Special report on the achievements realized by researchers of Chinese Academy of Sciences in the field of energy storage technologies

Xianfeng Li[a,*], Guanglei Cui[b,*]

[a] *Division of Energy Storage, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, PR China*
[b] *Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao, PR China*

ABSTRACT

The inevitable depletion of non-renewable fossil fuels and serious environmental pollution promote the wide application of renewable energies. Most of the renewable energy sources, such as solar and wind power, suffer from uncontrollable as well as complicated situations (Yang et al., 2011) [1]. Electrochemical energy storage technologies are crucial to solve these problems, as they can efficiently store electricity in chemicals and release it according to the users' demands (Yang et al., 2011; He et al., 2006)[1,2]. Moreover, energy and environmental challenges have stimulated great interest to replace gasoline engine powered vehicles by plug-in hybrid vehicles (PHEV) and electric vehicles (EVs). Therefore, it is vital to improve the performance of energy storage systems, which depends on the development of key materials for the various batteries and new energy storage strategies. Researchers from Chinese Academy of Science (CAS) have dedicated to the researches of energy storage systems for decades and made significant process. We will introduce the progress on energy storage systems of CAS in recent two years, which covers the key materials of Lithium ion battery (LIB), Lithium-oxygen (Li-O$_2$) battery, Lithium-sulfur (Li-S) battery, Lithium ion capacitor, Sodium ion battery, and Flow battery.

1. Lithium ion batteries

1.1. Cathode

The key materials of lithium ion batteries (LIBs) mainly include cathode, anode, electrolyte and separator. The output voltage of the battery is determined by the difference in electrochemical potentials between the cathode and anode [3]. In commercial LIBs, the cathode is the provider of lithium ions, which is also called "lithium sources". So the capacity of LIBs mainly depends on cathode materials. So far, cathode materials can be classified into three categories: (I) Lithium oxide compounds with layer structure LiMO$_2$ (M = Co, Ni, Mn), such as LiNi$_x$Co$_y$Mn$_z$O$_2$ (NCM) [4]; (II) Spinel structure compounds, typically like LiMn$_2$O$_4$ [5] and so forth; (III) Polyanionic structure compounds, typically like LiFePO$_4$ [6] and so on. The main researches on cathode materials are developing new derivative materials on the basis of traditional cathode materials, to improve their performance by doping, coating, *etc.*

LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ has been widely studied due to its low cost, high capacity, good rate performance, milder thermal stability, and good cycling stability [7–9]. However, its low rate capability, poor cycling performance and thermal stability at high cut-off voltage still need to be solved to meet the requirement of high power LIBs. Xiao et al. from University of CAS, prepared a dual functional coating layer of Li$_2$SiO$_3$ and carbon on LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ material [10]. Li$_2$SiO$_3$& C double coating layer served as a protection layer, which could protect the cathode material from the electrolyte and avoid unfavorable interfacial side reactions. Besides, the Li$_2$SiO$_3$ and carbon worked as the Li-ion and electron conductor, in favor of the transport of lithium ions and electrons. The rate capability of the cathode material was thus increased. The LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ coated with Li$_2$SiO$_3$&C exhibited high discharge capacity, coulombic efficiency (CE), and capacity retention. This strategy is convenient and universal, which can also be applied in other layered cathode materials to improve their electrochemical performance.

Lithium-rich layered oxide xLi$_2$MnO$_3$·(1-x)LiMO$_2$ (M = Ni, Co, Mn), can deliver a discharge capacity of 250 mAh g^{-1} in the voltage range of 2–5 V, even 200 mAh g^{-1} when the cut-off voltage is 4.6 V, which is higher than that of layered structure materials LiMO$_2$ (M = Co, Ni, Mn). Nevertheless, these materials initially suffer from the huge irreversible capacity and poor rate performance. In order to overcome these drawbacks, Xia et al. from Ningbo Institute of Materials Technology & Engineering, CAS, proposed doping B^{3+} in the lithium-rich layered oxides to block the migration of the transition metal ions. The

tetrahedral interstitial was occupied and the oxygen vacancy was maintained, in order to stabilize the crystal structure and suppress the voltage decay of the materials [11]. Li-rich layered materials with boron-doping manifested their excellent cycling performance and voltage stability, because of their good crystal structural stability under high voltage. And the transition phase from layered to spinel was inhibited by incorporated boron. In addition, the incorporated boron in the Li-rich layered oxides also plays a positive role in forming a more favorable SEI layer with low interfacial resistance.

Polyanionic cathode materials, especially the phosphate, monoclinic $Li_3V_2(PO_4)_3$ (LVP) has attracted more and more interest for its superior structure stability, high working voltage, low cost and environmental benignity [12,13]. But then, the practical application of LVP cathode materials in LIBs is impeded by several critical issues [14,15]. The VO_6 octahedron segregated by the PO_4 tetrahedron leads to the low conductivity of LVP, resulting in the worse rate and cycling performance. More critical problem is the complicated synthesis process of high-performance LVP materials [16,17]. Zhang et al. from Dalian Institute of Chemical Physics, CAS, prepared highly crystalline submicro-sheet LVP/C with homogeneous size and ordered morphology by a novel phase-change method [18]. The thin sheet structure with the length of 1–2 μm could shorten the Li^+ diffusion distance in the certain direction, accelerating the electrochemical reaction. Besides, the submicron sheets were stacked and crossed with each other, forming space for the penetration of electrolytes and enhancing the contact of electrode and electrolyte. And these properties exerted significant influence on the electrochemical performance of LVP cathode materials in LIBs. This phase-change method offered a new low-cost and easy-to-control synthesis process for the preparation of cathode materials for high-power lithium ion rechargeable batteries.

1.2. Anode

The physicochemical properties of the anode materials affect the battery behavior significantly and thus must be controlled appropriately. The carbon-based materials usually serves as anode materials, owing to their abundance, thermal and chemical stability, good electronic conductivity, good reversibility and low cost [19]. On the other hand, advanced anode materials are still highly demanded for exceptional energy, such as the Si-based anode and lithium metal anode.

Silicon is a kind of promising materials to replace the current anode materials thanks to its high theoretical capacity of 4200 mAh g^{-1} and high abundance [20]. At the same time, Si-based anode has a higher lithiation voltage plateau at 0.2–0.3 V *vs.* Li/Li$^+$ than the graphite anode (0.1 V vs. Li/Li$^+$), which could avoid the undesired dendrite formation, consequently alleviate the safety concern of LIBs [21–23]. Nonetheless, when Si particles are exerted stress and strain, fast capacity fading and low CE are caused. In order to solve these problems, many strategies have been proposed, such as reducing the particle size, detecting surface modifications, regulating the SEI film and so on [24–31]. Guo et al. from Institute of Chemistry, CAS, fabricated Si/nitrogen-doped carbon/carbon nanotube (SNCC) nano/micro-structured spheres by a polyacrylonitrile (PAN) assisted electrospray method, where the rice husk-derived Si nanoparticles were used as raw material [32]. These SNCC spheres could deliver a high reversible specific capacity. The carbon matrix built by CNTs and N-doped carbon layers could provide sufficient conductive pathways for electron diffusion and fast lithium ion transportation, enabling a high specific capacity at high charge/discharge current. Besides, the flexible CNTs and the robust N-doped carbon framework functioned as the structural reinforcement, which could maintain the whole integrity to overcome the mechanical breakage caused by the huge volume changes of Si. Moreover, the utilization of waste resources and facile preparation method made the SNCC anode cost-effective for possible industrial applications.

SiO_x-based anodes are particularly promising because of its longer cycle life compared with that of Si, which sacrifices some capacity ($\sim$2200–2500 mAh g^{-1}) [19]. Even though the formation of irreversible Li_2O and lithium silicate decreases the specific capacity, it acts as a natural volume buffer matrix to Li_xSi, which improves the cycling stability and capacity retention of batteries [33–35]. Besides, SiO_x-based anodes have much smaller volume change of $\sim$160% during the lithiation/delithiation process. Nowadays, SiO_x is dispersed along with Si in the SiO_x materials with 3D structures, where Li ions migrate through lithium silicate or Li_2O layer after the first cycle, leading to poor rate performance. Liu et al. from Ningbo Institute of Materials Technology and Engineering, CAS, proposed an innovative design of sheet-like Si/SiO_2 nanocomposites, showing Si nanodomains were well confined within the amorphous SiO_2 matrix (in brief nano-Si/a-SiO_2) to realize a two-dimensional silicon suboxides nanocomposites with moderate volume variation and better electrons and lithium ions kinetics [36]. The sheet-like nano-Si/a-SiO_2@C anodes could exhibit high initial CE and capacity, stable cycling performance and excellent rate capability. This could be ascribed to the synergistic effect of Si nanodomains, the amorphous SiO_2, the surface carbon coating layer and the sheet-like structure. The proposed sheet-like nano-Si/a-SiO_2@C anode verified the limited volume expansion and structure deformation, fast electron and Li^+ diffusion mobility all together leading to remarkable cycle stability and rate performance, making it very attractive for the next-generation LIBs.

Besides Si-based anode materials, lithium metal anodes with ultrahigh specific capacity of 3860 mAh g^{-1} have been widely researched. Additionally, they have a very low redox potential and a small gravimetric density of 0.534 g cm^{-3} [37,38]. Compared with volume changes of graphite and silicon anodes, the relative volumetric change of Li metal anode is virtually infinite, because Li metal is 'hostless'. The stress and strain generated from volume change, along with the surface heterogeneity of lithium foils will result in the fracture of SEI, resulting in irreversible capacity loss and low CE. Moreover, dendritic lithium during repeated Li plating/striping will not only induce "dead Li" with capacity loss, but also have the potential to penetrate through the separator and contact with cathode directly, causing a short circuit of the battery [39–41]. Wang et al. from Ningbo Institute of Materials Technology and Engineering, CAS, have prepared a lithium fluoride (LiF)-rich artificial protective layer to improve the stability of Li metal surface [42], since it has been known that the presence of LiF on Li surface could be promising to stabilize SEI layer and enable smooth Li deposition and dissolution [43,44]. Conventional LiF-containing layers formed during cycling process by adding electrolyte additives such as fluoroethylene carbonate (FEC), hydrofluoric acid (HF), and a trace amount of H_2O, are so vulnerable, which cannot protect Li metal anodes with long cycling proceeding [45–47]. The transplantable LiF-rich layer (TLL) film was composed of cross-linked nanoscale LiF domains, which could be easily peeled off from the Cu substrate by electrochemical reduction of NiF_2. The Cu/Li cell with the TLL-protected Li metal exhibited stable charge-discharge curves with high CE during more than 300 cycles and the LiFePO$_4$/Li cell demonstrated stable cycling behavior within 1000 cycles. This improvement in battery performance by the TLL should be related to the formation of a matrix cross-linked by nanosized LiF domains in the presence of Ni, with its remarkable effect of blocking solvent permeation. These results demonstrated that using a TLL could effectively limit the side reactions, stabilize Li metal/electrolyte interfaces, and inhibit dendrites growth, promoting its application in more practical operating conditions.

1.3. Electrolyte

The role of electrolytes is the medium for the transfer of charges, which are in the form of ions, between cathode and anode. Based on the states of matter at room temperature, there are basically three types of electrolytes used for LIBs: liquid, solid and gel electrolytes. At present, the commercial electrolyte used in lithium ion batteries is organic liquid electrolyte, which mainly includes LiPF$_6$, ethylene carbonate (EC),