buffer the strain caused by volume change. On the other hand, hybridizing ZnS with carbon materials is another way to enhance its electrical performance. Here we designed a novel nanocomposite by combining all three strategies into one to address the problem. The composite was prepared by a simple method, which includes the co-precipitation of Zn<sup>2+</sup>, Co<sup>2+</sup> and 2-methylimidazole in the presence of CNTs to form a Zn-Co-ZIFs@CNTs as precursor and subsequent simultaneously in situ pyrolysis and sulfidation of precursor at high temperature to obtain the final starfish-like Zn<sub>x</sub>Co<sub>1-x</sub>S nanoparticles rooted in porous carbon framework and strongly coupled with carbon nanotubes (Zn<sub>x</sub>Co<sub>1-x</sub>S@C@CNTs).

**Results:** When evaluated as anode materials for lithium ion batteries, Zn<sub>x</sub>Co<sub>1-x</sub>S@C@CNTs exhibited an excellent reversible capacity of 635 mA h g<sup>-1</sup> at a high current density of 1.2 A g<sup>-1</sup> after 1000 cycles and good high-rate capability (890 mA h g<sup>-1</sup> at 3.2 A g<sup>-1</sup> and 750 mA h g<sup>-1</sup> at 6.4 A g<sup>-1</sup>, respectively).

**Conclusions:** The high capacity, excellent cycling stability and rate capability of Zn<sub>x</sub>Co<sub>1-x</sub>S@C@CNTs can be ascribed to the unique hierarchically porous structure which integrates the high theoretical capacity of Zn<sub>x</sub>Co<sub>1-x</sub>S and the excellent conductivity as well as mechanical stability of CNTs. And the doped Co-ions have improved the intrinsic electrical conductivity of metal sulfides by increasing donor density. We believe that the strategy presented here can be extended to other metal oxide/sulfide-based composites for the preparation of high-performance anodes for lithium ion batteries.

### A01-40

#### 高容量储氢材料的热力学和动力学调控

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基于固态储氢材料的储能方式具有储能密度高和安全性能好的优势，是极具发展前景的储能技术。各种移动和固定式储氢装置不仅要求较高的重量/体积储氢容量、适宜的工作氢压，同时要求较低的工作温度和快速吸/放氢速率，因此迫切需开发具有良好热力学和动力学性能的高容量储氢材料。针对含 Mg, Li, Na, Al, B, N 等轻元素的金属氢化物、络合氢化物、氨基氢化物、化学氢化物等高容量储氢材料，世界各国学者发展了多种行之有效的热力学与动力学改善策略。本文重点介绍镁基金属氢化物的热力学与动力学性能研究进展，一方面探讨了合金化、多相反应、纳米尺度弹性约束对镁氢化物反应焓、反应熵、平衡压等热力学参数的调变效果，另一方面则重点讨论不同纳米技术及催化剂对镁氢化物吸/放氢反应的促进作用及机理。我们认为在多相复合体系中综合运用多种策略实现氢化物热力学与动力学性能的同时调控是未来储氢材料的重要发展方向。

#### A01-41

##### **A new AB<sub>4</sub>-type single-phase superlattice compound for electrochemical hydrogen storage**

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Metal-hydride (MH) based hydrogen storage materials have recently been designed for rechargeable batteries where protons serve as charge carriers. However, the MHs generally suffer from poor cycling stability during electrochemical hydrogen storage process. Herein, we report, for the first time, a new AB<sub>4</sub>-type single-phase La<sub>0.78</sub>Mg<sub>0.22</sub>Ni<sub>3.67</sub>Al<sub>0.10</sub> MH superlattice compound with excellent electrochemical hydrogen storage properties. This MH compound is able to deliver a high discharge capacity of 393 mAh g<sup>-1</sup>, according to its hydrogen gas absorbability (1.50 wt%), and exhibit a superior rate capability of 180 mAh g<sup>-1</sup> even at 1.8 A g<sup>-1</sup>. In addition, the compound retains its crystalline structure when subjects to electrochemical cycling and shows strong anti-oxidation ability in alkaline electrolyte, indicative of excellent cyclability. Our results demonstrate that the AB<sub>4</sub>-type superlattice structure MH can be a promising electrode material for hydrogen storage, and provide a new avenue for the applications of MH batteries.

#### A01-42

##### **Design and effective catalysis of hybrid catalyst on hydrogen sorption kinetics of magnesium-based hydride**

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Hydrogen storage has been regarded as the key to the utilization of hydrogen energy. Reversible hydrogen storage by magnesium-based hydride has been widely studied due to several advantages, including large hydrogen storage capacity, abundant resource and low cost. However, the high operating temperature and slow hydrogen sorption kinetics still restrict its application. To solve this, we have designed several hybrid catalysts, including bimetallic catalyst, carbon supported nano metal or metal oxide, metal/metal halide, etc. The as-prepared hybrid catalyst was added into magnesium-based hydride by mechanical milling. Then, the structural and hydrogen storage performances of the Mg-based hydride composite were studied systematically. Compared with the single-component catalyst, the multi-component hybrid catalyst exhibits superior catalysis on hydrogen sorption kinetics of magnesium-based hydride. In particular, the obvious synergistic catalytic effect between the catalyst components has been clarified. Owing to the effective catalysis of the as-prepared hybrid catalyst, the magnesium-based hydride shows greatly improved hydrogen sorption kinetics. Moreover, the catalytic activity can be well remained upon repeated hydrogenation/dehydrogenation cycling. Our results show that the magnesium-based hydrides enhanced by hybrid catalyst are promising for solid-state hydrogen storage.

#### A01-43

##### **Superwetting Nanoarray Electrodes for Gas-involving Electrocatalysis**

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Electrochemical gas-involving reactions are now of great importance in energy conversion processes and industries. Besides

highly active catalysts, the fast diffusion of reactants/intermediate and desorption of products on the catalyst surface are of critically importance. Based on this principle, micro/nano-engineering of the catalyst directly on the current collector are fabricated. Specifically, we demonstrated the effectiveness of the low-adhesion surface according to the structural designing (MoS<sub>2</sub>, Pt, Cu, layered double hydroxide nanoarray) with superaerophobic properties, which exhibit excellent HER, OER and HzOR performance. These electrodes significantly decrease the surface solid fraction and cut triple phase (solid–liquid–gas) contact line into discontinuous dots, and thus small bubble's volumes and low viscosity between electrode and gas bubbles are realized, thereby achieving enhanced electrocatalytic activity. On the contrary, providing an unobstructed gas-diffusion pathway to continually supply enough gas reactant to the active catalytic sites is vital for gas consumption reactions. A micro-/nanostructured and PTFE-modified CoNCNTs arrays with superaerophilic properties, which accelerate the gas-diffusion process as well as electron transport, shows superior ORR performance in both base and acid media. In summary, rational structural design of both highly activity and surface wettability is critically important for highly efficient and stable heterogeneous electrochemical reactions.

#### A01-44

##### **Layered/Spinel Lithium-Rich Oxide Nanowires as Excellent Performance Cathode Materials for Lithium-Ion Batteries**

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Lithium-rich cathode materials have attracted great attention due to their less environmental impact, low cost, high capacity and wide working voltage range. However, their low cycling performance, poor rate capability and severe voltage decaying impede their commercial applications.<sup>[1, 2]</sup> To cure these issues, herein we report an efficient strategy to fabricate high-rate and cycling-stable lithium-rich oxide nanowires with layered/spinel heterostructure by using a solvothermal method and subsequent high-temperature calcination technique. The structure and electrochemical performance of this cathode have been systematically investigated and the results reveal that the layered/spinel heterostructured nanowires are a kind of self-assembly of a lot of nanoparticles, and the Li<sub>4</sub>Mn<sub>5</sub>O<sub>12</sub> spinel phase is embedded inside the layered structure, which are in favor of Li<sup>+</sup> transport kinetics and structural stability during the charge/discharge process. Benefitting from the unique architecture, this novel cathode material reciprocates a high initial reversible capacity (289 mAh g<sup>-1</sup>), excellent cycling performance (94% capacity retention after 200 cycles at 0.5 C) and mitigated voltage fading. Moreover, it exhibits an outstanding rate capability and can achieve about 63.7% (184 mAh g<sup>-1</sup>) of the capacity at 0.1 C during ultrafast charging/discharging (10 C). The favorable results provide a feasible route to enhance the electrochemical performance of lithium-rich cathode material for constructing the high-energy and high-power lithium-ion batteries.

References:

- [1] S. Chu, Y. Cui, N. Liu, The path towards sustainable energy, *Nat. Mater.* 16 (2017) 16-22.
- [2] J. Lee, D.A. Kitchaev, D.-H. Kwon, C.-W. Lee, J.K. Papp, Y.-S. Liu, Z. Lun, R.J. Clément, T. Shi, B.D. McCloskey, J. Guo, M. Balasubramanian, G. Ceder, Reversible Mn<sup>2+</sup>/Mn<sup>4+</sup> double redox in lithium-excess cathode materials, *Nature*, 556 (2018) 185-190.

#### A01-45

##### **Microchanneled supporting electrodes of solid oxide cells: fabrication and applications**

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Solid oxide cells, including solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs), have a sandwich structure supported on an electrode, cathode or anode. The electrode-supporting configuration has replaced the initial electrolyte-supporting cells to reduce cell resistance. However, the thick supporting electrodes (0.5~1 mm) can cause gas diffusion limitation during cell operation. Firstly, electrolyte film supported on electrodes is densified *via* high temperature sintering of the double layers, which causes the low porosity of the supporting electrodes. Particulate pore former is employed to increase porosity, but it is not efficient because the formed pores have low connectivity. Gas diffusion pathway through tortuous pore channels greatly extends gas diffusion distance to 2~5 times. In addition, applying nanocatalysts over electrodes is an effective way to accelerate electrode reaction, which is prepared by infiltrating catalyst precursor solution into porous electrodes. However, it is not efficient to deliver catalyst precursor

to the electrode/electrolyte interface like the gas diffusion.

Some researchers had devoted to develop new electrode microstructure to improve gas diffusion. Porosity-graded anodes include several layers with different porosities, and these layers were prepared with different pore former amounts and/or ceramic particle sizes [1]. In addition to multistep preparation, sintering shrinkage match among layers need to be carefully considered to avoid deformation or crack formation. A channeled microstructure of anode supports was formed by freeze-drying, forming channel sizes ranging from 10 to 20  $\mu\text{m}$ , which is not ideal for supporting dense electrolyte and constructing three-phase-boundary within electrode reaction zone [2]. A phase-inversion process has been used to prepare hollow fibre anodes with embedded finger-like pores with the consequence that it cannot perform gas diffusion effectively due to a less-porous skin layer [3]. Efforts have been made to open the finger-like pores, requiring additional steps or accurate control of phase-inversion process.

Our group, for the first time, developed phase-inversion process to prepare planner ceramic membranes as oxygen separation membrane and supporting electrodes of solid oxide cells. With the aid of stainless steel mesh during the phase-inversion, microchanneled membranes have been developed with an integrated structure formed by a single process; numerous parallel channels are formed with one end open on one side and the other end closed with a separation layer on the other side of the membrane [4, 5]. The as-prepared oxygen separation membranes exhibited high oxygen permeation fluxes owing to improved gas diffusion compared with conventional porous supported membranes [6]. The microchanneled membranes have been demonstrated as anode supports of SOFCs and cathode supports of SOECs, providing channels as fast gas diffusion pathways [7, 8]. Additionally, the channels facilitate catalyst delivery to the electrode reaction zone for  $\text{CO}_2$  electrolysis [9, 10].

A second generation of microchanneled membranes has been developed by modifying the phase-inversion process [11], and the membranes have a dendritic pore channel structure. The pore channels start from one side of the membranes and gradually split into small channels like tree root while crossing the membrane, ending up with a thin layer about  $5\mu\text{m}$  in thickness on the other side of the membranes. The naturally formed channel structure provide efficient mass transfer pathway for gas diffusion and catalyst delivery. Compared to the cell prepared with the first generation of the membranes, the cells with dendritic pore channels have demonstrated higher performances under both SOEC and SOFC modes in terms of gas diffusion and electrode polarization resistance. The microstructure optimization of the supporting electrodes has been attempted to achieve high cell performances. The potential applications of the second generation membranes will be discussed.

## **A01-46**

### **A stability study of flat-tubular solid oxide fuel cells with double-side cathodes**

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#### 1. Objectives

Fuel cells are capable of directly converting chemical energy in fuels to electricity with high efficiency and low pollutant emission. Among various kinds of fuel cells, solid oxide fuel cells (SOFCs) have been attracting intensive attentions from academic and industrial communities due to their unique advantages compared with other kinds of fuel cells. The most important characteristic of SOFCs is that SOFCs employ metal oxides, exemplified by yttria-stabilized zirconia (YSZ), as the electrolytes. Since the oxide electrolytes gain sufficient ionic-conductivity only at high temperatures, current SOFCs are mainly operated 600-800  $^{\circ}\text{C}$ . Such high operating temperatures lead to significant challenges to the stability of SOFCs: (1) chemical stability and compatibility; (2) mechanical stability under severe temperature variation; (3) mechanical stability against redox cycle of Ni-based anode. The chemical stability and compatibility are mainly guaranteed by selecting suitable materials for the components. On the other hand, the cell structure plays key role on the mechanical stability of SOFCs.

In previous research, our group developed a novel flat-tubular SOFC structure with double-sided cathodes (DSC cells). Such cell structure integrated the advantages of planar and tubular cells namely ease for current collecting and sealing. Compared with the flat-tubular structure developed by Kyocera, two cathodes are deposited symmetrically on double side of the cell. As a result, the cell gains larger cathode area. Moreover, the integration of cells into a stack becomes much easier.



In this study, the stability and durability of the DSC cells with the cathode area of 180 cm<sup>2</sup> were investigated in three aspects: (1) long-term performance; (2) resistance to thermal cycling test; (3) resistance to sudden fuel cut-off.

## 2. Methodes

DSC cells with a dimension of 10 cm \*10 cm\*0.6 cm were used for the tests. The total area of two symmetric cathodes was 180 cm<sup>2</sup>. Air and pure hydrogen were supplied to the cathode and anode, respectively. For long-term stability test, the cell was discharged at 36 A at 750°C for 500 h. A thermal cycling test between room temperature and 750°C was conducted for the cell. The OCV and *I-V* characteristics of the cell were measured to evaluate the cell performance after thermal cycle test. The cell was discharged for a short period under a sudden fuel cut-off condition. Then, the fuel supplied was recovered and the OCV was monitored. Such operation was repeated for 13 cycles and subsequently the *I-V* characteristics were measured.

## 3. Results

1. long-term performance under constant discharge current and temperature: the degradation of the cell at 500 h was negligible, demonstrating the good long-term stability of the novel cell structure.

2. Resistance to the thermal cycling test: After 4 cycles, the OCV of the cell remained unchanged, indicating the sealing condition was not damaged. After the first cycle, some performance degradation was observed by *I-V* characteristics. However, the subsequent three thermal cycles did not cause more performance degradation.

3. Resistance to fuel cut-off: the results revealed that the new cell structure provide a good resistance for the discharge at low current density under fuel cut-off condition. However, the cell was damaged rapidly when the discharge current increased.

## 4. Conclusions

The novel cell structure was proved to possess good durability and stability to three kinds of operating conditions.

### A01-47

#### **The Rational Design of Nanocarbon and Metal Composite Materials for Lithium–Sulfur Battery Cathode: Li- or S-Binding?**

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Lithium–sulfur (Li–S) battery is considered as an ideal next-generation energy storage device for its high energy density. However, the poor electroconductivity of sulfur and its reduced products (Li<sub>2</sub>S and Li<sub>2</sub>S<sub>2</sub>) and the well-known “shuttle” of soluble sulfides have resisted its practical applications. Conductive materials, like carbon nanotube, graphene, and their hybrids, have been used to increase the conductivity of cathode materials, but these materials cannot provide strong binding effects towards soluble lithium polysulfides. We apply first-principles calculations to systematically investigate heteroatom-doping (B, N, O, F, P, S) effect in enhancing the binding between cathode materials and polysulfides. Then an implicit volcano plot is obtained to describe the dependence of binding energies on electronegativity of dopants and the N, O co-doping strategy is predicted to achieve even stronger interfacial interaction to trap lithium polysulfides. The strong anchoring effect between N/O-doped nanocarbon and polysulfides was further verified induced by the Li-binding, called “Li bond”. Besides, various metal composites have been considered as additives to enhance the binding effects and promoting the conversion of high-order polysulfides. An analogous periodic law of anchoring strength was find in 3D-metal sulfide system, which can be extended well to the 3D-metal oxide system well, and VS was predicted to be an excellent polar host candidate for sulfur cathodes. This finding provides a general and practical principle for rational design of advanced sulfur cathode materials, which is expected to be an effective toolbox to screen composite sulfur cathode for Li–S batteries with high energy density and long cycle life.

### A01-48

#### **Improved structural reversibility and cycling stability of Li<sub>2</sub>MnSiO<sub>4</sub> cathode materials for lithium-ion batteries**

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Li<sub>2</sub>MnSiO<sub>4</sub> cathode material possesses a high theoretical capacity ~330 mAh/g for lithium ion batteries. However, Li<sub>2</sub>MnSiO<sub>4</sub> suffers from structural collapse caused by irreversible transition of [MnO<sub>4</sub>] tetrahedrons to [MnO<sub>6</sub>] octahedrons and layer exfoliation

upon full delithiation. In addition,  $\text{Li}_2\text{MnSiO}_4$  is generally accompanied with impurities, such as  $\text{Li}_2\text{SiO}_3$ ,  $\text{Mn}_2\text{SiO}_4$  and  $\text{MnO}$ , which inevitably results in capacity loss. Pure  $\text{Li}_2\text{MnSiO}_4$  has been successfully synthesized by a two-step method. A central goal is to alleviate the structural collapse during cycling and thus achieve a stable cycling performance. We have exploited *Ti and S substitution* for high Coulombic efficiency, cycling stability and structural reversibility.

*For alleviating the irreversibility of  $[\text{MnO}_x]$  polyhedrons:*  $[\text{TiO}_4]$  tetrahedrons and  $[\text{TiO}_6]$  octahedrons coexisted  $\text{Li}_2\text{MnSiO}_4$  has been synthesized.  $[\text{TiO}_x]$  pillared  $\text{Li}_2\text{MnSiO}_4$  presented greatly improved cycling stability, especially  $[\text{TiO}_6]$  enriched  $\text{Li}_2\text{Mn}_{0.85}\text{Ti}_{0.15}\text{SiO}_4$ , which achieved a high initial Coulombic efficiency (86%) and excellent capacity retention (89% at 8<sup>th</sup> cycles for instance). Moreover,  $\text{Li}_2\text{Mn}_{0.85}\text{Ti}_{0.15}\text{SiO}_4$  exhibited excellent rate performance and retained 85% of initial discharge capacity after 50<sup>th</sup> cycles at C/2 rate. *Ex-situ* XPS revealed  $[\text{TiO}_x]$  pillars, especially  $[\text{TiO}_6]$  pillars facilitated the reversible transition of  $[\text{MnO}_x]$  during cycling. *Ex-situ* XRD demonstrated the enhanced structure reversibility of  $[\text{TiO}_6]$  enriched sample.

*For relieving the layer exfoliation:* we introduced S into O sites of  $\text{Li}_2\text{MnSiO}_4$ . The solid solubility of S was proved to be limited and excess S resulted in MnS impurity. The existence state and site of S element in  $\text{Li}_2\text{MnSiO}_4$  was also confirmed. It was found that S doping significantly improved not only the electronic and ionic conductivity but also the structural reversibility and cycling stability. 1mol% S doped sample exhibited a remarkable initial Coulombic efficiency (88.3%), capacity retention (98% at 10<sup>th</sup> cycles for instance) and rate performance.

#### A01-49

##### A First-principle Study towards Understanding Surface Reactions in Li-I Batteries.

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Hunan University

Large-scale stationary energy storage urgently demands to develop rechargeable batteries with low cost, high energy density, and enhanced cycling stability. Beyond conventional Li-ion batteries, secondary Li-I2 batteries based on the conversion reaction mechanism is considered as a promising next-generation energy storage device. However, Li-I2 batteries also suffer shuttle effect caused by the high solubility of iodine in the organic electrolyte.

A first-principles approach is employed to probe the effect of I2 molecules on corroding the metallic Li anode surface. It is found that the I2 molecule always tends to dissociate to two I atoms on the Li surface. Electrons in the metallic substrate spontaneously migrate to I atoms, resulting in the self-discharge. According to the *ab-initio* molecular dynamics simulation, the metallic Li surface can be oxidized to LiI species. LiI species cannot binding to the metallic substrate strongly and will be exfoliated easily, leading to the loss of active materials and irreversible capacity fade. According to the present simulation,  $\text{LiNO}_3$  additive can also prevent the Li surface from the iodization corrosion. The  $\text{NO}_3^-$  group can completely dissociate and penetrate into the Li substrate, result in forming a protective ternary compound layer. This layer can provide a strong affinity to LiI species, leading to alleviating the loss of active materials. Beyond  $\text{LiNO}_3$  additive, using N-doped graphene is another strategy to improve the battery performance. The N dopant can provide a strong attraction to trap I2 molecules. In addition, the N heteroatom can shift the Fermi energy level above the pi-antibonding states, which can enhance the reduction and dissociation of the I2 molecule.

#### A01-50

##### Multilevel structures of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{c-p}$ nanocomposites derived from low-cost, hybrid v-mofs for long-life lithium ion batteries

Zhaoyang Wang\*

Wuhan University of Technology

Fast charge/discharge rate and service life performances are still challenges for Li ion batteries. In this paper, Multilevel structures of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{carbon-phosphorus}$  (LVP/C-P) nanocomposites were synthesized using low-cost, hybrid vanadium metal-organic frameworks (V-MOFs) as precursor via a hydrothermal-assisted sol-gel method. Spheroidals, foams, prism and hydrangea like structures are found in the nanocomposite, which were characterized by SEM, TEM, Raman, XRD and Mapping analysis. The nanocomposites delivered a remarkably long service life, exhibiting a discharge capacity of 65 mAh g<sup>-1</sup> at 10 C with nearly 90% capacity retention after 1100 cycles. The excellent cycling stability is attractive for application in rechargeable lithium ion batteries. More importantly, our results demonstrated that glass fiber drawing wastewater could be facilely transformed into treasure of multilevel structure nanocomposites for cheap Li ion batteries.

## A01-51

### Stable operation of Ag-based anode solid oxide fuel cells on propane

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Ni-based anode is commonly used in solid oxide fuel cells (SOFCs) operated on hydrogen. However, when an SOFC operates directly with more available carbon-containing fuels such as propane, Ni promotes carbon deposition which deconstructs the anode, resulting in performance failure. To avoid this problem, an effective approach is to use some alternative anode material.

In this work, a cermet of silver and gadolinium-doped ceria (GDC) is investigated as the anode material of a SOFC directly operated on propane. The ambient air is used as the oxidant. Their electrochemical and durability performances of the SOFC are tested and compared to those of an SOFC with conventional Ni-GDC anode.

Experimental results show that the initial performances of the SOFCs, respectively with Ag-GDC and Ni-GDC anode, are similar, while quite different over operating time. The open circuit voltage (OCV) of a SOFC with Ag-GDC anode is stable at ~1 V while that with Ni-GDC anode continuously drops from the initial 1.2 V to 0.85 V in 140 min. A SOFC with Ag-GDC anode has been stably operated on propane at a constant current density of 103 mA cm<sup>-2</sup> for more than 160 h while that with Ni-GDC anode for only 50 h (Fig.1b). SEM examination shows Ni-GDC anode is destroyed by carbon deposition during operation on propane, while Ag-GDC anode is well conserved and has a carbon layer, with some breakages, built on its surface.

It is concluded that the performance degradation of a SOFC operated on carbon-containing fuel is not caused by carbon deposition covering the active sites of anode. The stable operation of SOFCs with Ag-GDC anode on dry propane is realized because, not like on Ni-based anode, carbon deposition on Ag-GDC does not reconstruct the structure of the anode. Therefore, the SOFC with Ag-based anode can survive even though there is carbon deposition on the anode.

## A01-52

### Solid state lithium sulfur battery and its in-situ mechanism study

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Solid state lithium sulfur (Li-S) batteries, as a next-generation high energy density storage system, has generated great interest due to its signally theoretical energy density (2600 Wh/kg), high capacity (1675 mAh/g), and the availability of low-cost sulfur. However, the soluble polysulfides forming in the cathode will transport to the anode where they are reduced to Li<sub>2</sub>S, namely shuttle effect, which results in the loss of active material and poor cyclability. Moreover, uncontrolled dendritic and mossy lithium growth seriously threaten the security and hinder the practical application of Li-S batteries. Strategies for avoiding shuttle effect and achieving dendrite-free lithium anode are of significant attracting and have driven investigation in multiple fields in the past decades.

Previous researches have been devoted to preventing the dissolve or transport of polysulfides. In the development of this solution, the most popular strategy is composing sulfur with carbonaceous materials, but it still suffers from rapid capacity fading over long-term cycling, because the nonpolar carbon can only provide weak physical adsorption to the polar lithium polysulfides (LiPSs). The lithium protection is a significant and effective subject considering the spontaneous side reactions between highly reactive Li metal and liquid electrolytes. Electrolyte additives such as LiNO<sub>3</sub>, ILi and P<sub>2</sub>S<sub>5</sub> also have been shown to efficaciously delay the onset of crude dendritic deposition on Li surface through the growth of solid electrolyte interphase (SEI). In this talk, I will mainly talk about the recent progress in solid state lithium sulfur battery and its in-situ mechanism will be also discussed.

## A01-53

### 2D Materials in Energy and Environmental Applications: Piezocatalysis and Water Splitting

Jyh Ming Wu\*

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The decomposition of organic pollutants serves as an increasing challenge in chemistry, and a major impact for environmental

purification associated with industrial wastes. A variety of semiconductor photocatalysts have been utilized for the advanced oxidation process to generate the reactive oxygen species, by producing the hydroxyl (OH $\cdot$ ) radical via the illumination of the UV light and the visible light, as it can oxidize the organic pollutants, a major remediation for environmental purification. This work, I will report that the non-centrosymmetric structure of the catalyzing material was applied by an external force, an electric field was therefore built up instantly inside the piezoelectric crystal due to its spontaneous polarization, which can efficiently separate the electron and hole pairs to trigger the catalyzing process for destroying the organic matters and producing radicals species in the dark. The non-centrosymmetric structure have been discovered in 2D materials such as, MoS $_2$ , MoSe $_2$ , and WS $_2$  etc.. The piezoelectric response in the odd number of layers in 2D material possess the uniquely piezo-catalyst effect by applying a mechanical deformation, which provides a great potential role in the energy and environmental applications without any lighting assistance.

#### **A01-54**

##### **Active, durable nanostructured bismuth oxide decorated cobaltite oxygen electrode of reversible solid oxide cells**

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Solid oxide cells (SOCs) are a device of choice for efficient storage and regeneration of renewable sources by alternatively operating in solid oxide electrolysis cell and solid oxide fuel cell modes. Cubic bismuth oxide such as Er and Y stabilized bismuth oxide (ESB and YSB) possesses excellent surface exchange capability and highest ionic conductivity among the electrolyte materials of SOC. However, the high reactivity between bismuth oxide and cobaltite oxygen electrodes is a bottleneck in developing active and reliable bismuth oxide-cobaltite composite oxygen electrodes for SOC. In this presentation, a Sr-free Sm $_{0.95}$ Co $_{0.95}$ Pd $_{0.05}$ O $_{3-\delta}$  (SmCPd) oxygen electrode decorated with nanoscale ESB is synthesized and assembled on barrier-layer-free Y $_2$ O $_3$ -ZrO $_2$  (YSZ) electrolyte film. The cell with the ESB decorated SmCPd composite electrode exhibits a peak power density of 1.81 and 0.58 W cm $^{-2}$  at 750 and 650 °C, respectively. More importantly, excellent operating stability is achieved in fuel cell mode at 600 °C for 500 h, in electrolysis mode and reversible mode at 750 °C for 200 h. The results demonstrate the feasibility of applying bismuth oxide-cobaltite composite oxygen electrodes in developing high performing and durable SOC.

#### **A01-55**

##### **N-p-MCNTs Supported Mn $_3$ O $_4$ Quantum Dots ORR Electrocatalysts for Zn-air Batteries**

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High efficient and low-cost electrocatalysts that favor a four-electron pathway for oxygen reduction reaction (ORR) are essential for high-performance metal-air batteries. Herein, we show an ultrasonication-assisted synthesis method to prepare Mn $_3$ O $_4$  quantum dots (QDs, ca. 2 nm) that anchored on nitrogen-doped partially exfoliated multi-wall carbon nanotubes (Mn $_3$ O $_4$  QDs/N-p-MCNTs) as a high-performance ORR catalyst. The Mn $_3$ O $_4$  QDs/N-p-MCNTs facilitated the four-electron pathway for the ORR and exhibited sufficient catalytic activity with an onset potential of 0.850 V (*vs.* RHE), which is only 38 mV less positive than that of Pt/C (0.888 V). In addition, the Mn $_3$ O $_4$  QDs/N-p-MCNTs demonstrated superior stability than Pt/C in alkaline solutions. Furthermore, a Zn-air battery using the Mn $_3$ O $_4$  QDs/N-p-MCNTs cathode catalyst successfully generated a specific capacity of 704 mA h g $^{-1}$  at 10 mA cm $^{-2}$  without the loss of voltage after continuous discharging for 105 hours. The superior ORR activity of Mn $_3$ O $_4$  QDs/N-p-MCNTs can be ascribed to the homogeneous Mn $_3$ O $_4$  QDs loaded onto the N-doped carbon skeleton and the synergistic effects of Mn $_3$ O $_4$  QDs, nitrogen, and CNTs. In addition to the high ORR activity, the cost of production of Mn $_3$ O $_4$  QDs/N-p-MCNTs is low, which will broadly facilitate the real application of metal-air batteries.

#### **A01-56**

##### **First-principles study on the core-shell cathode for solid oxide fuel cell**

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Solid oxide fuel cell (SOFC) is considered to be one of the most promising new energy technologies with its clean, efficient and wide fuel source. Current research activities focus on developing electrode materials operating at intermediate temperature (650~850 °C) in order to meet the requirements of the commercialization of cost and stability. At present, the perovskite type cathode materials are widely used in intermediate temperature SOFC, including  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$  (LSM),  $\text{Ba}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$  (BSCF) and so on. BSCF has good catalytic activity at low temperature, but its stability is poor in air, while LSM has good stability, but it has little ionic conductivity at low temperature. Therefore, we have prepared a composite cathode with core-shell structure, in which the surface of BSCF is densely coated with LSM to achieve the dual optimization of material stability and high catalytic activity. In this work, the interfacial atomic structure, oxygen adsorption and diffusion properties of the cathode-shell structure cathode have been studied by the first principles method.

In the core-shell structure, there is an interface between the shell and the core. The binding energy of the La-O plane of the LSM (100) surface and the Co-O plane of the BSCF (100) surface is 9.12 eV, greater than the other interface binding energy, suggesting that such a combination is the most possible composite structure. The O<sub>2</sub> molecular can be adsorbed on the LSM (100) more easily than on the BSCF (100) surface. In the study of the interface model, the oxygen vacancy formation energy of LSM is 2.24 eV, and 1.58eV for BSCF, thus the oxygen vacancy is more likely to be formed in BSCF, which is also one of the reasons why BSCF oxygen ion conductivity is better than LSM. At the interface between LSM and BSCF, the conductance of oxygen ions is accomplished by migration of oxygen ion (vacancy) from LSM to BSCF. The oxygen diffusion barrier is determined to be 0.66eV, indicating that the transmission of the oxygen ion in the interface is relatively easy.

In summary, we have used first-principles density functional theory to study the process of cathode bonding and reaction of core-shell structures: interfacial binding and bulk diffusion. It can be concluded that LSM@BSCF is a promising cathode material that can be applied to intermediate temperature SOFC.

#### **A01-57**

##### **直接碳固体氧化物燃料电池锑基阳极及其电极过程**

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直接碳燃料电池(DCFC)是一种燃料来源极其广泛、发电效率极高的能源转化技术,然而碳传质一直是其发展的技术瓶颈。高温熔融金属锑(Sb)阳极特殊的电极过程是解决以上问题的有效手段,具有结构简单、易于传质和工业放大等优点。本报告将深入研究熔融锑阳极表面 Sb<sub>2</sub>O<sub>3</sub> 还原、电解质表面 Sb 电化学氧化过程实现电池的长期稳定运行。首先,通过引入参比电极探讨 YSZ 电解质缓慢腐蚀的微观机制及掺杂离子的影响规律,采用化学法和物理法得到能够稳定运行的电极体系;其次,通过高温原位技术研究碳种类、结构对阳极浸润性的影响,通过 TPR 及在线色谱等技术探讨不同碳燃料氧化锑还原动力学行为,再借助于 SEM、XPS 及 EDS 技术得到碳中 Ni、V 及 S 杂质对电极过程的影响规律;最后,阐述利用锑和氧化锑密度差实现阳极自然对流并阐明阳极过程的控制步骤,实现其长期稳定运行。本报告提出的熔融锑阳极是解决 DCFC 碳传质问题切实可行的方法,是一种既能得到较高放电功率又能长期稳定运行的电池体系。相信报告的内容对于解决 DCFC 碳传质问题提供一种新的启示。

#### **A01-58**

##### **The investigation on stabilization mechanism of long-term operation of solid oxide fuel cell stacks**

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Solid oxide fuel cell (SOFC) is an efficient and clean energy conversion system. The key to commercialization is to reduce the degradation rate of the stack. There are important influencing factors relating to performance degradation, including of oxidation of metal interconnects, the reliability of high-temperature sealing, and the interfacial stability of adjacent components. In the study, the oxidation kinetics rate of interconnect are reduced by controlling the chemical composition, phase structure and micro-morphology of the oxide scale on the surface of the interconnect alloy, and the effect of Cr poisoning cathode was inhibited. A new type of flexible SOFC seals is developed which can enhance high temperature sealing stability and eliminate interfacial gas leakage. It has been investigated on the mechanism of temperature gradient and thermal stress on the sealing performance. A flexible interface layer

between the interconnect and the cell cathode is constructed to achieve improved interface electrical contact and thermal stress dissipation, which is beneficial to reach long term operation and thermal cycle stability of stack. The relationship between stack stability and the above factors is clarified, which provides a theoretical basis for the manufacture and evaluation of high-performance stack.

#### **A01-59**

##### **Thermoelectric properties of SnSe thin films**

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SnSe single crystals have been demonstrated to possess excellent thermoelectric properties. In this work, we demonstrate a grain size control method in growing nanocrystalline SnSe thin films through a glancing angle pulsed-laser deposition approach. Structural characterization reveals that the SnSe film deposited at a normal angle has a preferred orientation along *a* axis, while by contrast, the SnSe film deposited at a 80° glancing angle develops a nanopillar structure with the growth direction towards the incident atomic flux. The glancing angle deposition greatly reduces the grain size of the thin film due to a shadowing effect to the adatoms, resulting in significantly increased power factor for more than 100%. The maximum Seebeck coefficient and power factor are 498.5  $\mu\text{V K}^{-1}$  and 18.5  $\mu\text{W m}^{-2}\text{K}^{-2}$ , respectively. The enhancement of thermoelectric property can be attributed to the potential barrier scattering at grain boundaries owing to the reduced grain size and increased grain boundaries in the film. Given this enhanced power factor, and considering the fact that the nanopillar structure should have much lower thermal conductivity than a plain film, the *zT* value of such made SnSe film could be significantly larger than the corresponding single crystal film, making it a good candidate for thin film-based thermoelectric device.

#### **A01-60**

##### **Fabrication and Supercapacitive Properties of N/P Co-doped Carbon Materials**

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Supercapacitors have attracted great attention due to their high power density, superior rate capability and long operation life. Improving the energy density of carbon-based supercapacitors is one of the most urgent demands for developing high-power energy supplies, which in general requires delicate engineering of the carbon composition and textures. In the present work, by pre-functionalization of graphene nanosheets and successive one-step  $(\text{NH}_4)_3\text{PO}_4$  activation, we prepared a type of nitrogen and phosphorus co-doped graphene (NPG) with high specific surface areas, hierarchical pore structures as well as tunable N and P contents. The as-obtained NPG shows high specific surface areas of up to 320  $\text{m}^2\text{ g}^{-1}$  and efficient N/P co-doping as high as 3.7 at.% for N and 1.3 at.% for P. Our results demonstrate that the NPGs exhibit high specific capacitances of 219  $\text{F g}^{-1}$  ( $123\text{ F cm}^{-3}$ ) at 0.25  $\text{A g}^{-1}$  and 175  $\text{F g}^{-1}$  ( $98\text{ F cm}^{-3}$ ) at 10  $\text{A g}^{-1}$ , respectively. Accordingly, the NPG-based symmetrical supercapacitor device, working at a potential window of 1.3 V, could deliver an enhanced energy density of 8.2  $\text{Wh kg}^{-1}$  ( $4.6\text{ Wh L}^{-1}$ ) at a power density of 162  $\text{W kg}^{-1}$  ( $91\text{ W L}^{-1}$ ), which still retains 6.7  $\text{Wh kg}^{-1}$  at 6.5  $\text{kW kg}^{-1}$ . In particular, under a current density of 5  $\text{A g}^{-1}$ , the device endows an 86% capacitance retention of initial after 20,000 cycles, displaying superior cycle stability. Our results imply the feasibility of NPG as a promising candidate for high-performance supercapacitors.

#### **A01-61**

##### **Hollow Nanostructures for Applications in Li/Na-Ion Batteries**

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Energy storage devices play a significant role in conserving fossil fuel and reducing greenhouse gas emission. Among various feasible energy storage technologies, lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs), as representatives of the current- and next-generation rechargeable batteries, have attracted intensive interests due to their (potential) applications in portable electronic devices, new-energy vehicles, military equipment etc. The main challenge for them is the development of electrode materials with

superior electrochemical performances. Recently, hollow nanostructures (such as carbonaceous materials and transition metal oxides) and their hybrid materials have shown great advantages for applications as anode materials in LIBs and SIBs due to their high surface/volume ratio, high electrical conductivity and large void space. Here, by using template-removal methods, we synthesized hybrid materials of NiO nanoparticles/carbon nanohelmets (NiO/CNHs) for LIBs and Ni-NiO nanoparticles/porous carbon nanosheets (Ni-NiO/PCNs) for SIBs, which show high reversible specific capacity, superior cycling stability and rate performance, attributed to their ingenious architectures. The facial strategies reported here provide new insights for rationally developing novel hollow structures for advanced energy storage devices.

#### **A01-62**

##### **Investigation of Catalytic Activity Mechanism of Cathode Materials for Fuel Cells by Synchrotron Radiation Soft X-ray Absorption Spectroscopy and High Temperature In Situ Photoelectron Spectroscopy**

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Synchrotron radiation soft X-ray absorption spectrum (soft-XAS) has the advantages of deep detection depth, signal sensitivity, etc. for the electronic valence states, spin states and coordination states of electrons in 3d metal oxides. The working temperature of the fuel cell is at high temperature, and the high-temperature in-situ photoelectron spectroscopy (XPS) technology can detect the electronic structure at the actual operating temperature. Compared with the normal temperature XPS spectrum, it can reflect the real electronic structure characteristics. The Ruddlesden-Popper phase layered oxide  $\text{La}_3\text{Ni}_2\text{O}_7$  has excellent conductivity, but has poor catalytic activity. By doping Co ions at the B site, the catalytic activity is improved which is manifested that the polarization resistance of  $\text{La}_3\text{Ni}_{1.9}\text{Co}_{0.1}\text{O}_7$  is  $1.12 \Omega \text{ cm}^2$  while that of  $\text{La}_3\text{Ni}_{1.6}\text{Co}_{0.4}\text{O}_7$  is only  $0.35 \Omega \text{ cm}^2$  measured at  $650 \text{ }^\circ\text{C}$ . By analyzing the photoelectron spectroscopy of oxygen at high temperature, it was found that Co doped samples exhibit higher intensities of chemically adsorbed oxygen at high temperatures, which indicates that doping of Co is beneficial to maintain a certain amount of oxygen defects at high temperatures to absorb the environment oxygen. The presence of oxygen vacancies at high temperatures provides oxygen adsorption sites and oxygen ion diffusion channels during oxygen reduction reactions, thereby enhancing catalytic activity. At the same time, through the X-ray absorption spectrum, we found that Co shows a +3 value at a certain doping amount, and the +3 Co ions have a certain local effect on electrons. We have demonstrated this feature by measuring the electrical conductivity and magnetic properties. The localized electrons indicate that the 3d metal ions tend to covalently interact with oxygen, which favors the adsorption of oxygen by metal ions during the oxygen reduction reaction, thereby enhancing the catalytic activity. This design and characterization method provide direct evidences for exploring the catalytic reaction mechanism of fuel cells, and provide ideas for the design of cathode materials.

#### **A01-63**

##### **Prussian Blue-Based Cathodes for Sodium Ion Batteries**

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Rechargeable sodium ion batteries (SIBs) are emerging as one of the promising candidates for applications in large-scale energy-storage systems. Prussian blue analogues have been considered as potential cathodes because of their rigid open framework and low-cost synthesis. Nevertheless, PBAs suffer from inferior rate capability and poor cycling stability resulting from the low electronic conductivity and deficiencies in the framework. Crystallinity and electronic conductivity are challenging issues for PBAs to be tackled.

Nickel substitution is an efficient method to improve the cycle stability of PB and activated the low spin  $\text{Fe}^{2+}/\text{Fe}^{3+}$  couple. Further regulation of the distribution of the substituted nickel ions generates PB with a gradient nickel substitution, which features a high-Ni-content outer layer and low-Ni-content inner layer in a single grain. The outer layer prevents side reactions, ensuring excellent cycling stability, while a small amount of nickel ions in the inner layer efficiently activates the low spin Fe for achieving high capability. Growing the nanosized PB cubes directly on carbon chains is also a promising way in improving PB's crystallinity and electronic conductivity. First-principles computation revealed that the electrochemical activity of the low spin Fe couple is

closely associated with the  $[\text{Fe}(\text{CN})_6]$  vacancies in the PB crystal.

Through the incorporation of nickel ions into PB structure, the low-spin Fe ( $\text{Fe}^{\text{LS}}$ ) couple is sufficiently activated for sodium storage, which leads to higher capacity contribution at larger potential and more stable redox energy. Moreover, iron-nickel hexacyanoferrate ( $\text{FeNiHCF}$ ) is better crystallized with less water content compared with single metal hexacyanoferrate of  $\text{FeHCF}$  and  $\text{NiHCF}$ . As a result, the  $\text{FeNiHCF}$  cathode exhibits synergistic advantages of high capacity, excellent cycling stability, high rate performance and  $\sim 100\%$  Coulombic efficiency. Through the unique gradient nickel substitution on PB, higher performance in sodium storage is obtained. The implications of Ni substitution in protecting the active material can be twofold. First, the electrochemically inert Ni can efficiently inhibit the side reaction with electrolyte occurring at high voltage. Second, alleviation of the volume change on account of the larger volume of the Ni–N octahedron than the Fe–N octahedron is also beneficial to prolonging the cycle life. Furthermore, the nickel ions across the entire grain of PB play an important role in activating  $\text{Fe}^{\text{LS}}$  redox couple and promoting the electrochemical kinetics of the electrode. The resultant Ni-substituted PB electrode achieves a capacity as high as  $114 \text{ mA h g}^{-1}$  under a current density of  $100 \text{ mA g}^{-1}$  with 100% coulombic efficiency up to 600 cycles. In addition, a high capacity of  $84 \text{ mA h g}^{-1}$  is retained after 1000 cycles with 90% capacity retention. An ultrahigh-rate and long-life sodium ion battery cathode consisting of PB@C was developed through a facile in situ synthesis. The nanosized PB cubes directly grown on carbon chains were well crystallized with a low vacancy content. The small size and intimate contact of the PB cubes with the carbon matrix assured both a shortened Na-ion diffusion length and fast electron transfer within the electrode. The low  $[\text{Fe}(\text{CN})_6]$  vacancy content in PB@C was verified to greatly activate the electrochemical reactions associated with the  $\text{Fe}^{\text{LS}}$  redox couple using first-principles calculations. The density of states (DOS) of  $\text{Fe}^{\text{LS}}$  atoms neighboring the vacancy was largely affected by it and the unoccupied peak states of  $\text{Fe}^{\text{LS}}$  nearly disappeared, indicating the electrochemical activity of the neighboring  $\text{Fe}^{\text{LS}}$  had dramatically degraded for reaction with Na. The superior reaction kinetics in the redox reactions of the high spin Fe ( $\text{Fe}^{\text{HS}}$ ) couple were demonstrated, which relied on the partial insertion of Na ions enhancing the electron conduction. Once one Na ion had been inserted into the crystal cell, the enhancement of the electronic conduction of the electrode greatly improved the insertion kinetics and correspondingly resulted in a superior rate capability at the low voltage plateau contributed by the  $\text{Fe}^{\text{HS}}$  couple. With the synergistic effect of structure and morphology improvements, the resultant PB@C composite achieved an unprecedented rate capability ( $77.5 \text{ mAh g}^{-1}$  at 90 C,  $90 \text{ mAh g}^{-1}$  after 2000 cycles with 90% capacity retention at 20 C) with outstanding cycling stability.

References:

1. Shenglan Yu, Yong Li, Yunhao Lu, Ben Xu, Qiuting Wang, Mi Yan, Yinzhu Jiang\*, "A promising cathode material of sodium ironnickel hexacyanoferrate for sodium ion batteries," *J. Power Sources* 2014, 275, 45.
2. Yinzhu Jiang\*, Shenglan Yu, Baoqi Wang, Yong Li, Wenping Sun, Yunhao Lu\*, Mi Yan, Bin Song, Shixue Dou, "Prussian Blue@C Composite as an Ultrahigh-Rate and Long-Life Sodium-Ion Battery Cathode," *Adv. Funct. Mater.* 2016, 26, 5315.
3. Baoqi Wang, Yu Han, Yuting Chen, Yanjun Xu, Hongge Pan, Wenping Sun, Shuangyu Liu, Mi Yan, Yinzhu Jiang\*, "Gradient substitution: an intrinsic strategy towards high performance sodium storage in Prussian blue-based cathodes," *J. Mater. Chem. A*, 2018, DOI: 10.1039/C8TA02291G.

#### A01-64

##### The effects of external stresses and chemical stresses on the lithium ion diffusion in battery electrodes

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On account of the high energy density and light weight, Lithium ion battery has attracted wide attention in recent years. However, deformation can be induced due to the electrochemical processes of Li insertion and extraction in the electrodes. Meanwhile, lithium ion diffusion in battery electrodes is easy to be affected by external load. For example, external stresses and chemical stresses can affect the reaction rate and energy storage density of lithium ion batteries. In this presentation, based on the thermodynamic theory and Finite Element Method, we develop a two-dimensional model that couples mechanics and electrochemistry in anode materials, with the goal to analyze the effect of external stress on the lithium ion diffusion. Results show that the external stress can significantly influence the electrochemical performance of lithium ion battery, including lithium ion concentration and diffusion rate.



## A01-65

### Electrochemical synthesis of titanium carbide -polyaniline composite film with high capacitance performance

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Rational design of composite has been confirmed as an effective and economical pathway to achieve high performances of titanium carbide ( $Ti_3C_2T_x$ )-based electrode materials. Herein, we report a new composite of titanium carbide-polyaniline ( $Ti_3C_2T_x$ -PANI) film by one-step method of *in-situ* electrochemical polymerization bestows high gravimetric capacitance. The as-prepared binder-free  $Ti_3C_2T_x$ -PANI film exhibits a high specific capacitance of  $2813.5 \text{ F g}^{-1}$  at a current density of  $5 \text{ mVs}^{-1}$  in  $3 \text{ M H}_2\text{SO}_4$  solution in a three electrodes test system. Moreover, the efficiency of  $96.3 \%$  remains even after 10000 cycles at a current density of  $100 \text{ A g}^{-1}$ . The capacity and cycle performance overwhelms the majority of MXene ( $Ti_3C_2T_x$ ) and MXene-based composite. These outstanding properties of the as-synthesized composites are attributed a unique sandwich architecture, which not only provides a wide lamellar distance for facilitating fast ion transport, and a large number of effective sites for high capacities, but also extends cycling life by preventing sheet agglomeration, and improving its conductivity.

## A01-66

### 手性介观结构无机材料及其手性响应性

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手性是自然界的基本属性之一。手性与宇宙的所有活动都息息相关，自然界最神秘而最普遍的结构或形貌。自然界的基本现象和定律都是由手性构成。介观结构材料，其特殊的组装结构及空间限域效应赋予了其多方面的独特性能，为人们提供了一个调控材料物理化学性质的崭新平台。手性介观结构无机材料，随着材料化学，纳米科学和物理学的发展而出现，备受化学界、生理学界、材料界科学家们广泛的关注，成为近十年里最重要研究课题之一。

通过氨基酸表面活性剂、DNA 以及手性小分子等为模板剂或诱导剂与无机源的协同共组装合成了各种无机手性介观结构材料。引入共结构导向剂概念，组装出三级手性介孔二氧化硅材料，提出了由于受到螺旋堆积所产生的扭曲张力形成螺旋柱状体，发现了模板剂手性堆积而产生的超分子手性印记及其手性诱导功能。通过 DNA 与无机物种进行协同共组装合成出罕见的二维正方结构；发现了在金属离子的诱导下 DNA 矿化形成类胆甾型液晶相多级无机螺旋结构；提出了基板晶向引导定向生长三维手性介孔材料薄膜的方法，发现了其光学活性及其增强机理。特殊性质的无机材料的多维、多尺度、“手性叠手性”的多级手性膜结构，具有基于不同机理的多重光学活性，并且其间协同作用极大地增强材料对光响应的手性选择性。

手性响应性是手性材料的基本属性，也是手性材料的应用基础。小于 Bohr 激子半径的半导体纳米晶体以小于 Bohr 激子半径的距离紧密堆叠形成手性多级结构时，其激发态在手性组装体上离域，将与左右圆偏振光产生不同的相互作用而产生基于电子跃迁吸收和发射的光学活性。基于以上思路设计并组装成功了多种半导体纳米颗粒从原子级别到微米级别的多级三维手性介观结构。提出了在不对称场作用下，手性多级结构半导体材料的电子从价带到导带跃迁时选择性吸收圆偏振光而产生光学活性；发现了纳米花的多级手性结构及其光学活性；合成成功了多维、多尺度、“手性叠手性”的多级手性膜结构，发现了基于发射的无机物光学活性，提出了多重光学活性协同增强原理；发现了多级结构手性无机材料对不对称小分子的选择。

## A01-67

### Solid polymer electrolytes for all solid state lithium ion battery

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Solid polymer electrolyte (SPE) with outstanding performances is considered as one of the ideal electrolytes for LIBs due to its excellent safety performance, good flexibility and light weight. Furthermore, the SPE can not only successfully overcome the disadvantage of traditional liquid electrolyte, such as leakage of liquid and corrosion of electrodes, but also exhibit the good flexibility and wonderful film-forming properties, which makes it possible to be applied in many occasions with the special request

for the shape of cells. However, the SPE still confronted with several problems which limit its application in lithium ion batteries, such as the weakness of lithium ion conductivities of polymers and the failure of PEO-based polymer membranes in blocking the growth of lithium dendrite across the cathode.

To overcome this problem, we proposed to fabricate the PEO-based electrolyte by organic doping, inorganic doping and structure design. Firstly, practical, high-yield mesoporous organic polymer (MOP) spheres were successfully synthesized by a novel self-template method, which can be used as fillers to prepare poly (ethylene oxide) (PEO)-based polymer electrolytes membranes. Secondly, the mechanically robust, thermally stable electrolytes with high ionic conductivity were prepared by blending MOP with the polyethylene oxide. Thirdly, to further enhance the electrochemical performance of the electrolytes, we design a symmetrical sandwich-like electrolyte and an asymmetric electrolyte by inorganic doping, respectively, and the electrochemical performance of the electrolytes were compared. Finally, we try to prepare a new polymer solid electrolyte with three-dimensional network by UV irradiation, and also the electrochemical performance of the electrolytes before and after inorganic doping were compared. All the above method show the potentials in enhancing the electrochemical performance of the solid polymer electrolytes.

#### **A01-68**

##### **An all-organic aqueous battery based on quinone- adsorption**

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The intermittency of wind and solar energy prohibits it as sole, stable power supply. Safe and inexpensive energy storage with a long life as well is thus necessary for the development of renewable energy. Supercapacitors can deliver high power and long cycle lives, but a low energy density. In this study, based on the architecture of conventional supercapacitors, we design an all-organic aqueous battery by adsorbing quinones onto porous carbon electrodes. By using two inexpensive low-molecular-weight organic compounds, it is possible to reduce costs while substantially increasing energy density. In addition to the formation of the double layer, protons shuttle between the two electrodes of Pyrocatechol-3,5-disulfonic acid disodium salt and 9,10-Anthraquinone-2,7-disulfonic acid disodium salt during charge and discharge which contributes capacity. The battery delivers a capacity 3 times larger capacity than that of a supercapacitor. The work demonstrates a new strategy of designing low-cost, safe means of energy storage.

#### **A01-69**

##### **Effects of combination method on the electrochemical performance of graphene-CaTi<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub> electrode material**

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As a new electrode for energy storage device, CaTi<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub> has better electrochemical performance in our previous report. To further improve its electrochemical properties, the graphene which has excellent electrical conductivity is chosen. Effects of the graphene-CaTi<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub> combination method on the electrochemical properties of the electrode are studied. The microstructure of the samples are analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The electrochemical properties of the samples are tested by galvanostatic charge discharge (CP) and cyclic voltammetry (CV). The experiment results show that compared to other methods e.g. impregnation method and solvothermal method, the electrochemical performance of the graphene-CaTi<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub> composite sample electrode prepared by solid phase mixing method is the optimum specific capacitance of 300.15 F\*g<sup>-1</sup> at the current density of 5A/g, which is increased by 81.22% compared with specific capacitance value of the pure CaTi<sub>2</sub>O<sub>4</sub>(OH)<sub>2</sub> electrode (165.63F\*g<sup>-1</sup>).

#### **A01-70**

##### **CO<sub>2</sub> Plasma-Treated TiO<sub>2</sub> Film as an Effective Electron Transport Layer for High-Performance Planar Perovskite Solar Cells**

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Perovskite solar cells (PSCs) have received great attention due to their excellent photovoltaic properties especially for the comparable efficiency to silicon solar cells. The electron transport layer (ETL) is regarded as a crucial medium in transporting electrons and blocking holes for PSCs. In this study, CO<sub>2</sub> plasma generated by plasma-enhanced chemical vapor deposition (PECVD) was introduced to modify the TiO<sub>2</sub> ETL. The results indicated that CO<sub>2</sub> plasma treated compact TiO<sub>2</sub> layer exhibited better surface hydrophilicity, higher conductivity, and lower bulk defect state density in comparison with the pristine TiO<sub>2</sub> film. The quality of the stoichiometric TiO<sub>2</sub> structure was improved and the concentration of oxygen-deficiencies induced defect sites was reduced significantly after CO<sub>2</sub> plasma treated for 90 s. The PSCs with TiO<sub>2</sub> film treated by CO<sub>2</sub> plasma for 90 s exhibited simultaneously the improved short-circuit current (*J*<sub>sc</sub>) and fill factor (FF). As a result, PSC based TiO<sub>2</sub> ETL with CO<sub>2</sub> plasma treatment affords a power conversion efficiency (PCE) of 15.39%, outperforming that based on pristine TiO<sub>2</sub> (13.54%). These results indicate that the plasma treatment by PECVD method is an effective approach to modify ETL for high performance planar PSCs.

#### **A01-71**

##### **Effect of Microstructural feature of Precipitate on the Strength and Toughness Relationship**

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Effect of microstructural feature of precipitate on the strength-toughness relationship of drill-pipe steel was investigated using optical microscopy (OM), transmission electron microscopy (TEM) and *In-situ* tensile testing in a TEM, based on alloy composition design and severe plastic deformation. The results show that the strength-toughness relationship is distinctly different from the general observations when tempered from 580°C to 625°C, of which strength reaches to 150ksi, and impact toughness still remains 151J at 625°C. Microstructural examinations reveal that ferrite with fine grain and dispersive precipitates were observed when tempered from 580 to 625°C. However, precipitate segregated along grain boundaries and formed banded structure when tempered from 650 to 680°C. On closer examination, rod-shaped precipitate formed at 580°C, spherical and rod-shaped precipitates occurred at 625°C, and spherical precipitates appeared at 650-680°C. During *in-situ* tensile testing in a TEM, a straight path of crack propagation formed along rod-shaped precipitate boundary. However, this path changed into zigzag due to the obstruction of spherical precipitate. Finally, the mechanism responsible for the unusual strength-toughness relationship is discussed.

#### **A01-72**

##### **Ions Transportation through MOF Membranes and Its Applications in Li-S batteries and fuel cells**

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Metal-organic frameworks (MOFs) have attracted much attention recently since their unique channel structure and tunable properties. The fabrication of MOF membranes has extended their applications. The self-confined conversion method was employed to prepare MOF membranes. Positively charged metal hydroxide nanostrands were used as metal source of MOF and negatively charged function molecules, such as polystyrene sulfonate (PSS) and DNA, could easily assemble with them. Then the metal hydroxide nanostrands film converted to well-intergrown MOF membranes when soaked in ligands solution. Meanwhile, the function molecules would be encapsulated in MOF membranes.

Since MOFs are generally poor ionic conductors with low ion conductivity, the PSS and DNA were encapsulated into HKUST-1 and ZIF-8 membranes, respectively, to improve their ion conductivities by building hydrogen-bond networks. The continuous well-intergrown MOF membranes are promising for separators of energy storage and conversion devices, attributed to the porous structure and ions selectivity.

The PSS@HKUST-1 membrane demonstrated high Li<sup>+</sup> conductivity with excellent ions separation factor, due to the size sieving effect and ion affinity of sulfonate groups. The Li<sup>+</sup> conductivity can reach up to 5.53×10<sup>-4</sup> Scm<sup>-1</sup> at 25°C, 1.89×10<sup>-3</sup> Scm<sup>-1</sup> at 70°C, and the membrane present nice property of blocking polysulfide during the cycles of Li-S batteries to mitigate the shuttle effect. The Li-S cell assembled with PSS@HKUST-1 membrane and regular sulfur/super P carbon cathode exhibits outstanding cyclability with a negligible capacity decay of 0.05% per cycle over 500 cycles at 0.5 C and excellent rate capability up to 5 C, which

are far superior to that of commercial Celgard separator. Moreover, a high areal capacity over 7 mAh cm<sup>-2</sup> is achieved when areal sulfur loading reaches 11.27 mg cm<sup>-2</sup> at 0.5 C, surpassing that of commercial Li-ion batteries and superior to most interlayer-related or modified separator-based Li-S batteries.

DNA@ZIF-8 membranes were also synthesized by the self-confined conversion method. The linear DNA molecules significantly improve the proton conductivity of DNA@ZIF-8 membranes through the generated hydrogen-bond networks between the incorporated water molecules and these hydrophilic groups from the DNA molecules inside the cavities. Because the pore entrance aperture of the DNA@ZIF-8 membrane is smaller than the size of the methanol molecule, methanol crossover has been significantly blocked through the membrane. The well-ordered crystalline structure of the DNA@ZIF-8 membrane shows no swelling after the water uptake. The DNA@ZIF-8 membrane has high proton conductivity of  $3.40 \times 10^{-4}$  S cm<sup>-1</sup> at 25 °C and the highest one ever reported of 0.17 S cm<sup>-1</sup> at 75 °C, under 97% RH, but low methanol permeability of  $1.25 \times 10^{-8}$  cm<sup>2</sup> s<sup>-1</sup>. In addition, for the first time, an MOF-based PEM was assembled for DMFC with maximum power density of 9.87 mW cm<sup>-2</sup>.

The approach developed here is universal, which will significantly facilitate extensive research on the exploration of other polymer functionalized MOF-based membranes and eventually produce some advanced materials for the energy storage and conversion devices.

### A01-73

#### Lower-Dimensional Perovskites for Solar Cells and Optoelectronics

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Lower-dimensional organic-inorganic hybrid halide perovskites have recently attracted great attention due to high photo- and electroluminescence and photovoltaic potential.<sup>[1,2]</sup> However there is still a lack of understanding of some fundamental material/physical/chemical properties of these lower-dimensional materials, which are critical to optoelectronics and high efficiency solar cells. Here I will discuss our recent studies toward a better understanding and control of chemical structure, crystallization, charge dissociation and transport and device performance for a variety of lower-dimensional (A)<sub>2</sub>(A')<sub>n-1</sub>Pb<sub>n</sub>X<sub>3n+1</sub> perovskites. Our findings suggest an important role of the chemical structure and precursors crystallization in charge dissociation and transport in quantum-well structure. In addition, we will briefly discuss the relationship of properties-device performance for (A)<sub>2</sub>(A')<sub>n-1</sub>Pb<sub>n</sub>X<sub>3n+1</sub> film in terms of solar cells and optoelectronics.

### A01-74

#### Mechanical properties and microstructure of epoxy resin enhanced oil-well cement stone

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the present work aims to mixed epoxy resin with oil-well cement, evaluating possible improvements on their mechanical properties, microstructure and ultimately coming up with an ideal and effective concentration for future applications. Epoxy resin dosage vary from 10% to 50%, and the mass fraction of the epoxy resin were used to replace the quality of the cement, cured at 50°C, 70°C with 100% relative humidity for 3days, 7days, 14days and 28days, respectively. The oil-well cement stone prepared with the various amounts of epoxy resin were analyzed by scanning electron microscopy (SEM), mechanical testing, X-ray diffraction (XRD), infrared spectrum analysis (FTIR), and thermal stability analysis. The compressive strength of the sample with 30%, 10% cured at 50°C, 70°C for 7 days, respectively, increased 71% and 100.6%. These improved the mechanical properties of the oil-well cement stone primarily because of forming the three-dimensional structure of epoxy resin curing.

### A01-75

#### Low-Temperature-Gradient Crystallization for Multi-Inch High-Quality Perovskite Single Crystals for Record Performance Photodetectors

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With their excellent optoelectronic properties, the practical application of single-crystalline organolead halide perovskite materials is now limited by the lack of a method to prepare high-quality perovskite single crystals in large dimension. Herein, we report our development of a low-temperature-gradient crystallization (LTGC) method for high-quality  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  ( $\text{MAPbBr}_3$ ) perovskite single crystals with lateral dimension as large as two inches. The theoretical analysis suggests that a small temperature gradient should be used to restrain the growth condition, particularly the solution concentration, within the optimal single-crystal-growth (OSCG) zone. The solubility curve as a function of temperature reveals a sharp turning point at  $\sim 60^\circ\text{C}$ , across which the first-order solubility derivative ( $dC/dT$ ) shows very different behaviors: below this temperature, the  $dC/dT$  changes dramatically as the temperature increases, while above this temperature, the  $dC/dT$  enters a plateau where further temperature change has little effect on the derivative, meaning that one can attain both a substantial crystal growth rate and crystallization yield below this temperature. Utilizing this discovery, a  $\text{MAPbBr}_3$  single crystal as large as  $47 \times 41 \times 14$  mm is obtained with high quality *via* the LTGC method. The single crystal exhibits the best optoelectronic quality among all  $\text{MAPbBr}_3$  materials reported in the literature, including the best trap state density, mobility, carrier lifetime, and diffusion length. These superior optoelectronic properties are further transferred into a high performance planar photodetector. The device exhibits high operational stability, high external quantum efficiency (13453%), excellent detectivity as high as  $8 \times 10^{13}$  Jones, and a fast response speed as quick as 15.8  $\mu\text{s}$ . To our knowledge, both the detectivity and the response speed are the best among all  $\text{MAPbBr}_3$  devices reported to date. The unique synthesis method and excellent crystalline quality of the perovskite single crystals make them promising candidates for the next generation of optoelectronic devices.

#### A01-76

##### **Influence of Manganese Dioxide Catalyst on Electrochemical Performances of Magnesium Air Battery**

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Magnesium air battery is a promising electrochemical energy storage and conversion device due to its high energy density, high safety, environmental benignity, and earth abundance of Mg. Low-cost, earth-abundant electrocatalysts of the oxygen reduction reaction (ORR) at the cathode is essential for magnesium air battery. Electrolytic manganese dioxide (EMD) is the most attractive for ORR due to its cheaper price.

The electrochemical properties of  $\text{MnO}_2$  materials strongly depend on their crystal structure and morphology. In this study, the influences of ball-milling and thermal treatment on the structure and discharge performance of commercial EMD were studied.

It is found that the morphology of commercial EMD was obviously changed from irregular shape to spherical particles with a significant decrease in particle size after ball-milling, and the crystal phase of commercial EMD converted from  $\gamma\text{-MnO}_2$  to  $\beta\text{-MnO}_2$  via thermal treatment. EMD as electrocatalyst by ball-milling or heat treatment in magnesium air battery exhibited much higher discharge performance in comparison with the commercial EMD.

Consequently, controlling the morphology and crystal structure of electrolytic manganese dioxide as cathode catalysts of magnesium air battery is important for both fundamental research and technological applications.

#### A01-77

##### **Highly conductive $\text{NiSe}_2$ nanostructures for all-solid-state battery-supercapacitor hybrid devices**

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Battery-supercapacitor hybrid (BSH) comprises of a battery-type electrode offering plenty energy density and a capacitor-type electrode with ample power density. Transition metal oxides/hydroxides, as a kind of available battery-type electrode materials, whose low electronic and ionic conductivity have already become the principal restriction to the development of high-performance hybrid devices. The objective of this research is to synthesize high conductivity  $\text{NiSe}_2$  nanostructures serving as electrode materials for hybrid devices, which is expected to be a potential candidate for all-solid-state energy storage devices.

The NiSe<sub>2</sub> nanostructures were synthesized by a simple hydrothermal procedure. Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and SeO<sub>2</sub> were dissolved in deionized water to form homogeneous solution. Subsequently, the solution was transferred into a Teflon-lined stainless autoclave with a piece of pretreated nickel foam immersed into, and then the autoclave was sealed and heated. Finally, the NiSe<sub>2</sub> sample was washed and dried to obtain the final products.

The NiSe<sub>2</sub> nanostructures are composed of the NiSe<sub>2</sub> films uniformly covered on the Ni foam and the NiSe<sub>2</sub> nanopyrramids directly grown from the bottom films. The NiSe<sub>2</sub> nanopyramid electrode exhibits a high specific capacity of 240.83 mAh g<sup>-1</sup> at 1 A g<sup>-1</sup>. The small values of the internal resistance (0.85 Ω) and charge transfer resistance (0.41 Ω) demonstrate the excellent charge transfer rate and electrical conductivity. The hybrid device delivers a high energy density of 0.196 mWh cm<sup>-2</sup> at a power density of 1.6 mW cm<sup>-2</sup>. The equivalent series resistance (ESR) of the all-solid-state hybrid device is 1.52 Ω, which firmly reveals the nature of low resistance and high conductivity for BSH devices. Meanwhile, connecting two hybrid devices in series is able to drive a red LED for more than 3 minutes after charging for 9 seconds.

A facile one-step hydrothermal strategy has been carried out to synthesize pyramid-like NiSe<sub>2</sub> nanostructures on nickel foam. The NiSe<sub>2</sub> nanopyramid electrode exhibits a significant specific capacity, good rate capability and high conductivity. The all-solid-state hybrid device integrates the merits of high energy density at a high power density and low internal resistance. These results demonstrate the pyramid-like NiSe<sub>2</sub> nanostructure is expected to be an ideal high-specific-capacity electrode material, representing a type of promising electrode for energy-storage hybrid devices with wide-scale applications, particularly in all-solid-state energy storage devices and portable electronic devices.

## 墙展

### A01-P01

#### Effects of neutron irradiation on the elastic modulus of reactor pressure vessel steels

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The elastic modulus of material performance parameters are taken as the design input to perform the stress analysis and structural integrity evaluation of reactor pressure vessel (hereinafter referred to as RPV). Fast neutron irradiation damage is one of the main reasons leading to the deterioration of RPV material performance. The influence of irradiation on the elastic modulus of RPV steel and its variation in the whole in service life of RPV has been the focus for nuclear power designers. The neutron accelerated irradiation test of RPV steel was carried out at 290 °C by irradiation test reactor. Then, the elastic modulus, Poisson's ratio, shear modulus and longitudinal wave velocity of RPV steels after irradiation were tested by ultrasonic resonance spectrometer in the hot laboratory. The results showed that the elastic modulus and other parameters of Hualong No.1 RPV do not change significantly during the whole in service life, and the fast neutron irradiation damage has no effect on the above materials performance. The conclusion is helpful to improve the reliability of the integrity evaluation results of RPV during the long term service, and provide support for RPV life extension demonstration in the future.

### A01-P02

#### Microstructures and Properties of Zn-Al-Mg Alloys with Different Mg and Al Contents

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Zn-Al-Mg coating is the highest corrosion resistance new coating of the Zn-based coating and the surface is beautiful, it has broad application prospects in the industry. The addition of Mg has a certain influence on the structure and properties of the coating, but Mg has a strong affinity for oxygen and is easily oxidized. Therefore, Zn-Al-Mg alloys with different Mg and Al contents were smelted in the electrical resistance furnace by heating the mixture of pure Zn ingot, pure Al ingot and Mg<sub>11</sub>Zn alloy to 600°C, holding temperature for half an hour, sampling and cooling. Through component analysis, the actual composition was close to the target. The microstructure and chemical composition of the Zn-Al-Mg alloys was analyzed by scanning electron microscopy (SEM) and energy

dispersive spectrometer (EDS), respectively. Electrochemical polarization experiments were carried out on the samples. The Tafel polarization curves were exported to judge the corrosion resistance of the samples. As the Mg content in the Zn-Al-Mg alloy increasing, more lamellar and fine Zn/Al/MgZn<sub>2</sub> eutectic structure replace dendritic and coarse Al-enriched structure in the alloys. Also the charge transfer resistance shows differently values which concludes that the alloy contains 6 wt.% Al has the biggest anti-corrosion ability.

#### **A01-P03**

##### **A high-performance hybrid Mg<sup>2+</sup>/Li<sup>+</sup> battery based on hierarchical copper sulfide microflowers conversion cathode**

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Hybrid Mg<sup>2+</sup>/Li<sup>+</sup> batteries featuring dendrite-free Mg anode and Li-storage cathode are promising safe energy storage systems. However, improving the energy density remains a grand challenge due to the quite limited capacities of traditional Li-intercalation cathodes. To circumvent this limitation, a new type of conversion cathode for hybrid Mg<sup>2+</sup>/Li<sup>+</sup> batteries, microflower-like Cu<sub>9</sub>S<sub>5</sub>, is reported herein. The Cu<sub>9</sub>S<sub>5</sub> cathode is compatible with the dual-salt Mg<sup>2+</sup>/Li<sup>+</sup> electrolyte and delivers a high reversible capacity of 300mAh g<sup>-1</sup> at 50mA g<sup>-1</sup> via electrochemical conversion reaction, with 94% capacity retention over 100 cycles in hybrid Mg<sup>2+</sup>/Li<sup>+</sup> batteries. The electrode also shows an outstanding rate capability providing 155mAh g<sup>-1</sup> at 1000mA g<sup>-1</sup> and a superior long-term cyclability over 1000 cycles. This excellent performance is attributed to the hierarchical architecture of Cu<sub>9</sub>S<sub>5</sub> which facilitates the reversible conversion reactions and stabilizes the electrode structure during discharge/charge process. This work provides new insight for the nanostructure design of stable conversion electrodes and opens a new avenue for building safe and high-performance hybrid Mg<sup>2+</sup>/Li<sup>+</sup> batteries for practical applications.

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#### **A01-P04**

##### **Nanoencapsulated phase change materials with polymer-SiO<sub>2</sub> hybrid shell materials: compositions, morphologies, and properties**

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Organic-inorganic hybrid materials are promising for encapsulation of phase change materials (PCMs) to achieve exceptional capsule properties. In this work, novel polymer-SiO<sub>2</sub> hybrid shelled nanoencapsulated PCMs (NanoPCMs) were fabricated in one-pot, through sequentially executed interfacial hydrolysis-polycondensation of alkoxy silanes and radical polymerization of vinyl monomers. The morphologies, chemical compositions, and crystal structures of the NanoPCMs were characterized by SEM, TEM, FT-IR, and XRD methods. The thermal energy storage capability, thermal reliability, and thermal conductivity were tested by DSC, accelerated thermal cycling test, and heat flux method, respectively. The leakage proof property and mechanical property were evaluated by seepage test and nanoindentation test, respectively. Compared with NanoPCMs with SiO<sub>2</sub> shell, the NanoPCMs with polystyrene (PS)-SiO<sub>2</sub> shell possess smaller size and bowl like shape, while NanoPCMs with poly(hydroxyethyl methacrylate) (PHEMA)-SiO<sub>2</sub> shell possess larger size and perfect spherical shape. The polymer types have great impact on the supercooling behavior of the NanoPCMs. The polymer-SiO<sub>2</sub> hybrid shell materials endow the NanoPCMs with improved thermal reliability, thermal conductivity, and leakage proof property. More importantly, the compressive load at yield increases remarkably from 14.7 μN for nanocapsules with SiO<sub>2</sub> shell, to >34.6 μN for that with PS-SiO<sub>2</sub> shell, and 65 μN for that with PHEMA-SiO<sub>2</sub> shell.

#### **A01-P05**

##### **Electrochemical Performance of Polypyrrole Nanowires/Nitrogen Functionalized Graphene Composite supercapacitor electrodes**

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Conducting polypyrrole (PPy) nanowires have been electrodeposited on nitrogen functionalized graphene (NFG) surface and

obtain the PPy/NFG composites. The scanning electron microscope (SEM) results demonstrate that PPy nanowires with 80 nm in diameter. The direct and close contact between electroactive material and conductive current collector is beneficial to improve specific surface area and the conductivity of supercapacitor electrodes. The obtained PPy/NFG composites exhibit good capacitive behavior with specific capacitance of 1058 and 910 F/g at current densities of 0.5 and 10 A/g. However, the PPy nanowires and NFG present specific capacitance of 309 and 160 F/g, 265 and 185 F/g, respectively. Symmetric supercapacitor device based on the PPy/NFG composite also presents a high specific capacitance (601 F/g at a current density of 0.5 A/g), large energy density (83.5 Wh/kg) and power density (10 kW/kg). Moreover, the supercapacitor shows excellent charge/discharge rate and good cycling stability, retaining over 93% of its initial capacitance after 3000 cycles.

#### **A01-P06**

##### **Novel core/shell CoSe<sub>2</sub>@PPy nanoflowers for high-performance fiber asymmetric supercapacitors**

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Objectives: Portable and wearable electronic products are attracting more and more attention in recent years. Here we reported a high performance flexible fiber asymmetric supercapacitor (FASC) assembled from a CoSe<sub>2</sub>@PPy core/shell positive electrode and an electrochemically activated carbon fiber (EACF) negative electrode.

Methods: Nanostructured CoSe<sub>2</sub> chrysanthemum flowers are synthesized via hydrothermal reaction. The highly hierarchical and electrochemically active material is electrodeposited with PPy to produce high performance nanostructured core/shell CoSe<sub>2</sub>@PPy flower electrode.

Results: The lightweight and flexible fibre-shaped asymmetric supercapacitor CoSe<sub>2</sub>@PPy//EACF exhibits high volumetric energy density, superior flexibility and long lifespan, which provides a stable output voltage of 1.6 V and achieves a high energy density of 2.63 mWh cm<sup>-3</sup> at 14 mW cm<sup>-3</sup>, a high volumetric capacitance (7.6 F cm<sup>-3</sup>) at 18 mA cm<sup>-3</sup> and good capacity retention (~80%) after 15,000 charging/discharging cycles. The resulting FASC has been used to power a mini-scale flexible photodetector.

Conclusion: These encouraging results open up new opportunities for the novel nanostructured core/shell electrode as next generation high performance flexible and lightweight SCs and other energy storage devices.

#### **A01-P07**

##### **Facile Synthesis of Carbon Supported Nano-Ni Particles with Superior Catalytic Effect on Hydrogen Storage Kinetics of MgH<sub>2</sub>**

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Metal nano-catalysis is an effective method to enhance the hydrogen storage properties of magnesium hydride (MgH<sub>2</sub>), and the catalytic effect can be further improved by a matrix materials supported nano-metal. In this work, carbon supported nano-Ni (Ni@C) was synthesized by calcination of dimethylglyoxime dinickel chelate, and then it was doped into MgH<sub>2</sub> to improve the de/re-hydrogenation kinetics. It shows that the homogeneously distributed Ni with refined particle size in carbon base leads to superior catalytic effects on hydrogen absorption/desorption of MgH<sub>2</sub>-5 wt.% Ni@C. The MgH<sub>2</sub>-5 wt.% Ni@C starts to desorb hydrogen at 187 °C, which is 113 °C lower than that of as-milled MgH<sub>2</sub>. Moreover, it takes only 500 s to thoroughly desorb hydrogen at 300 °C, which is 3000 s faster than as-milled MgH<sub>2</sub> under the same dehydrogenation conditions. According to the Kissinger's method, the apparent activation energy for desorption of the MgH<sub>2</sub>-5 wt.% Ni@C is 66.5±1.8 kJ·mol<sup>-1</sup>, which is about 79.9 kJ·mol<sup>-1</sup> lower than that of as-milled MgH<sub>2</sub>. Cycling experiments show that the capacity retentions of hydrogen absorption and desorption after 10 cycles at 275 °C are 91 % and 93 %, respectively. Transmission electron microscope analysis shows part of Ni transformed to Mg<sub>2</sub>NiH<sub>4</sub>/Mg<sub>2</sub>Ni during hydrogen absorption/desorption cycles.

#### **A01-P08**

##### **The diffusion phenomenon of cathode components in YSZ electrolyte of SOFC**

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Solid oxide fuel cell (SOFC) is a new type of power generation technology that directly converts chemical energy into electrical energy. It has clean, high-efficiency advantages and broad application prospects. The energy conversion efficiency of SOFC is not limited by the Carnot cycle and can reach 60 to 70%, becoming a hot spot for energy research. The electrolyte needs to have high chemical and structural stability, high ionic conductivity, and low electronic conductivity at the operating temperature. Add a certain amount of  $Y_2O_3$  to zirconia  $ZrO_2$ , on the one hand, the introduction of low-priced  $Y^{3+}$  ions stabilizes tetragonal zirconia, and on the other hand it provides a large number of oxygen vacancies, which improves the oxygen ion conductivity. Therefore, yttria-stabilized zirconia (YSZ) has become the most widely used solid electrolyte material.

In recent years, although research on the flat-panel SOFC has made great progress, the attenuation problem is still the major bottleneck restricting its technological development. There are few studies on the diffusion of metal elements in the electrolyte induced by the current in the discharge state of SOFC.

This paper mainly studies the diffusion of Mn of a lanthanum strontium manganite (LSM) cathode in YSZ electrolyte after polarization test and the effect of diffusion on the mechanical properties of YSZ electrolyte. It is necessary to study the phenomenon of diffusion in electrolytes under the function of current, and find out the influence of polarization time and current density on the diffusion of elements, so as to make the suitable discharge state for the long time stable work of the SOFC.

The polarization test was respectively performed at a current density of  $1A/cm^2$  for 100h, 250h, 500h and 1000h, then using scanning electron microscope (SEM) to observe the microscopic morphology of the sample, and using the Energy-dispersive X-ray spectroscopy (EDX) linear scanning spectrometer attached to the SEM and electron probe microanalysis (EPMA) to analyze the interface between the electrode and the electrolyte. The effect of current density and polarization time on the diffusion depth is obtained.

The effects of current density and polarization time on the vickers hardness and fracture strength of YSZ electrolyte were studied by indentation test and ring-on-ring test. Through the microscopic observation of the fracture mode by SEM and X-ray photoelectron spectroscopy (XPS), the data is obtained and the curve fitting is carried out, and the corresponding relationship between the time of electricity and the strength and hardness of the fracture is obtained and the phenomenon is explained.

Finally, it is found from experiments that under the function of polarization current, the Mn can diffuse into YSZ. With the increase of polarization time and the increase of current density, the depth of diffusion is larger. In addition, the diffusion of Mn has an effect on the mechanical properties of YSZ, and the different polarization time and current density have different effects on mechanical properties.

#### **A01-P09**

##### **Fe<sup>3+</sup> doped TiO<sub>2</sub> octahedrons derived from a metal-organic framework toward visible-light photocatalytic conversion of CO<sub>2</sub> into solar fuel**

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With the fast development of MOFs in the field of photocatalysis during the past several decades, MOFs have been considered as a good template or precursor in the synthesis of new photocatalytic materials. But the majority of the work were focused on the thermal decomposition of MOFs and MOFs composites by heat treatment. In this work, Fe<sup>3+</sup> doped TiO<sub>2</sub> octahedrons with lengths of 300-600 nm, were prepared by a hydrothermal route in the presence of HF, using MIL-101(Fe) as template and the source of Fe. The Fe<sup>3+</sup> doped TiO<sub>2</sub> octahedrons show great potential in photocatalytic reduction of CO<sub>2</sub> to CH<sub>4</sub> under visible light. On the one hand, the morphology of octahedron has a large specific surface area. On the other hand, the doping of Fe<sup>3+</sup> reduces the band gap of TiO<sub>2</sub> and makes it responsive in visible light. After annealing, the oxygen vacancies of the samples increased because of the increase of Fe doping content. Photocatalytic reduction of CO<sub>2</sub> under visible light and the yield of CH<sub>4</sub> is up to 5.70  $\mu$ mol/g.

#### **A01-P10**

##### **Surfactant dependent zinc cobalt sulfide: high performance charge storage material for asymmetric supercapacitors**

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Composite electrode materials,  $\text{Co}_3\text{S}_4/\text{Zn}_{0.76}\text{Co}_{0.24}\text{S}$ , with different morphologies on three dimensional nickel foam by a facile hydrothermal and subsequent ion exchange techniques method. With the hexamethylenetetramine (HMT) serving as alkaline source, different surfactants such as ammonium fluoride ( $\text{NH}_4\text{F}$ ) or poly-vinylpyrrolidone (PVP) will contribute to develop various morphologies. The morphologies, structures and crystalline phase, specific surface area and electrochemical performance will be analyzed to research the superiority of thin kind of material. The  $\text{NH}_4\text{F}$  actuated a flower like Zn-Co-S, expressing a superior electrochemical performance of  $2798.16 \text{ F g}^{-1}$  in  $5 \text{ mA cm}^{-2}$  and retaining 93.8% after 7000 cycles, which is better than the branch like Zn-Co-S actuated by PVP. The fabricated asymmetric supercapacitor, flower like Zn-Co-S //RGO, effectively improve the voltage window up to 1.6V and consequently lead to a high energy density of about  $62.22 \text{ Wh kg}^{-1}$  at a power density of  $800 \text{ W kg}^{-1}$ , excellent specific capacitance of  $175 \text{ F g}^{-1}$  at  $1 \text{ A g}^{-1}$ , and long cycle life (retain 86.29% after 8000 cycles).

#### A01-P11

##### Basic Properties of Proton Conductor BZCYYb Material

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Proton conductor BZCYYb( $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ ) have a wide range of applications in SOFC due to its resistance to carbon deposition and good electrical conductivity, while less research is conducted on the basic properties of BZCYYb materials. In this paper, the water storage capability, oxygen vacancy concentration, phase transition, chemical stability and conductivity of BZCYYb were studied. In a steam atmosphere, a 1.4% weight gain was observed in the experiment of heating up to  $650^\circ\text{C}$  and holding for one hour. The  $\delta$  in BZCYYb measured by the iodometric method at room temperature was 0.215 to 0.216. Thermogravimetric analysis at high temperature found that BZCYYb material has weightlessness, indicating the precipitation of oxygen in the material. Oxygen vacancies and water absorption are the key factors affecting the resistance to carbon deposition. In addition, DTA and thermal expansion tests have found 5 phase change points from room temperature to  $1100^\circ\text{C}$ .

#### A01-P12

##### A novel perovskite $\text{Nd}(\text{Ba}_{0.4}\text{Sr}_{0.4}\text{Ca}_{0.2})\text{Co}_{1.6}\text{Fe}_{0.4}\text{O}_{5+\delta}$ as cathode for proton-conducting solid oxide fuel cells

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Layered perovskite oxides have received extensive attention as promising cathode materials for solid oxide fuel cells (SOFCs) because of their faster diffusion coefficient and oxygen transport kinetics. A novel perovskite  $\text{Nd}(\text{Ba}_{0.4}\text{Sr}_{0.4}\text{Ca}_{0.2})\text{Co}_{1.6}\text{Fe}_{0.4}\text{O}_{5+\delta}$ (NBSCaCF) is fabricated by simultaneously doping strontium (Sr) and calcium (Ca) in the layered perovskite  $\text{NdBaCo}_{1.6}\text{Fe}_{0.4}\text{O}_{5+\delta}$  and initially examined as a cathode for proton-conducting fuel cells (H-SOFCs) based on a  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$  (BZCYYb) electrolyte.

NBSCaCF is synthesized by the sol-gel method and its structural characteristic, electrical property and redox behavior are investigated. Anode supported single cell (Ni-BZCYYb anode, BZCYYb electrolyte, and NBSCaCF - BZCYYb cathode) and symmetrical fuel cell (NBSCaCF - BZCYYb electrodes and BZCYYb electrolyte) are fabricated and their performances are measured. The interfacial polarization resistance for the symmetrical fuel cell is as low as  $0.41 \Omega \text{ cm}^2$  under open circuit conditions, at  $650^\circ\text{C}$ .

This study reveals a novel strategie for layered perovskites` doping and demonstrates the potential of NBSCaCF - BZCYYb as a cathode material for proton-conducting intermediate-temperature solid oxide fuel cells.

#### A01-P13

##### First-Principles Study of the Surface Stress and the Surface Strain of Pt Catalysts

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Using the first-principles density functional theory calculations, we have conducted a systematic study of the surface stress and the surface strain of the stepped Pt surfaces. We examined both  $n(111) \times (110)$  type and  $n(111) \times (100)$  type stepped surfaces. We found

that, for both cases, the surface stresses are similar to that of (111) in the direction along the steps, but smaller than that of (111) in the direction perpendicular to the steps with the dependence on the number of terrace atoms  $n$ , i.e. there is a linear relationship between the surface stress and the inverse of the terrace width  $1/n$ . The stress in the direction perpendicular to the steps induces a compressive strain of the surface atoms, which increases with the decreasing width of terrace ( $n$ ). As surface strain modulate the surface electronic structure and energetics of adsorbed reaction intermediates, we will discuss the implication of the surface strain on the catalytic activity of various Pt surfaces, using oxygen reduction as an example, and further compare with available experimental results.

#### A01-P14

##### **Hydrogen desorption properties of MgH<sub>2</sub> promoted by the hydrogen-induced Al\* formed in situ from Al<sub>12</sub>Mg<sub>17</sub> in hydriding combustion synthesis**

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The effects of the hydrogen-induced Al\* formed in situ from Al<sub>12</sub>Mg<sub>17</sub> in hydriding combustion synthesis (HCS) on the dehydriding properties of MgH<sub>2</sub> were investigated. Thermal analysis showed that the peak temperature of dehydriding of the as-milled MgH<sub>2</sub> prepared by HCS was reduced by 15.2 °C when commercial 20 at% Al was introduced by mechanical milling. It would be further reduced by 24.9 °C when 20 at% Al\* was introduced in situ from the hydriding of Al<sub>12</sub>Mg<sub>17</sub> during HCS. Isothermal desorption measurements showed much better dehydriding kinetics of MgH<sub>2</sub>-20 at% Al\* than MgH<sub>2</sub>-20 at% Al, that is, 4.14 and 2.92 wt% hydrogen were desorbed at 300 °C after 60 min for MgH<sub>2</sub>-20 at% Al\* and MgH<sub>2</sub>-20 at% Al, respectively. It revealed that the Al\* resulted in a finer grain size of MgH<sub>2</sub> and a uniform distribution of aluminum which is beneficial greatly for a reduction of hydrogen diffusion length and for its high thermal conductivity. Furthermore, the apparent activation energy was reduced from 144.4 kJ/mol for the MgH<sub>2</sub> to 133.2 kJ/mol for the MgH<sub>2</sub>-20 at% Al\*

#### A01-P15

##### **Hierarchical core-shell structure of the FeCo<sub>2</sub>S<sub>4</sub>@Ni(OH)<sub>2</sub> arrays for all-solid-state asymmetric supercapacitors**

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Supercapacitors (SCs) have attracted tremendous interests owing to their long cycle life, high power density and fast recharge capability compared with other commercial batteries.<sup>[1, 2]</sup> Herein, a hierarchically core-shell and ultrathin double-layer FeCo<sub>2</sub>S<sub>4</sub>@Ni(OH)<sub>2</sub> three-dimensional (3D) network on Nickel foam (NF) was successfully prepared for the first time by a simple method. The morphology, composition and structure of the prepared hybrid are characterized by SEM, TEM, EDS, XRD, and XPS. The FeCo<sub>2</sub>S<sub>4</sub>@Ni(OH)<sub>2</sub>/NF electrode exhibits a high specific capacitance of 2984 F/g at 5mA/cm<sup>2</sup> and shows a remarkable cycling stability (about 95.7% of capacity retention after 5000 cycles at the current density of 50 mA/cm<sup>2</sup>). The as-fabricated ASC using FeCo<sub>2</sub>S<sub>4</sub>@Ni(OH)<sub>2</sub>/NF as the positive electrode and reduced graphene oxide as the negative electrode delivers a considerable energy density of 64 Wh/kg at a power density of 800 W/kg and superior cycling performance (about 92.9% of capacity retention after 10000 cycles at 6 A/g), which output voltage can achieve 1.6 V, and two ASCs connected in series can power a light-emitting diode (LED). Our strategy provide a facile method for fabricating hierarchically multicomponent heterostructures with unique structural superiority for prospective energy storage devices.

#### A01-P16

##### **Phosphorus-Based Materials for Sodium-ion Batteries**

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Sodium-ion battery is one of the most promising candidates to replace lithium-ion battery for large-scale electrochemical energy storage, because of their similar electrochemical performance, but the natural abundance of sodium raw material. Excellent electrochemistry performance and low-cost sodium-ion batteries are highly desirable for a wide range of applications including electric vehicles, hybrid vehicles, and renewable energy storage systems. Until now, a great number of researches have been devoted to developing alternative anode materials with superior electrochemical properties since the anode materials used are closely related to the capacity and safety characteristics of the batteries. In spite of many challenges, the development of sodium-ion batteries is relatively slow and immature in comparison to lithium-ion batteries primary due to the large radius of  $\text{Na}^+$  (1.09 Å vs. 0.76 Å of  $\text{Li}^+$ ). The electrode materials with high specific capacity, long cycle life but low cost, which are significant important for large-scale electrochemical energy storage.

With regard to anode materials, the limited theoretical specific capacity (372 mAh g<sup>-1</sup>) of the traditional commercial graphite significantly hampers the progress of electrochemical energy storage. Phosphorus takes the advantage of high theoretical specific capacity of 2596 mAh g<sup>-1</sup>, which is considered to promising anode material for sodium-ion batteries. Such a high theoretical specific capacity and three electron transfer reaction of phosphorus with  $\text{Na}^+$  forming  $\text{Na}_3\text{P}$ . Generally speaking, solid phosphorus has three main allotropes, including white phosphorus, red phosphorus and black phosphorus. Due to the chemical instability, white phosphorus is in no doubt impossible to be employed as electrode materials. Moreover, the synthesis of bulk phosphorus materials are more complicated. Similar to silicon as anode materials for lithium-ion battery, the key points of the red phosphorus for sodium-ion battery are the low conductivity and severe structural destruction caused by large volume change during electrochemistry cycles.

Graphene, a carbon monolayer packed into a two-dimensional honeycomb lattice, with numerous advantages including superior electronic conductivity, large surface area, and excellent mechanical strength, leading to a wide range of application as a conductive additive in electrochemical energy storage application. In contrast with graphene, graphene oxide can be easily dispersed in many solvents, through chemical method, the functionalization of graphene oxide with active materials to form hybrid graphene oxide materials, which leading to extensive use as conductive additive in electrochemical energy storage. In all case, graphene oxide matrix seems to enhance the electronic and ionic transport properties, thus improving the cycle and rate capability.

Herein, we reported the synthesis of hybrid red phosphorus/graphene oxide anode materials. When applied as anode material for sodium-ion battery, the related cyclic voltammetry, cycle performance, rate capability and electrochemical impedance spectroscopy were investigated.

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#### **A01-P17**

##### **Nitrates induced stress corrosion cracking in tubing from oil well**

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The 110 Ksi tubing failed in use when reservoir acidification reconstruction and production testing were performed in a HPHT oil well, which is longitudinal cracking of coupling. Failure analysis was conducted on the coupling. The failure zone was studied by means of macroscopic analysis, metallographic, scanning electronic microscope, energy dispersive spectrometer and X-ray diffraction analysis etc. The results indicated that the failure of the coupling is caused by stress corrosion cracking (SCC). SCC initiated from the exterior surface of coupling and displayed the fracture feature of intergranular crack propagation. The corrosion products at the grain boundaries were found to be mainly some oxides. The failure is in connection with the completion fluid composition, which are mainly nitrates.

#### **A01-P18**

## Surface-engineering enhanced sodium storage performance of Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> cathode via in-situ self-decorated conducting polymer route

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The rapid development of new energy sources requires efficient energy storage technology. Among the various technologies, Na-ion batteries are the most promising alternative because of low cost and wide-spread availability of Na.

Since the 1980s, a variety of polyanionic materials have attracted much attention. Among them, NASICON-type Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (NVP) received considerable attention because of its high reversible capacity of 117 mAh g<sup>-1</sup> and high potential plateau at 3.4 V vs. Na<sup>+</sup>/Na. Conducting polymers are ideal coating agents because they not only improve the electrical conductivity, but also provide mechanical flexibility. Among the conductive polymers, poly(3,4-ethylene-dioxythiophene) (PEDOT) is a commonly used conductive intermediate because of its high electrical conductivity. Therefore, NVP@PEDOT composite was prepared for the first time using an in-situ self-decorated conducting polymer route that does not require further calcination.

Bare NVP was prepared by ball mixing and subsequent calcination method. NVP@PEDOT was prepared by in-situ surface-self-decorated method. To partially oxidize NVP, NO<sub>2</sub>BF<sub>4</sub> was used as the oxidizing agent. The coating content of PEDOT can be controlled by tuning the oxidizing state of NVP using different molar ratios of NVP and NO<sub>2</sub>BF<sub>4</sub>. In this study, two different molar ratios of NVP and NO<sub>2</sub>BF<sub>4</sub> (5:1 and 5:2) were selected, marked as NVP@PEDOT-1 and NVP@PEDOT-2, respectively.

NVP@PEDOT-1 electrode showed the best electrochemical performance, reaching a reversible capacity of as high as 89, 79, and 58 mAh g<sup>-1</sup> at high rates of 5, 10 and 20 C, respectively, while the bare NVP electrode only delivered 25, 13, and 5 mAh g<sup>-1</sup>, respectively. When the current was returned to a low rate, the initial capacity of the three electrodes was recovered, exhibiting excellent structural stability. The cycling behaviors of bare NVP and NVP@PEDOT electrodes were also investigated. NVP@PEDOT-1 electrode delivered a high discharge capacity of 100 mAh g<sup>-1</sup> at the initial capacity and 93 mAh g<sup>-1</sup> after 100 cycles at 1 C rate, corresponding to a capacity retention of 93%, while only 89% and 59% for NVP@PEDOT-2 and NVP electrodes, respectively. Even after 200 cycles, NVP@PEDOT-1 electrode exhibited a capacity retention of 82%. The enhanced electrochemical performance of the electrode with PEDOT coating can be explained as follows: the coated PEDOT improves the electronic conductivity and buffers the structural change during the Na- ion insertion and extraction.

The experimental results show that the conducting polymer-coated NVP can be used as a low-cost, high-energy, and long-cycling-life cathode material for the construction of cost-effective Na-ion batteries. This facile self-decorated synthetic method has a potential to achieve an in-situ conducting coating on the surface of materials in the energy storage, catalysis, and biomass fields.

### A01-P19

## A Scalable Strategy to Develop Advanced Anode for Sodium-Ion Batteries: Commercial Fe<sub>3</sub>O<sub>4</sub> Derived Fe<sub>3</sub>O<sub>4</sub>@FeS with Superior Full-Cell Performance

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Sodium-ion batteries (SIBs) have recently attracted a great interest as a promising alternative to lithium-ion batteries (LIBs) for large-scale energy storage applications owing to their low cost and abundant Na resource. However, the larger diameter of Na ion than that of the Li one hampers the electrochemical kinetics of SIBs electrodes, making it difficult to achieve the reversible insertion/extraction of Na ions into/out the crystalline host. Hence, it's still a huge challenge to find the appropriate and scalable anode materials with high specific capacity, outstanding Na-storage reversibility and excellent rate capability.

Herein, a novel core-shell Fe<sub>3</sub>O<sub>4</sub>@FeS composite with the morphology of regular octahedra has been prepared via a facile and scalable strategy by using commercially available Fe<sub>3</sub>O<sub>4</sub> (C-Fe<sub>3</sub>O<sub>4</sub>) as the low-cost precursor. When investigated as anode material for SIBs, the prepared Fe<sub>3</sub>O<sub>4</sub>@FeS exhibits the much improved Na-storage performance, which combines the high capacity of FeS and the excellent cycling stability of Fe<sub>3</sub>O<sub>4</sub>. It delivers a reversible Na-storage capacity of 169 mAh g<sup>-1</sup> after 750 cycles at 0.2 A g<sup>-1</sup> with a capacity retention of 90.8 % and a Coulombic efficiency of around 100 %. Furthermore, it is disclosed that such outstanding electrochemical properties should be attributed to the partially pseudocapacitive behaviors in the kinetic of FeS shell and the

synergies between Fe<sub>3</sub>O<sub>4</sub> and FeS in the core-shell structure. Furthermore, the full cells are assembled by coupling the prepared Fe<sub>3</sub>O<sub>4</sub>@FeS anode with our previously reported Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>O<sub>2</sub>F (NVPF) cathode. The Fe<sub>3</sub>O<sub>4</sub>@FeS/NVPF full cell delivers a reversible capacity of 157 mAh g<sup>-1</sup> after 50 cycles at 0.5 A g<sup>-1</sup> with a capacity retention of 92.3 %. The good performance, simple preparation and low cost raw, carbon-free, make Fe<sub>3</sub>O<sub>4</sub>@FeS become a promising anode material for SIBs and it is expected to large-scale commercial applications.

References:

- [1] WANG Y-Y, HOU B-H, GUO J-Z, et al. An Ultralong Lifespan and Low-Temperature Workable Sodium-Ion Full Battery for Stationary Energy Storage [J]. *Advanced Energy Materials*, DOI: 10.1039/c8ta01132j.
- [2] HOU B H, WANG Y Y, GUO J Z, et al. A Scalable Strategy To Develop Advanced Anode for Sodium-Ion Batteries: Commercial Fe<sub>3</sub>O<sub>4</sub>-Derived Fe<sub>3</sub>O<sub>4</sub>@FeS with Superior Full-Cell Performance [J]. *Acs Appl Mater Interfaces*, 2018, 10(4): 3581-9.
- [3] WANG Y-Y, HOU B-H, WANG Y-N, et al. Multiple heterointerfaces boosted de-/sodiation kinetics towards superior Na storage and Na-Ion full battery [J]. *J Mater Chem A*, 2018, 6(15): 6578–86.
- [4] HOU B-H, WANG Y-Y, GUO J-Z, et al. Pseudocapacitance-Boosted Ultrafast Na Storage in Pie-Like FeS@C Nanohybrid as Advanced Anode Material for Sodium-Ion Full Batteries [J]. *Nanoscale*, DOI: 10.1039/C7NR09674G.

## A01-P20

### Co<sub>3</sub>O<sub>4</sub> nanofasciculus consisted of nanowire on carbon fibers as electrode materials for long-life pseudocapacitors

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Among these electrical energy storage systems, supercapacitors have been paid more and more attention as the most promising power sources compared to other energy storage devices (such as Li-ion, Pb-acid, and Ni-MH batteries) in terms of higher power density, short charge time and long cycle life<sup>[1]</sup>. Electrode material is one of the key factors that affect the capacitive performance of supercapacitors. Therefore, the regulation of material morphology, composition and specific surface area has become an important way to study and develop high performance electrode materials<sup>[2]</sup>.

Redox-active transition metal oxides and hydroxides, such as RuO<sub>2</sub>, MnO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, CoO, NiO, CuCo<sub>2</sub>O<sub>4</sub>, Co(OH)<sub>2</sub> and Ni(OH)<sub>2</sub>, are the most fascinating candidates as pseudocapacitor electrode materials in virtue of their high theory specific capacitances and power densities relied on the fast redox reaction on the surface<sup>[3]</sup>. Cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) is believed to hold a high capacitance up to 3560 F/g and an excellent redox reversibility according to theoretical predict<sup>[4]</sup>. In this work, Co<sub>3</sub>O<sub>4</sub> nanofasciculus consisted of nanowire on carbon fibers was been prepared by hydrothermal. The loading amount of active material is 1.0 ± 0.1 mg/cm<sup>2</sup>. All the electrochemical measurements were performed with an electrochemical workstation (CHI 660E) under a conventional three-electrode cell with 6 M KOH aqueous solution as an electrolyte at room temperature.

Almost all of the CV curves have a pair of obvious redox peaks within the rang of 0 to 0.6 V. The reactions in charge/discharge may be described as (Co<sub>3</sub>O<sub>4</sub> + 4OH<sup>-</sup> ↔ 3CoO<sub>2</sub> + 2H<sub>2</sub>O + 4e<sup>-</sup>). The specific capacitance can achieve 604.6 F/g and 425.5 F/g at the current densities of 4 and 32 A/g. After cycling 40000 times at a big current density of 32 A/g, the specific capacitance still retains 117 % of its initial capacitance. The results prove that the novel nanofasciculus structure is promising candidate materials for high-performance pseudocapacitor.

Reference:

- [1] *Nat. Mater.* 2008 , 7, 845
- [2] *J. Mater. Chem. A*, 2015, 3, 13114–13188
- [3] *Journal of Power Sources* 263 (2014) 338e360
- [4] *Adv. Mater.* 2017, 29, 1604167

## A01-P21

### Carbon-coated Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> Microspheres as a Superior Rate and Long Cycle Lifespan Cathode Material for Sodium Ion Batteries

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Sodium ion batteries have been of great interest in recent decades on account of the richer natural abundance, lower price and similar electrochemical mechanism to lithium-ion batteries. Nevertheless, the energy density and cyclic stability of existing cathode material haven't reached a satisfactory level due to poor conductivity and low average discharge voltage. NASICON type materials with high Na ionic conductivity and stable 3D framework have been widely investigated as sodium ion battery materials. Among them,  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  with an average operating potential of 3.4 V and high cycling stability, is considered as a promising cathode material for sodium ion battery. However, inferior electronic conductivity limits rate capability and reversibility, which hinders its practical application.

In this contribution, carbon-coated  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  microspheres (denoted as NVP@C) are synthesized by a facile spray-drying method. NVP@C appear near-perfect spheres, which could improve effectively the surface area NVP@C composites. The carbon layer was uniformly coated on the surface of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  particles by using glucose as carbon source. When used as cathode for SIBs, NVP@C microspheres exhibits excellent electrochemical performance in voltage range of from 2.0 V to 3.9 V. The reversible capacity of  $108.7 \text{ mA h g}^{-1}$  was obtained at a current rate of 0.2C (1C corresponds to  $117 \text{ mA h g}^{-1}$ ). Even at 50 C, the electrode can deliver a specific discharge capacity of  $62.1 \text{ mA h g}^{-1}$ . After the long-term 7000 cycles at the rates of 10 C, the reversible capacity can reach  $70.2 \text{ mA h g}^{-1}$ , corresponding to capacity retention of 74.2%. The superior electrochemical performance is ascribed to the 3D carbon matrix which could promote the electronic conductivity of the electrode and accommodate effectively volume variation during Na insertion/extraction.

#### A01-P22

##### Water-in-salt electrolyte enables aqueous supercapacitors

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Electrolyte is the charge carrier in electrolyte, which has a key effect on the overall performance of the capacitor. There are many factors that affect the performance of electrolyte, such as concentration of electrolyte salt in electrolyte, electric potential window of electrolyte, ionic conductivity of electrolyte, etc. At present, organic electrolyte (2.7 V) and ionic liquid electrolyte (3.5 V) is widely applied, but it is restricted of ionic conductivity, short cycle life and low toxicity, so the development of low cost, environmental protection, high-performance water electrolyte is promising. However, the decomposition voltage of water system electrolyte is only 1.23V. Herein, comparing the linear sweep voltage(LSV) window of different electrolyte(LiTFSI,  $\text{Li}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ), different scan rate (100mv/s, 50mv/s, 10mv/s) and different concentration (0.1m, 0.5m, 1.0m) in three-electrode system, which uses glassy carbon electrode as the working electrode, graphite electrode as the counter electrode and Ag/AgCl as the reference electrode. When increasing the concentration of LiTFSI from 1M to 18M, the linear scanning voltage window can reach up to 2.6V.

#### A01-P23

##### A 0.5LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>·0.5Li<sub>2</sub>MnO<sub>3</sub> composite electrode with high voltage and stability

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Li-rich manganese-based oxide materials have been considered as the most promising cathode materials for next lithium-ion batteries because they can deliver a high capacity more than  $250 \text{ mAh g}^{-1}$ . However, they suffer from serve capacity fading and voltage decay upon cycling. In this study, we propose a new strategy to mitigate capacity fading and voltage decay by combine  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  with  $\text{Li}_2\text{MnO}_3$ .

As a result, the  $0.5\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2 \cdot 0.5\text{Li}_2\text{MnO}_3$  (NCA-LRMO) composite electrode shows high stability (94% capacity retention and 197 mV voltage decay after 100 cycles at 0.1C) and high voltage (3.71V average discharge voltage). In contrast, the NCM111-LRMO ( $0.5\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2 \cdot 0.5\text{Li}_2\text{MnO}_3$ ) electrode shows 63% capacity retention and 436 mV voltage decay in the same condition.

By employing cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and transmission electron microscopy

(TEM), we revealed that the high stability of the NCA-LRMO electrode is due to its high Ni content, which could suppress the activity of Mn and inhibit the structure to transform from layered to spinel-like structure.

#### A01-P24

### A Practicable Li/Na-Ion Hybrid Full Battery Assembled by a High-Voltage Cathode and Commercial Graphite Anode: Superior Energy Storage Performance and Working Mechanism

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Nowadays, although Li-ion batteries (LIBs) are still dominating the market of energy storage and Na-ion batteries (NIBs) are regarded as a promising alternative of LIBs especially in the large-scale energy storage applications owing to the low cost and abundance of Na resources, both have their own shortcomings, such as higher and higher prices of LIBs due to the low and unevenly distributed Li resources, and relatively poor electrochemical properties of NIBs due to the large ionic radius of Na and sluggish Na-diffusion kinetics.<sup>1-4</sup> Hence, it is highly imperative to develop other advanced electrochemical energy storage devices. Amongst them, hybrid Li/Na-ion batteries (HLNIBs) should be a highly effective design concept to overcome their each disadvantages and give full play to the advantages of both LIBs and NIBs.<sup>5,6</sup>

In this study, we propose a new design of Li<sup>+</sup>/Na<sup>+</sup>-hybrid full battery composed of a high-voltage and lithium-free Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>O<sub>2</sub>F (NVPOF) and commercially available graphite (MCMB) as cathode and anode, respectively. The assembled HLNIBs exhibit two high working voltage at about 4.05 and 3.69 V with a specific capacity of 112.7 mA h g<sup>-1</sup>. Its energy density can reach up to 328 W h kg<sup>-1</sup> calculated from the total mass of both cathode and anode materials. Moreover, the HLNIBs show outstanding high-rate capability, long-term cycle life and excellent low-temperature performance. For example, at a very high current density of 2.6 A g<sup>-1</sup>, the delivered discharge capacity is 73.9 mA h g<sup>-1</sup>, and the corresponding capacity retention is above 66% compared to the value at the low current density of 0.065 A g<sup>-1</sup>. After even 2000 cycles at 1.3 A g<sup>-1</sup>, the capacity retention is still about 86.3%, implying a very low capacity fading rate of only 0.0068% per cycle. At -25 °C, the capacity retention is up to 80.6 % in comparison to room temperature. In addition, the reaction kinetics and Li/Na-insertion/extraction mechanism into/out NVPOF is preliminarily investigated by the galvanostatic intermittent titration technique and ex situ X-ray diffraction, and these test results reveal the fast Li/Na-migration kinetics of NVPOF electrode as well as the high reversibility and stability of NVPOF lattice during the successive Li/Na-intercalation/extraction processes. This work provide a new and profound direction to develop advanced hybrid batteries.

References:

[1] J. M. Tarascon, M. Armand, *Nature* 2001, 414, 359-367.

[2] C.-X. Zu, H. Li, *Energy Environ. Sci.* 2011, 4, 2614-2624.

[3] J.-Z. Guo, P.-F. Wang, X.-L. Wu, X.-H. Zhang, Q. Yan, H. Chen, J.-P. Zhang, Y.-G. Guo, *Adv. Mater.*, 2017, 27, 1701968.

[4] F. Wan, J.-Z. Guo, X.-H. Zhang, J.-P. Zhang, H.-Z. Sun, Q. Yan, D.-X. Han, L. Niu, X.-L. Wu, *ACS Appl. Mater. Interfaces* 2016, 8, 7790-7799

[5] Q. An, F. Xiong, Q. Wei, J. Sheng, L. He, D. Ma, Y. Yao, L. Mai, *Adv. Energy Mater.* 2015, 5, 1401963

[6] K. Du, H. Guo, G. Hu, Z. Peng, Y. Cao, *J. Power Sources* 2013, 223, 284-288

#### A01-P25

### Hydrogen storage properties of AB<sub>4</sub>-type single-phase La–Nd–Mg–Ni–Al-based alloy

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Superlattice RE–Mg–Ni-based alloys have been considered as one of the promising hydrogen storage materials. Herein, we obtained a new rhombohedral AB<sub>4</sub>-type single-phase La–Nd–Mg–Ni–Al alloy by induction melting method followed by annealing treatment. The structural characteristics of the AB<sub>4</sub> phase involved in the hydrogen absorption/desorption and its electrochemical hydrogen storage properties are studied.

The hydrogen storage capacity at the 303 K of this alloy is 1.75 wt.% and the corresponding plateau pressure is 0.15 MPa. With



the test temperature increases to 343 K, the hydrogen storage capacity increases to 2.21 wt.% and the plateau pressure decreases to 0.09 MPa. Moreover, the reversible hydrogen desorption amount is high to 95 % at 343 K. The electrochemical discharge capacity of the alloy electrode is 390 mAh g<sup>-1</sup> and the capacity retention rate at the 100<sup>th</sup> cycle is 90%.

The rhombohedral AB<sub>4</sub>-type superlattice structure is consisted by three CaCu<sub>5</sub>-type [AB<sub>5</sub>] subunits and one C15-type [A<sub>2</sub>B<sub>4</sub>] subunit stacking along the c-axis. The component [AB<sub>5</sub>] subunits could be divided into two patterns: the bilateral layer [AB<sub>5</sub>] subunit connected to the [A<sub>2</sub>B<sub>4</sub>] subunit ([AB<sub>5</sub>]<sup>1</sup>) and the middle layer [AB<sub>5</sub>] subunit neighbored to the inner [AB<sub>5</sub>] subunits ([AB<sub>5</sub>]<sup>2</sup>). Refinement results show that the volume of [AB<sub>5</sub>]<sup>2</sup> subunit gets larger than those of [AB<sub>5</sub>]<sup>1</sup> subunit. It is believed that the participation of the C15-type [A<sub>2</sub>B<sub>4</sub>] subunit in the stacking sequence results in the lattice deformation of [AB<sub>5</sub>]<sup>1</sup> and [AB<sub>5</sub>]<sup>2</sup> subunit. As the RE–Mg–Ni-based alloys store hydrogen by the H atoms entering the crystal lattice interstice, the lattice distortion certainly would impact the hydrogen storage properties. It is believed that the increased volume of [AB<sub>5</sub>]<sup>2</sup> subunit results in the improvement of the hydrogen storage capacity.

#### **A01-P26**

##### **A new type of composite electrolytes with high specific capacity and good air-stability for room-temperature solid-state lithium battery**

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Solid-state lithium batteries call for polymer electrolytes with high energy density, easy processing and excellent flexibility. However, the low ionic conductivity and high interfacial impedance hinder its further application. Therefore, we utilized lithium bis(oxalate)borate (LiBOB) to prepare the PEO-LLZTO-LiBOB solid electrolytes via the solution pouring method. Compared with the traditional LiPF<sub>6</sub> as a lithium salt, the BOB<sup>-</sup> anion could stabilize the Al fluid. And the solid-state electrolytes with LiBOB as lithium salt held a higher ionic conductivity and a wide electrochemical window. Moreover, the fabricated solid-state LiFePO<sub>4</sub>|Li batteries delivered a higher specific capacity and excellent cycle performance (165.9mAh g<sup>-1</sup> with capacity retention of 84.6% after 100 cycles) at room temperature. The larger volume of BOB<sup>-</sup> anions lead to weaker binding force with Li<sup>+</sup>, which resulted in the easy dissociation of lithium salt and the improvement in the conductivity of the whole system. These results provided a new prospect for solid polymer electrolytes of solid-state lithium-ion electrolytes at room temperature.

#### **A01-P27**

##### **Effect of carbon nanotubes on the microstructural evolution and hydrogen storage properties of Mg(BH<sub>4</sub>)<sub>2</sub>**

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As an important member of complex hydrides, Mg(BH<sub>4</sub>)<sub>2</sub> has a high gravimetric capacity (14.9 wt%). In this study, the Mg(BH<sub>4</sub>)<sub>2</sub> was synthesized by the ion exchange method. Afterwards, the Mg(BH<sub>4</sub>)<sub>2</sub> composites with different amounts (2, 5, 10, 25 and 50 wt%) of carbon nanotubes (CNTs) were prepared by mechanical milling. Effects of the CNTs on the microstructural evolution and hydrogen storage properties were investigated. The onset temperature of the Mg(BH<sub>4</sub>)<sub>2</sub>-5 wt% CNTs is decreased to lower temperature around 120 °C from 275 °C. The desorption plateau of Mg(BH<sub>4</sub>)<sub>2</sub>-5 wt% CNTs is the highest, which ascribes that CNTs causes the reaction pathway change. Additionally, the Mg(BH<sub>4</sub>)<sub>2</sub>-5 wt% CNTs shows the best dehydrogenating kinetics properties, and can desorb 6.04 wt% hydrogen within 2000 s at 300 °C. The dehydrogenation activation energy of the Mg(BH<sub>4</sub>)<sub>2</sub>-5 wt% CNTs is decreased to 130.2 kJ/mol H<sub>2</sub>, which is much lower than that of pure Mg(BH<sub>4</sub>)<sub>2</sub>.

#### **A01-P28**

##### **Triboelectric nanogenerator based on turbine structure for efficient water wave energy harvesting and self-powered water flow velocity sensing**

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With the gradually depletion of fossil fuels, researchers have worked on related environmental problems and looked for alternative renewable energy sources. Water wave energy is promising clean energy source, which is difficult to collect effectively. In this work, we demonstrated a turbine-triboelectric nanogenerator using silicone rubber, epoxy resin and flexible electrode which generates electricity from the motion of water flow. Turbine-triboelectric nanogenerator is an energy collection device based on the coupling between contact electrification and electrostatic induction of triboelectric materials, converting the water flow energy into electrical energy.

Turbine-triboelectric nanogenerator is composed of basement, fan blade, electrodes and turbine support. When the water flows through the turbine, the triboelectric materials on the fan blades will be contact each other. At the same time, the electrodes have potential and the charges will transfer between the electrodes. On the surfaces of the triboelectric layers, we prepared the nano-fiber structure, which can increase the contact area of the friction material and enhance the output of the turbine-triboelectric nanogenerator. In addition, CNTs were added into silicon rubber to increase the surface charge density of triboelectric materials of turbine-triboelectric nanogenerator.

With the size of the blades of a turbine of  $4 \times 3 \text{ cm}^2$ , the peak-to-peak short circuit current of  $3 \mu\text{A}$  and the peak-to-peak open circuit voltage of  $50\text{V}$  and the maximum power density of  $12.5 \mu\text{W}/\text{cm}^2$  at a load resistance of  $100 \text{ M}\Omega$  can be obtained from the turbine-triboelectric nanogenerator under the velocity of  $30\text{L}/\text{min}$ . 50 light-emitting-diodes (LEDs) can be completely lit up and  $2.2 \mu\text{F}$  capacitor can be easily charged to  $2.8\text{V}$  in  $9\text{s}$ . Due to the output current and voltage change with the water flow velocity, turbine-triboelectric nanogenerator can be applied to self-powered velocity sensor of water flow. The turbine-triboelectric nanogenerator has the advantages of low price, small size, high sensitivity and simple preparation process. The results obtained in this work open the prospects for the future development and optimization of an effective strategy of water flow, as well as the possibility of using as sensors to monitor the water supply system, which can use the energy generated by the water movement in the pipeline to work and send data. Additionally, turbine-triboelectric nanogenerator can be miniaturized for technology of microfluidics.

#### **A01-P29**

##### **The Design of Minitype Broadband Micro-Energy Generator**

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Micro-energy harvesting has become the key technology for extending the endurance of mobile terminals. Unlike the traditional chemical batteries, Micro-energy harvesting system could generate unlimited power as long as there is mechanical energy. The traditional micro-energy harvesting system has many problems such as large size, low sensitivity and poor efficiency, because it is mainly composed of electromagnetic generators(EMGs), triboelectric nanogenerators(TENGs) and piezoelectric nanogenerators(PENGs), and the limitation of EMGs is a major factor causing these problems. Therefore, the traditional micro-energy harvesting system only converts low-frequency mechanical energy into electrical power.

In this work, a novel generator harvesting both low and high-frequency mechanical energy is demonstrated. The main structure consists of two strong magnets and a support rod with a limiter. The strong magnets are placed with opposite polarity, resulting in one of the magnets is levitated. The coil is wrapped in rubber film, which attached to an electrode surface and placed on one of the magnets, and another electrode is placed on the other magnet. Due to the restriction of the limiter, the gap between to magnets is narrow and the gradient of the magnetic field becomes larger. Therefore, the coil will output huge power when the levitation has a small shock. Besides, the TENG composed of the two electrodes and the rubber produces electric power efficiently under the coupling effect of vibration and repulsion generated by the magnetic field.

The whole size of the minitype broadband micro-energy generator is  $4.5 \times 4.5 \times 2.2 \text{ cm}^3$  and its weight is about  $60 \text{ g}$ . In the verification experiment, the generator produces peak output power of  $42 \text{ mW}$ , and the frequency response range of the device is from  $2\text{Hz}$  to  $200\text{Hz}$ , which is extremely sensitive for micro-energy generators. The other dynamic response characters are analyzed in this paper.

#### **A01-P30**

##### **Highly efficient synergetic catalysis of graphene supported nickel on hydrogen storage of Mg90Al10 composite**

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Mg-based materials are a very promising candidate for hydrogen storage. However, its application is severely restricted by its high thermodynamic stability and sluggish hydrogen sorption-desorption kinetics. Compounding with transition metal elements has been adopted to improve the performance of Mg-based materials for hydrogen storage to resolve urgently these above problems. In the present work, the graphene supported Ni (Ni@rGN) was introduced to the Mg<sub>90</sub>Al<sub>10</sub> composite by hydriding combustion synthesis and mechanical milling (HCS+MM). The Ni@rGN catalysts were synthesized by a facile chemical reduction method. The microstructures of the composites show that Ni nanoparticles are well supported on the surface of graphene and the graphene supported Ni catalysts are dispersed uniformly on the surface of MgH<sub>2</sub> particles. Moreover, it is revealed that there is a synergistic effect of Ni, Al and graphene on the hydrogen storage properties of the composites. The Mg<sub>90</sub>Al<sub>10</sub>-8wt.% Ni@rGN shows the optimal hydriding/dehydriding properties, requiring only 100 s to reach its saturated hydrogen absorption capacity of 6.1 wt.% at 473K, and desorbing 6.4 wt.% hydrogen within 1200 s at 573 K.

#### **A01-P31**

##### **Synthesis and electrochemical properties of Sn/RGO composites as lithium-ion battery anodes**

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Among various available anode materials, metallic tin (Sn) has long been considered as alternatives due to its high theoretical capacities (Li<sub>4.4</sub>Sn: 993 mAh g<sup>-1</sup>), low cost, environmental benignity and high electrical conductivity. However, tin electrodes often behave rapid capacity decay and weak cyclability during cycling process because of the large lithiation/delithiation associated volume change. In our recent research, crystalline tin (Sn) nanostructures and tin/reduced graphene oxide (Sn/RGO) composites have been synthesized via two reduction methods separately (liquid reduction method and gamma-ray reduction technique). Comparing with Sn, the cycling stability of Sn/RGO composites is greatly improved to perform a long cycling life. For instance, Sn/RGO electrode, in which Sn spherical nanoparticles with the diameter of ~ 5 nm disperse uniformly on the surface of RGO, delivers a reversible discharge capacity of 355 mAh g<sup>-1</sup> at the end of 50 cycles at 200 mA g<sup>-1</sup>. (Some results and details can be seen in our recent article: International Journal of Electrochemical Science, 13(2018), 2366-2378)

#### **A01-P32**

##### **An Ultralong Lifespan and Low-Temperature Workable Sodium-Ion Full Battery for Stationary Energy Storage**

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In order to substitute the currently market-dominant lithium ion batteries (LIBs), which would become unaffordable to consumers due to the low abundance and uneven distribution of Li resources in the Earth's crust and therefore the higher and higher prices, sodium-based batteries (SBBs) have drawn great attentions of energy-storage scientists. Traditionally, SBBs are the molten-sodium batteries, mainly including the high temperature sodium-sulfur and sodium-metal halide batteries. Although high-T SSBs have been developed for the utilization in grid-scale energy storage, such a high operation temperature signifies the highly severe safety concerns in practical applications because the metallic sodium anode is in the liquid state with extremely high reactivity. Therefore, room-temperature (room-T) sodium-ion batteries (SIBs) were proposed and extensively studied to reduce/solve the safety hazards of high-T SBBs in recent years. In addition to high/room-T workability, low-temperature (low-T) Na storage is another principal concern for the wider applications of SIBs.

Herein, an outstanding anode material with superior low-T Na-storage performance was first prepared, and then an advanced low-T sodium-ion full battery (LT-SIFB) was assembled and studied via coupling such low-T anode with Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>O<sub>2</sub>F cathode. The prepared low-T anode material is a nanocomposite, in which amorphous selenium (*a*-Se) is evenly coated on the surface of 3D conductive network with open channels composed of reduced graphene oxide (rGO) nanosheets. Thereafter, it is abbreviated as

3DSG. The prepared 3DSG delivers outstanding Na-storage properties in terms of high capacity retention ( $C_r$ ) from room-T (25 °C) to -25 °C, long-term cycling stability, and superior rate capability. As expected, the assembled SIFB indeed exhibits superior low-T energy-storage performance as well as ultralong cycle life (e.g., after even 15000 cycles, the  $C_r$  is still up to 86.3% at 1 A g<sup>-1</sup>) and outstanding rate capability.

References:

- [1] WANG Y-Y, HOU B-H, GUO J-Z, et al. An Ultralong Lifespan and Low-Temperature Workable Sodium-Ion Full Battery for Stationary Energy Storage [J]. *Advanced Energy Materials*, DOI: 10.1039/c8ta01132j.
- [2] WANG Y-Y, HOU B-H, WANG Y-N, et al. Multiple heterointerfaces boosted de-/sodiation kinetics towards superior Na storage and Na-Ion full battery [J]. *J Mater Chem A*, 2018, 6(15): 6578–86.
- [3] HOU B H, WANG Y Y, GUO J Z, et al. A Scalable Strategy To Develop Advanced Anode for Sodium-Ion Batteries: Commercial Fe<sub>3</sub>O<sub>4</sub>-Derived Fe<sub>3</sub>O<sub>4</sub>@FeS with Superior Full-Cell Performance [J]. *Acs Appl Mater Interfaces*, 2018, 10(4): 3581-9.
- [4] HOU B-H, WANG Y-Y, GUO J-Z, et al. Pseudocapacitance-Boosted Ultrafast Na Storage in Pie-Like FeS@C Nanohybrid as Advanced Anode Material for Sodium-Ion Full Batteries [J]. *Nanoscale*, DOI: 10.1039/C7NR09674G.

### A01-P33

#### Ni/Co-LDH Modified PP Separator for High-Performance Li-S Batteries

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PP as the separator of lithium-sulfur (Li-S) battery has a large of pores. During typical discharge, the polysulfide being dissoluble in electrolyte migrates to anode through the pores, i.e. the so-called shuttle effect, which results in a series of side effects. Therefore, the specific capacity and stability of the battery are affected. It has become a research focus to improve the performance of the battery by introducing a dense barrier layer on the surface of PP separator to block the shuttle effect. At present, there are many reports on the modification of separator based on single carbon material or metal oxide.<sup>[1-4]</sup> Carboxylated multi-walled carbon nanotubes can increase the conductivity of the cathode and enhance the mechanical properties of the separator. In addition, nickel cobalt layered double hydroxide (Ni/Co-LDH) has strong affinity with polysulfide, and thus can inhibit the shuttle effect of polysulfide. In this study, we combined both to modify the commercialized PP separator through a facile filtration method, and the modified separator was used in the Li-S battery. The results show that the battery had a high initial specific capacity of 1039mAh g<sup>-1</sup> during 2C cycles, and the specific capacity of the battery can remain at 705mAh g<sup>-1</sup> after 100 cycles. Therefore, the stability and specific capacity of Li-S battery based on Ni/Co-LDH modified PP separator have been greatly improved.

References:

- [1] Vizintin A, Lozinšek M, Chellappan R K, et al. Fluorinated reduced graphene oxide as an interlayer in Li-S batteries[J]. *Chemistry of Materials*, 2015, 27(20): 7070-7081.
- [2] Peng H J, Zhang Z W, Huang J Q, et al. A cooperative interface for highly efficient lithium-sulfur batteries[J]. *Advanced Materials*, 2016, 28(43): 9551-9558.
- [3] Yao H, Yan K, Li W, et al. Improved lithium-sulfur batteries with a conductive coating on the separator to prevent the accumulation of inactive S-related species at the cathode-separator interface[J]. *Energy & Environmental Science*, 2014, 7(10): 3381-3390.
- [4] Ni X, Qian T, Liu X, et al. High Lithium Ion Conductivity LiF/GO Solid Electrolyte Interphase Inhibiting the Shuttle of Lithium Polysulfides in Long-Life Li-S Batteries[J]. *Advanced Functional Materials*, 2018, 28(13): 1706513.

### A01-P34

#### Metal-Organic Framework Template Derived Porous CoSe<sub>2</sub> Nanosheet Arrays for Energy Conversion and Storage

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Aims: With the development of modern society, the energy crisis and environmental problems are those we must face now. Developing highly effective electrocatalyst and supercapacitor are important method to solve these issues. However, transitional

metal oxides, metal hydroxides, and carbon material difficultly satisfy the requirement of electrocatalyst and supercapacitor. Compared with above transitional materials, metal selenides have attracted considerable attention with high electrochemical activity, good electronic conductivity, and stability. Among various metal selenides, CoSe<sub>2</sub> proved to possess good electrochemical activity and stability. Nevertheless, preparation of higher effective electrocatalyst and supercapacitor electrode material is still urgent. The strategy of constructing porous architecture is one of the effective method to improve electrochemical performance.

Methods: 1. Preparation of MOF-Co on CC. An aqueous solution containing 2-methylimidazole (C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>, 40 mL, 0.4 M) was quickly added into the aqueous solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (40 mL, 50 mM), after which a piece of clean CC substrate (1 × 1.5 cm<sup>2</sup>, the front of the CC was protected by glass slides) was immersed into the mixture solution. After reaction for 4 h, the sample was then taken out and cleaned with deionized water, finally dried in vacuum overnight. 2. Preparation of Porous CoSe<sub>2</sub> on CC. First, a piece of MOF-Co on CC (1 × 1.5 cm<sup>2</sup>) was etched by an etching reaction process in deionized water/ethanol solution followed with a thermal treatment for 4 min. Then, a piece of treated MOF-Co (1 × 1.5 cm<sup>2</sup>) was placed in the middle of tube furnace, and 0.6 g of Se powder was put in a crucible, and put in the side of a quartz tube inlet (the distance of MOF-Co and crucible is 16 cm). The tube furnace was heated to 450 °C at a fast ramping rate of 10 °C min<sup>-1</sup> and held for 2 h with argon flowing at 100 sccm. After cooling down to room temperature, porous CoSe<sub>2</sub> was successfully prepared.

Results: The porous CoSe<sub>2</sub> has both a larger specific surface area and outstanding electrical conductivity. As the catalyst for oxygen evolution reaction, the porous CoSe<sub>2</sub> achieves a lower onset potential of 1.48 V versus the reversible hydrogen electrode (RHE) and a small potential of 1.52 V (vs RHE) at an anodic current density of 10 mA cm<sup>-2</sup>. Especially, the linear sweep voltammogram curve of the porous CoSe<sub>2</sub> is in consist with the initial curve after durability test for 24 h. When tested as an electrode for supercapacitor, it can deliver a specific capacitance of 713.9 F g<sup>-1</sup> at current density of 1 mA cm<sup>-2</sup> and exhibit excellent cycling stability in that a capacitance retention of 92.4% can be maintained after 5000 charge-discharge cycles at 5 mA cm<sup>-2</sup>.

Conclusions: The results suggest that introducing Se atoms into electrode material could effectively alter the nanostructure, which can solve the problem of the lower electrical conductivity, thus dramatically enhancing the catalytic activity and durability. This porous structure fabrication strategy for metal selenides may be generally applied to the materials for diversified applications such as electrocatalyst, supercapacitor, and others.

#### A01-P35

##### Preparation and characterization of nano spherical V<sub>2</sub>O<sub>3</sub> powders

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The traditional methods of preparing V<sub>2</sub>O<sub>3</sub> powders exist many disadvantages, such as dangers of combustion, explosion or toxic gas leakage, and high requirement of equipment and cost, low production efficiency, which limited the prospect of industrial application. In this paper, the liquid phase reduction-thermal reduction has been used to prepare V<sub>2</sub>O<sub>3</sub> nanoparticles with spherical morphology to overcome these drawbacks. It is a novel method that the precursor was developed by Oxalic acid dehydrate (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O) reduction of V<sub>2</sub>O<sub>5</sub> powder in anhydrous ethanol. Nanoparticles of V<sub>2</sub>O<sub>3</sub> were successfully synthesized through thermal treatment of the precursor. The phase, composition, structure, and morphology of the as obtained samples were confirmed by XRD, FTIR, EDX, XPS and SEM measurements. Meanwhile, the process of the formation of nano spherical V<sub>2</sub>O<sub>3</sub> in the heat-treatment is briefly discussed by analyzing the DSC. The results show that the average size of particles of V<sub>2</sub>O<sub>3</sub> is about 40 nm~50nm. The possible formation mechanism of V<sub>2</sub>O<sub>3</sub> is proposed as follows: the reduction reaction prepared precursor Vanadyl oxalate(VOCO<sub>4</sub>) and thermal reduction of VOCO<sub>4</sub> obtained the Vanadium oxalate V<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>. Then the nano spherical V<sub>2</sub>O<sub>3</sub> was acquired by further thermal decomposition. It was found that the preparation of V<sub>2</sub>O<sub>3</sub> by the method of this paper is simple, effective, easy to operate, low cost and high efficiency. Besides, the utilization rate of raw materials and purity of the V<sub>2</sub>O<sub>3</sub> powder can be improved.

Keywords: nano spherical V<sub>2</sub>O<sub>3</sub> powders; liquid phase reduction; thermal reduction

#### A01-P36

##### 锂离子电池高镍三元正极材料的制备与改性研究

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镍钴锰三元正极材料由于其能量密度高、放电电压高、成本低廉等优点引起研究者的广泛关注，也因此得到了快速的发展。近年来，随着人们对锂离子动力电池能量密度的要求进一步提高，放电容量更高而成本更低的高镍三元材料备受关注。但由于其循环性能不够稳定、电导率和大倍率性能不佳等缺点，限制着其进一步广泛的应用。

采用水热法-高温固相法制备了高镍 811 型材料，以尿素作为沉淀剂，在外层包覆上一层钛酸锂，得到了改性的高镍三元正极材料。研究表明，使用水热法制备前驱体，之后再经高温烧结后的材料表现出较为优异的性能，材料的扫描电镜图像显示粒子为椭球状，长约 25 $\mu\text{m}$ ，宽约 14 $\mu\text{m}$ ，颗粒由直径 500nm 左右的球状一次粒子构成；从材料在包覆不同比例时的 XRD 图谱可以看出各个衍射峰位置都与纯相基本相同，说明包覆后材料晶体结构未发生改变；包覆前后材料在 0.5C 下的循环性能对比图可以发现包覆不同比例钛酸锂后高镍材料在前十圈左右容量保持率明显优于未包覆材料，且循环 50 圈后容量衰减小于未包覆的高镍材料，改性后材料在循环 50 圈后的放电容量为 159.8mAhg<sup>-1</sup>，而相同条件下纯相仅为 145 mAhg<sup>-1</sup>；掺杂前后的材料的倍率性能显示包覆钛酸锂同样改善了材料的倍率性能，包覆后材料在 2C 下的放电容量为 132.4 mAhg<sup>-1</sup>，而相同条件下纯相仅为 98. mAhg<sup>-1</sup>，且在回到小倍率充放电时，包覆后的材料具有更加优异的电化学性能。

参考文献：

- [1] R. Li, Y. Qin, X. Liu et al., *Electrochimica Acta*, 2018, 266: 202-211.
- [2] F. Wu, J. Tian, Y. Su et al., *Acs Appl Mater Interfaces*, 2015, 7: 7702-7708.
- [3] X. Jia, M. Yan, Z. Zhou et al., *Electrochimica Acta*, 2017, 254: 50-58.

#### A01-P37

##### 金属有机骨架负载硫化亚锡复合材料的制备及其电化学性能研究

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硫化亚锡作为锂离子电池负极材料具有 875mAhg<sup>-1</sup> 的放电比容量（石墨为 372 mAhg<sup>-1</sup>），但是由于其在充放电过程中具有较大的体积膨胀(300%)而限制了在实际生产中的应用。为了缓解硫化亚锡因体积膨胀而带来的容量衰减问题，人们通过设计缓冲空间为材料的膨胀提供空间以提高硫化亚锡负极的性能[1-3]。在这项工作中，我们利用金属有机骨架（MOFs）的空间结构为硫化亚锡提供缓冲空间，达到抑制其体积膨胀的以提升其性能的目的。

本文设计的金属有机骨架 MOFs 负载硫化亚锡具有优良的结构与电化学性能，经表征可以发现金属有机骨架与硫化亚锡紧密的结合在一起，且相较于纯相硫化亚锡，复合后材料的粒径明显变小，复合材料展现优良的循环稳定性，这是金属有机骨架为硫化亚锡纳米颗粒在充放电过程中提供的缓冲空间所致。

参考文献：

- [1] X.-L. Gou, J. Chen, P.-W. Shen, *Materials Chemistry and Physics*, 93 (2005) 557-566.
- [2] D.D. Vaughn, 2nd, O.D. Hentz, S. Chen, D. Wang, R.E. Schaak, *Chemical communications*, 48 (2012) 5608-5610.
- [3] Q. Li, L. Li, K.A. Owusu, W. Luo, Q. An, Q. Wei, Q. Zhang, L. Mai, *Nano Energy*, 41 (2017) 109-116.

#### A01-P38

##### 优化 La<sub>6.76</sub>La<sub>3</sub>Zr<sub>1.76</sub>Ta<sub>0.24</sub>O<sub>12</sub> (Ta-LLZO) 固态电解质的制备工艺

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石榴石结构的 Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZO) 固态电解质对锂稳定，电化学窗口宽，所以成为一种极具潜力的固态电池的电解质。Murugan 等[1]合成了 LLZO，在 25℃，离子电导率为 3×10<sup>-4</sup>S/cm。但相比于液态有机电解液的离子电导率(10<sup>-2</sup>—10<sup>-3</sup>S/cm) 还有一定差距。影响离子电导率[2]的因素包括锂离子浓度、离子迁移率以及致密度。

本工作钽 (Ta) 掺杂的 Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>(Ta-LLZO)的合成进行了优化，使其室温电导率达到了 4.2×10<sup>-3</sup>S/cm。立方相的 Ta-LLZO 合成经过两个阶段，首先在低温 950℃煅烧（6-12h）得到四方相的 Ta-LLZO 电解质，然后将四方相的电解质压成直径为 15mm，厚度为 1mm 的薄片，在母粉的埋覆下烧结，烧结温度为 1100℃，保温时间为 6-15h，最终得到立方相的 Ta-LLZO。对得到的 Ta-LLZO 进行了阻抗测试，在不同温度下的离子电导率，随着温度提高，电导率也在增加。100℃时电导率达到了

10-2S/cm, 已经达到目前锂离子电池的标准。室温下, 阻抗并没有出现规则半圆, 这是由于电解质的不致密导致的, 经过测量计算本工作所制备的 Ta-LLZO 电解质的致密度只有 89%, 所以接下来改善电解质的致密度会进一步提高电解质的离子电导率。

#### **A01-P39**

Preparation and characterization of barium strontium titanate powders

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The barium strontium titanate is the promising material for high energy density capacitor because of its high dielectric constant. The fine grain BST ceramic with high density shown the improved dielectric performance. Therefore it is essential to prepare BST nano-powders to obtain fine grain materials. The aim of this study is to prepare nanoscale BST powders by sol-gel method. The BST powders were characterized by TG-DSC, XRD, SEM, TEM and ICP-AES respectively. The results showed that the BST nano-powders with high purity and fine uniformity were obtained.

#### **A01-P40**

**High-temperature Transport Properties of  $\text{Ca}_{0.98}\text{Dy}_{0.01}\text{Re}_{0.01}\text{MnO}_3$  ceramics (Re=Nd, Gd, Yb)**

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Perovskite-type  $\text{Ca}_{0.98}\text{Dy}_{0.01}\text{Re}_{0.01}\text{MnO}_3$  (Re=Nd, Gd, Yb) ceramics were synthesized by co-precipitation method combined with the solid-state reaction. Their thermoelectric properties were evaluated from 300K to 973K. All the samples are single phase with an orthorhombic structure. The introduction of second doping elements will cause the lattice distortion and change the density of state near the Fermi level. As a result, the highest power factor is obtained  $3.28 \mu\text{Wcm}^{-1}\text{K}^{-2}$  at 973K for  $\text{Ca}_{0.98}\text{Dy}_{0.01}\text{Yb}_{0.01}\text{MnO}_3$  sample. Meanwhile, the dual doping can lead to a low thermal conductivity, so the best figure of merit 0.22 can be obtained for  $\text{Ca}_{0.98}\text{Dy}_{0.01}\text{Yb}_{0.01}\text{MnO}_3$  sample at 973K, which is an anticipated result for  $\text{CaMnO}_3$ .

#### **A01-P41**

**Free-standing N-doped carbon foam based highly compressible all-solid-state asymmetric supercapacitors**

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With the rapid development of flexible energy storage technology, the compressible all-solid-state supercapacitors have attracted much attention. Compressible electrodes require not only resilient property but also high capacitive performance. Here in, we fabricated compressible all-solid-state asymmetric supercapacitors (ASCs) composed by hierarchical structured Fe-Co-Ni ternary sulfides (Fe-Co-Ni TSs) coated three dimensional (3D) macroporous N-doped carbon foam (NCF) as positive electrode and vertical aligned carbon nanotubes (VACNTs) wrapped NCF as negative electrode in alkaline gel electrolyte. The as-assembled compressible ASC device exhibits a relatively high specific capacitance of  $\sim 150 \text{ F g}^{-1}$  at  $1 \text{ A g}^{-1}$  under a compression strain of 60% and desirable stability with 85% capacitance retention even after 5000 cycles. Due to complex and rich redox reactions and strong adhesion of the hierarchical structured Fe-Co-Ni TSs to the compressible 3D NCF, the Fe-Co-Ni TS/NCF electrodes exhibit excellent supercapacitive performances and ideal structural integrity under pressure deformation. Furthermore, the dense arrangement of VACNTs covered on 3D NCF provide a better flexibility and cross-linked conductive network which benefit to rapid transmission of ions/electrons during elastic deformation. These impressive results provide a great promise of controllable, low-cost preparation of compressible electrodes for future deformation-tolerant energy storage applications.

#### **A01-P42**

**mesoporous lamellar-shaped lithium-rich cathode material for lithium-ion batteries with exceptional rate capability and stability**

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With the development of society, the problem of energy has become more and more serious. Lithium-ion battery, acting as the new energy, has a lot of advantage, such as environment-friendly and portability. Although the lithium-ion battery has been researched for many years, the low energy density and severe cycle performance are also hardly meet the current requirement. Lithium-rich oxide layer material, which could exhibit the over 250 mAh g<sup>-1</sup> when the charge voltage reaches the 4.8 V, has become more and more attractive to researcher. However, the drawbacks of encountering structural reconstruction, sharp voltage decay during cycling as well as low packing density still exist, which retard their further commercial development. This paper presents a novel approach to construct mesoporous lamellar-shaped Li<sub>1.2</sub>Mn<sub>0.54</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>O<sub>2</sub> particles. One crucial step during the synthetic process is the usage of Hexadecyl trimethyl ammonium Bromide (CTAB) and Hexamethylenetetramine, which act as the precipitant and nucleate. And the key control parameter is time and temperature of hydrothermal reaction, which directly affects the morphology and size of particles. Of particular note is the desirable architecture which not only inherits the merits of hollow structures but also facilitates the tight particles packing. Owing to these advantages, mesoporous lamellar-shaped Li<sub>1.2</sub>Mn<sub>0.54</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>O<sub>2</sub> exhibits the excellent discharge capacity and cyclic stability. Under the 0.5 C rate, its initial discharge capacity reaches the 236.13 mAh g<sup>-1</sup>, and the capacity retention above 85.3 % over 150 cycles. These results reveal that structural design of cathode materials play a pivotal role in increasing the electrochemical performance of lithium-rich oxide layer material.

仅发表论文

#### A01-PO-01

##### **Comparative study of the discharge performance for magnesium alloy and aluminum alloy**

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Objectives: The light metal elements like magnesium, aluminum are abundant in the earth, and this kind of metals or alloys is extensively studied to be used as energy storage material. The energy of light metal can be released in the form of electric energy by using metal fuel battery. In this study, the purpose is to study the difference of the discharge performance for the magnesium alloy and aluminum alloy and to study the influence factors for different alloys.

Methods: In this work, magnesium alloy and aluminum alloy were prepared by vacuum-melting method. The prepared alloys were used as anodes in the metal fuel battery testing system, the MnO<sub>2</sub> catalysts was used in nickel foam based cathode, and the performance of electric energy conversion of these metals were studied. The short circuit current densities and open circuit voltages with different anodes were tested and analyzed. Scanning electron microscope (SEM) was used to characterize the microstructures of the alloy after discharging.

Results: The results revealed that the magnesium alloy and aluminum alloy had showed different discharge performance. The difference of the discharge performance for the magnesium alloy and aluminum alloy were analyzed according to the electrochemistry properties and the microstructures of the alloys. The battery with magnesium alloy anode exhibited relatively higher voltage about 1.5 V and the current density could reach up to 6 mA/cm<sup>2</sup>.

Conclusions: The discharge performance was determined by the electrochemistry characteristics of the metal element to a great degree. The microstructure of the alloy also influenced the discharge performance. The magnesium alloy and aluminum alloy can be applied in different fields according to different requirements.

#### A01-PO-02

##### **Research Progress of All-solid-state Thin Film Lithium Ion Battery**

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Compared with the traditional liquid lithium-ion battery, all-solid-state lithium-ion battery can significantly improve its safety, and has also been greatly improved in terms of specific energy, specific power and cycle performance. With the development of



smart society, the intelligent devices has become a trend, and the corresponding energy supply system has gradually attracted attention. Among them, the all-solid-state thin film lithium-ion battery is a better smart device energy unit. The all-solid-state thin-film lithium-ion battery adopts a physical film forming process, and the process is compatible with the manufacturing process of the micro-nano devices, which is conducive to the integration of the micro-device and the micro-energy source.

This article first introduced the advantages and key issues of all-solid-state thin film lithium-ion batteries. The electrolyte of the all-solid-state thin-film lithium-ion battery is a key factor that affects the battery performance. The electrolyte includes the inorganic solid electrolyte and the polymer electrolyte. The development of inorganic solid electrolytes includes three generations, of which the second generation of lithium-phosphorus-nitrogen is the most commonly used electrolyte in commercial batteries. The third-generation garnet-structured electrolyte has the best performance, but it needs further development. The interface problem is also an important factor that affects the performance of all-solid-state thin-film lithium-ion batteries.

Next, the preparation process of all-solid-state thin-film lithium-ion batteries is introduced, including RF magnetron sputtering, atomic layer deposition, pulsed laser deposition, template deposition, laser direct writing, thermal evaporation, and sol-gel method, chemical vapor deposition process. The batteries prepared by these processes can be small in size and have better performance and cycle characteristics.

Finally, the latest advances in the all-solid-state thin-film lithium-ion battery are described, including a flexible all-solid-state thin-film lithium-ion battery and a three-dimensional all-solid-state lithium-ion battery. The flexible battery can be applied to a wearable medical device, and the three-dimensional structure can significantly improve the battery's power density.

### **A01-PO-03**

#### **Lithium Storage property of Al-base alloy prepared by Mechanical Alloying**

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As an important part of the lithium-ion battery, the negative electrode material directly determines the energy density and cycle life of the battery. Aluminum-based metal materials have a high lithium storage capacity, but their cycle performance is poor. In this paper, pure Al, Cu and Fe powders were used as raw materials. AlCu and AlFe binary alloys were prepared by mechanical alloying(MA) method. The evolution of alloy structure during the mechanical alloying process was studied. The electrochemical lithium storage properties of different alloys were studied. XRD results show that the diffraction peak of elemental single phase gradually decrease with longer milling time for AlCu and AlFe alloy. Alloys form after milling for 30 hours. Electrochemical tests show that the discharge capacity of the alloy increased with the milling time. The cycle stability of alloy acquired by MA method is better than pure Al.

### **A01-PO-04**

#### **Nanosheets-assembled LaMnO<sub>3</sub>@NiCo<sub>2</sub>O<sub>4</sub> core-shell nanoflowers Architecture supported on Ni Foam as Advanced Electrodes for Supercapacitors**

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The effective composited materials with structural optimization have potential for improving the electrochemical performance of supercapacitors in recent years. Herein, we put forward a rational design to fabricate LaMnO<sub>3</sub>@NiCo<sub>2</sub>O<sub>4</sub> core-shell nanoflowers architecture supported on Ni foam substrate by facile hydrothermal processing. Owing to the synergistic contribution between LaMnO<sub>3</sub> nanoparticles and the porous nanosheets of NiCo<sub>2</sub>O<sub>4</sub>, the hierarchical electrodes with high oxygen vacancies achieved remarkable electrochemical performances with a wide potential window (-0.8-0.6 V). This makes such hybrid structure possess a high specific capacitance of 772 F/g at 0.5 A/g with capacitance retention of 73% after 10000 cycles at high current density of 20 A/g and nearly 100% coulombic efficiency in 6 M KOH electrolyte. It is noteworthy that the energy density of the asymmetric supercapacitor with activated carbon (AC) as the negative electrode is 36.6 Wh/kg at a power density of 800 W/kg, and the maximum of 25600 W/kg can be obtained with a remaining energy density of 19.4 Wh/kg. The capacitance retention of the as-prepared

LaMnO<sub>3</sub>@NiCo<sub>2</sub>O<sub>4</sub>//AC device is 144.8% after 10000 cycles, demonstrating its long cycle life, which is much superior than most of previously reported aqueous supercapacitors. Therefore, the proposed strategy of LaMnO<sub>3</sub>@NiCo<sub>2</sub>O<sub>4</sub> electrode on Ni foam paves the way for high-performance supercapacitors.

#### **A01-PO-05**

##### **Effects of H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> on the photoelectric conversion of TiO<sub>2</sub> nanotubes**

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Nanotube composite films of SiW<sub>12</sub>-TiO<sub>2</sub> were fabricated by electro-deposition a layer of H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> (SiW<sub>12</sub>) on TiO<sub>2</sub> nanotube films. The structure and morphology of as-prepared composite films were demonstrated by X-ray diffraction, Scanning electron microscopy and Infrared radiation. And then assembled such compounded film into a PV cell and determine their photoelectric conversion efficiency. The experimental results show that the photoelectric conversion efficiency of TiO<sub>2</sub> nanotube films modified with SiW<sub>12</sub> was 3.66%, which makes 10 times more than that of the non-modified (0.36%). Meaning that SiW<sub>12</sub> has a great effect on TiO<sub>2</sub> nanotube films, which makes its photoelectric conversion efficiency remarkably improved.

#### **A01-PO-06**

##### **Failure Analysis of X80 Helical Seam Submerged-arc Welding Pipe Leak Out**

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CNPC Tubular Goods Research Institute

One Φ1219mm X80 helical submerged-arc welding (HSAW) pipe leaked out abnormally in the process of hydrostatic burst test analysis. This paper gives a systematic investigation of the abnormal leaked HSAW pipe. Failure reason of the leaked HSAW pipe was researched through visual inspection, X-ray non-destructive inspection, chemical composition analysis, mechanical properties test, metallographic examination, fracture surface analysis and scanning electron microscope (SEM) with energy dispersive spectrometer (EDS). The results show that the HSAW pipe leaked out in the welding seam. The failure course was the large non-metallic inclusions, which from the outside and exists in the welding metal. Such inclusions undermining the continuity of the weld metal matrix, and causing stress concentration. At the same time provides the weakest parts for the destruction of the material. When the metal deformation, the cracks first formed in the inclusions, as the deformation increase, the further expansion of the cracks. In the end, the cracks penetrated through the wall thickness, finally HSAW pipe leaked out failure.

#### **A01-PO-07**

##### **In situ cross-linked polymerization of poly(ionic liquid)-based quasi solid electrolytes for lithium ion batteries**

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Lithium ion batteries have been widely used in fields ranging from portable electronics to electric vehicles due to their high energy density, high working voltage and long cycle life. However, the use of conventional liquid electrolyte with high volatility and flammability triggers serious security concerns such as fire, explosion and electrolyte leakage. The solid electrolyte with high energy density can mitigate lithium dendrite penetration due to its high mechanical strength which is currently expected to replace liquid electrolytes as a new type of safe electrolyte. However, the rigid nature of ceramics usually leads to high interfacial resistance and unstable electrolyte/electrode interface contact during charge-discharge cycles which limits its practical application in lithium batteries. In this regard, designing the solid electrolytes that possess both favorable ionic conductivity and optimized interfacial properties, yet a great challenge.

In this paper, we fabricated a transparent homogeneous elastic free-standing poly(ionic liquid)-based quasi solid polymer electrolyte (PIL-QSE) by in-situ cross-linked polymerizing imidazole ionic liquid in poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP) porous membranes prepared via phase inversion. The properties of the quasi-solid electrolyte membrane such as thermal stability, crystallinity, mechanical properties, ionic conductivity, electrochemical stability, and lithium ion transference

number under different preparation conditions were studied in detail. The interfacial characteristics between the electrolyte and the electrode material were also investigated. The results show the electrolyte membrane with the casting solution concentration of 20%, the plasticizer content of 80%, and the additive content of 15% exhibits optimal performance with an electrochemical window of 5.0 V and lithium ion transference of 0.52. The electrolyte membrane was assembled into LiFePO<sub>4</sub>|PIL-QSE|Li half-cell. It was found that the cell deliver a discharge specific capacity of 130 mAhg<sup>-1</sup> at 0.1C with 96.2% capacity retention after 100 cycles at 25 °C. The method of in situ polymerization provides an effective way to improve the interfacial properties between electrodes and electrolytes with good mechanical properties, favorable thermal stability and improved electrochemical performance.

#### **A01-PO-08**

##### **An Anode-Supported Planar Solid Oxide Fuel Cells Based on Double-Sided Cathodes**

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A planar solid oxide fuel cell (SOFC) is a multi-layered thin sheet with a composite structure. The coefficients of thermal expansion mismatches among the layers and materials in a traditional electrode-supported cell may result in thermal stress during operation and micro-cracks of ultra-thin electrolyte and operational damage. This work proposed a new symmetric planar SOFC design based on double-sided cathodes offset asymmetry of thermal stress from the structure. This structure has been applied to prepare an anode-supported SOFC that maintains integrity after two complete redox cycles. Its anti-fracture load is 20 times stronger than that of traditional ultra-thin cells. These properties are promising for applications under harsh operational environments.

#### **A01-PO-09**

##### **Porous Ni-Fe alloys as anode support for intermediate temperature solid oxide fuel cells: cell performance and stability**

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Huazhong University of Science and Technology

Porous nickel-iron alloy supported solid oxide fuel cells (SOFCs) are fabricated through cost-effective ceramic process including tape casting, screen printing and co-sintering. The cell performance is characterized with humidified hydrogen as the fuel and flowing air as the oxidant. The cell performance and stability under thermal and redox cycle are investigated from the point of view of structural stability. Single cells supported by nickel and nickel-iron alloy (50 wt.% iron) present relatively high discharge performance, and the maximum power density measured at 800°C is 1.52 and 1.30 W·cm<sup>-2</sup> respectively. Nickel supported SOFC shows better thermal stability between 200-750°C due to its dimensional stable substrate under thermal cycles. Post test analysis shows that a dense iron oxide layer formed at the surface of the nickel-iron alloy during the early stage of oxidation, which prevents the further oxidation of the substrate as well as the functional anode layer, and thus, making nickel-iron supported SOFC exhibits better redox stability at 750°C.

#### **A01-PO-10**

##### **Flower-shaped Nickel-Cobalt-Oxides/Polyaniline/Multiwalled Carbon Nanotubes as a Bifunctional Electrocatalyst for Zn-air Batteries**

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Beijing University of Technology

Rechargeable Zn-air batteries have attracted much attention due to the high theoretical energy density, low cost and environmental benignity. To improve the cycling life and efficiency of the battery, highly efficient and durable bifunctional catalysts for air cathodes are urgently needed. Supporting transition metal oxides on carbon nanotubes (CNTs) is an effective way to improve the activity of catalysts due to the high surface area and superior electrical conductivity of CNTs.

In this study, a novel flower-shaped nickel-cobalt-oxides/polyaniline/multiwalled carbon nanotubes (NiCoO/PANI/MWCNTs)

nanohybrids were prepared via a simple *in situ* method. Briefly, the solution containing Ni<sup>2+</sup> and Co<sup>2+</sup> was mixed with CNTs and aniline followed by subsequent borohydride reduction. The flower-shaped NiCoO and leucoemeraldine oxidation state of PANI supported on the surfaces of MWCNTs were obtained during the preparation.

The as-prepared NiCoO/PANI/MWCNTs exhibited enhanced activity for both oxygen evolution and reduction reaction in alkaline KOH electrolyte. When adopted as cathode catalyst for rechargeable Zn-air batteries, high power densities and excellent cycling stability over 80 h were obtained. High performance of the as-prepared catalyst could be attributed to the synergistic effect among transition metal oxides, PANI and MWCNTs.

This work outlined here contributes to the advancement of designing novel and inexpensive hybrid electrocatalysts for rechargeable metal-air batteries.

#### **A01-PO-11**

#### **Flower-shaped Nickel-Cobalt-Oxides/Polyaniline/Multiwalled Carbon Nanotubes as a Bifunctional Electrocatalyst for Zn-air Batteries**

Chenchen Zhao\*, Wenbo Du

Beijing University of Technology

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