Electrochemical energy storage technologies represented by lithium-ion batteries and electrochemical capacitors have played key roles in the modern smart-grid. However, the rapid development of the terminal markets, including electric vehicles and portable intelligent electronic devices, requires significant breakthroughs in respect to energy density, power density, cost, life cycle and safety, etc. This means an urgent need to go beyond the current energy-storage technologies of lithium-insertion and electrical double-layer chemistry. Because of the high energies involved, the alloy-type and conversion-type chemistries have caused widespread concern in recent years [1–5]. However, they often suffer more significant problems, including poor kinetics, large volume changes and the presence of soluble intermediates. To solve these issues, the major focus has been on material engineering by nanotechnology. Through morphology control and nanostructuring, many novel active materials have showed promising electrochemical performance in a laboratory cell [6–10]. However, nanotechnology that is cost-effective and can be used on an industrial scale is still lacking. On the other hand, in many studies, lithium metal was directly used as a counter electrode, which may form lithium dendries and cause significant safety issues, such as short-circuit, burning and explosion.

In this perspective, we will show that electrochemical modification can be a more efficient and beneficial way of developing high-performance energy-storage devices than material engineering. A schematic of electrochemical modification is shown in figure 1. The modified materials are then used as the cathode and anode in an electrochemical system where they are matched with a specific electrolyte and an auxiliary electrode. During modification, two individual circuits of anode//auxiliary electrode ($V_1$) and cathode//auxiliary electrode ($V_2$) are connected. Rational electrochemical-reaction techniques, i.e. galvanostatic discharge/charge, constant voltage discharge/charge, pulse charge, short circuit, etc., are conducted to produce changes in the electrode properties, such as surface chemistry, charge density and crystal structure. The auxiliary electrode plays the same role as a counter electrode, which should have a larger area than the modified electrode. As a result, the polarization of auxiliary electrode can be ignored during modification, and thus the modification can be conducted effectively. Moreover, the reaction products of auxiliary electrode should not affect the reaction of modified electrode. Common auxiliary electrodes includes the copper, platinum, lithium and so on. After modification, an advanced energy-storage device that combines the optimized cathode and anode ($V_3$) is obtained which gives an excellent electrochemical performance. Electrochemical modification has the following advantages. First, it can be performed after electrode preparation or even device assembly, which is compatible with the commercial fabrication. Second, the properties of the active materials can be quantitatively changed by controlling the parameters, such as potential, current density and capacity. At present, the electrochemical modification strategies have been widely used in the field of energy-storage and can be divided into three types: electrochemical coating, capacitive-type charge injection and battery-type charge injection.
1. Electrochemical coating

Electrochemical coating is important for protecting the anodes of lithium ion batteries. During a typical process, the electrolyte or electrolyte additive decomposes. The decomposition products are deposited on the surface of electrode to form a coating layer, which changes the electrode/electrolyte interface. This coating layer is ion-conducting and electron-insulating, and is also called a solid electrolyte interface (SEI) film [11]. It has been reported to be able to inhibit further decomposition of the electrolyte during cycling and widen the stable voltage window [12]. Currently, the formation of this layer can also be achieved by atomic layer deposition technology [2, 13]. However, the electrochemical coating is certainly the most economical.

The composition and structure of the coating layer are significantly affected by the electrolyte species, electrode material, current density, potential and temperature. Among these, the electrolyte species is the most important. For example, at an early stage, propylene carbonate (PC)-based electrolytes were used for lithium-ion batteries. During cycling, the graphite anodes were attacked by electrolyte decomposition and co-insertion of solvent molecules, leading to poor cycling stability [12]. Subsequently, it was found that ethylene carbonate (EC)-based electrolytes formed a stable SEI film composed of inorganic (LiO₂, LiF, Li₂CO₃) and organic components [11], which made the lithium ion battery in current use. Nowadays, to meet the demands of alloy-type and conversion-type anode materials, a series of novel electrolyte additives, including fluoroethylene carbonate (FEC), vinylene carbonate (VC), lithium oxalate borate (LiBOB) and lithium nitrate (LiNO₃) [14–17] has been developed to modify the SEI film. FEC and VC promotes the formation of highly crosslinked polyethylene oxide (PEO) polymers in the SEI film [18] and this highly elastic structure significantly improved the cycling stability of the Si anode. After 50 cycles, the Si anode in EC-based electrolyte only retained 58% of the initial capacity, whereas the capacity retention of Si anode in FEC- or VC-based electrolyte achieved 73%–81%. In addition, FEC is also used for sodium-ion batteries to improve stability of novel binary transition metal oxides [19, 20], where the electrodes suffer a larger volume change than ones in lithium-ion batteries during cycling due to the larger size of Na⁺ (1.02 Å) than Li⁺ (0.76 Å). For example, by adding 2 wt% FEC to EC-based electrolyte, nickel molybdate (NiMoO₄) anode can display a reversible capacity of 245 mAh g⁻¹ and a capacity retention of 82% at 50th cycle [20]. LiBOB and LiNO₃ were shown to improve the stability of the SEI film, and prevented destruction caused by soluble products [14, 16]. The former was used for high-voltage spinel full-cells to stabilize the SEI on graphite anode against the Mn dissolution problem. By adding one weight percent LIBOB to the EC-based electrolyte, the capacity retention of full-cells increased from 18%–80% at 30 °C and 5%–40% at 45 °C. The latter was used for lithium-sulfur batteries to paasivate the Li anode and thus prevent the continuous reaction between Li and polysulfides in electrolyte. In addition to the electrolyte species, its concentration is a crucial factor. For example, in a high concentration of lithium bis(trifluoromethanesulfon)imide (LiTFSI) (>20 M) aqueous electrolyte (‘water in salt’), the reduction potential of LiTFSI was changed from 1.4 V to 2.9 V vs Li/Li⁺ [21]. This allowed a SEI film to be formed before the anode reached the hydrogen evolution potential. Because of this, the stable potential of the anode was widened, and an ultra-high voltage (2.3 V) aqueous lithium-ion battery was obtained. This full cell delivered a high energy density of 100 Wh kg⁻¹ (based on the total electrode mass) and showed an excellent stability with high capacity retention of 68% after 1000 cycles.
The electrochemical coating strategy was also used for electrochemical capacitors using lithium (difluoroxalate)borate (LIODFB) [22]. During the coating process, LIODFB reduced at 1.7 V vs Li/Li$^+$ and formed a nanometer thick, ion-conducting coating layer on the surface of the graphene electrode. This solid/solid interface supported the establishment of a de-solvated electrical double layer, and ensured a wider stable potential window, coupled with a higher capacitance and a lower self-discharge rate [23, 24]. A dual-graphene lithium ion capacitor, assembled using coating graphene electrodes, had a high stability at 100% depth of discharge (0–4.3 V), whose capacity retention achieved 89% after 1000 cycles. Also, this full-cell delivered a battery-level energy density of 160 Wh kg$^{-1}$ (based on the total electrode mass), and self-discharge rate was reduced by half compared to normal one.

2. Capacitive-type charge injection

In the capacitive-type charge injection process, electrons or holes are injected into the electrode material by an electrical double-layer or surface redox reaction. This process is highly reversible. As the charge is injected, the properties of the material including its surface chemical structure and electronic structure also change. The mechanism of capacitive-type charge injection was initially studied by monitoring the change of the electronic conductivity of single-wall carbon nanotubes (CNTs) [25]. During the injection, a 1 M sodium chloride (NaCl) aqueous electrolyte was used. To inject holes, a positive-bias voltage was applied to the CNT electrode, while anions (Cl$^-$) were adsorbed on the CNT surface to form an electrical double-layer and maintain electrical neutrality. To inject electrons, a negative-bias voltage was applied to the CNT electrode, while cations (Na$^+$) were adsorbed on the CNT surface to form an electrical double-layer and maintain electrical neutrality. It was found that these electrical double layers remained stable even when the electrode left the electrolyte. This phenomenon demonstrates the practicality of capacitive-type charge injection [26]. The stability of the electrical double layer is closely related to the type of injected charge. Injected holes were more stable than injected electrons. In addition, the environment also had a significant effect on the stability. In a vacuum or deionized water, the electronic conductivity of single-wall carbon nanotubes decreased rapidly because of the quick desorption of the electrical double layer, while the electronic conductivity was relatively stable in air.

For electrochemical energy-storage, capacitive-type charge injection has been used to maximize the energy density of carbon-based electrochemical capacitors [27]. The porous carbon electrodes store charge using the electrical double layer and have a sloping charge/discharge profile, which means that there is a one-to-one correspondence between the electrode potential and the amount of injected charges (figure 2(a)). Therefore, it is possible to control the open circuit potentials of the anode and cathode in an electrochemical capacitor by capacitive-type charge injection, and this has a decisive influence on the operating voltage and energy density of the device. As shown in figure 2(b), in the organic electrolyte (1 M lithium hexafluorophosphate (LiPF$_6$) in ethylene carbonate/dimethyl carbonate (EC/DMC)), the open circuit potential of a carbon-based electrode is about 3 V (vs. Li/Li$^+$). During charging, the cathode first reaches the higher potential limit (4.5 V) and anode is still far from the lower potential limit (0.01 V), so the capacitor fails to wholly utilize the stable voltage window. The maximum operating voltage of the cell is only 3 V. In contrast, for a cell assembled using the injected electrode, the open circuit potential of both cathode and anode are optimized. This ensures that the potentials of both the anode and cathode can simultaneously reach the higher and lower potential limits during the charging process, leading to a maximum working voltage of 4.5 V. By using this method, the energy density of carbon-based electrochemical capacitors reached about ten times the original values, while the power density was also maintained. Besides, this method do not have to sacrifice the cycling stability. The CNT-based cell retained 91% at 2000th cycle of the initial energy stored. It is noted that this method is also applicable to pseudocapacitive-type metal oxides, which store charges by a surface redox reaction [28]. By this method, an aqueous asymmetric capacitor using 2 M LiNO$_3$ as the electrolyte and combining a vanadium pentoxide cathode and an activated carbon anode, achieved a maximum energy density of 46.35 Wh kg$^{-1}$ at 1.8 kW kg$^{-1}$ and 28.25 Wh kg$^{-1}$ at 18 kW kg$^{-1}$. After 10 000 cycles between 0–1.8 V, the capacity of cell was not reduced indicating an excellent stability. The excellent electrochemical performances are benefited from adjusting the open circuit potentials of the anode and cathode via capacitive-type charge injection, which ensure the full utilization of redox reaction of V$_2$O$_5$ cathode (~0.2 to 0.8 V vs. SCE).

3. Battery-type charge injection

During the battery-type charge injection process, electrons or holes are injected into the electrode materials through a bulk-phase redox reaction. At the same time, electrode materials are intercalated or extracted with oppositely charged ions, leading to significant structural changes and phase transitions. A typical example is
the lithiation of graphite. During the injection of electrons, graphite is intercalated by lithium ions to form intercalation compounds ($\text{Li}_x\text{C}_6$). As shown in figure 3, according to the number of intercalated lithium ions, four different intercalation compounds can be obtained, resulting in a significant change in the physical- and chemical- properties of the graphite. Compared with capacitive-type charge injection, the battery-type charge injection is less reversible.

Currently, battery-type charge injection has been used to activate electrode materials such as lithium sulfide ($\text{Li}_2\text{S}$) and lithium-rich layered oxides. $\text{Li}_2\text{S}$ is a promising active material with a high theoretical capacity but it is electrochemically inert due to its poor conductivity and low ion diffusion coefficient. It has been reported that the problem may be solved by high over-potential (~1 V) charging [30]. During this process, lithium is extracted from $\text{Li}_2\text{S}$, and a small quantity of polysulfide was thereby irreversibly produced. Polysulfides with a high ionic conductivity were present during subsequent cycles and promoted the kinetics of the conversion reaction ($\text{Li}_2\text{S}$ to S). Based on this, even 10 µm $\text{Li}_2\text{S}$ particles can be used as the active material of cathode, and delivered a high initial capacity of 800 mAh g$^{-1}$. On the other hand, Lithium-rich layer oxide materials are composed of two phases: $x\text{Li}_2\text{MnO}_3$, $(1-x)\text{LiNi}_{a}\text{Co}_{b}\text{Mn}_{c}\text{O}_2$ ($x < 1, a + b + c = 1$). The former is electrochemically inert. To be used as high-energy materials for cathodes, the materials need to be first charged to a high voltage (4.7 V) during which lithium ions and oxygen are irreversibly released, leading to the conversion of $\text{Li}_2\text{MnO}_3$ to electrochemically-active $\text{Li}_x\text{MnO}_y$ [31]. As a result the activated lithium-rich layer oxides achieved a specific capacity of 250 mAh g$^{-1}$, while the value for the pristine material was only 170 mAh g$^{-1}$ [32].

Battery-type charge injection has been also used to supplement lithium availability in a cell. The irreversible consumption of lithium ions during cycling is a significant problem for lithium ion batteries and lithium ion capacitors and leads to quick capacity decay. To solve this problem, an effective strategy is to reversibly intercalate lithium ions into the electrodes before the cell is used, which is known as pre-lithiation.
After pre-lithiation, original state of electrode changes from discharge state to charge state. These excess lithium ions can be released when electrochemical-active lithium in cell loses due to the formation of SEI film or side reactions, and improve the cycling stability of cell. At an early stage, pre-lithiation was performed using a lithium counter electrode. However, this process is not available for commercialization. Nowadays, many novel pre-lithiation techniques have been developed to avoid the used of a lithium counter electrode [33, 34].

4. Electrochemical modification for novel energy-storage systems

As discussed above, improving the electrochemical performance of energy storage devices by electrochemical modification is simple but effective. It is a cost-effective way to improve current electrochemical energy-storage technologies. Actually, in addition to optimizing electrode materials, this strategy can also provide ideas for the design of novel energy-storage systems, and help simplify research on the path from materials to devices. A quasi-symmetrical molybdenum disulfide (MoS$_2$) battery illustrates this [35]. It proposes an electrochemical activation modulation to decouple the covalent metal and sulfur elements in MoS$_2$ and activate their redox activity. This method involves a multiple-step battery-type charge injection. During modification, the MoS$_2$ electrode first underwent a conversion reaction with Li$^+$ to form Mo and Li$_2$S. It was then discharged to release the Li$^+$. Due to the sluggish kinetics, this conversion reaction has a poor reversibility, causing an intermediate phase composed of Li$_2$S, MoS$_2$, and Mo to be formed inside the electrode. After cycling, this intermediate phase in different and controlled potential windows, a sulfur-redox MoS$_2$ cathode and a metal-redox MoS$_2$ anode were obtained. The former achieved a capacity of 148 mAh g$^{-1}$, which is ten times the pristine MoS$_2$ cathode in the range of 1.7–3.1 V vs. Li/Li$^+$; while the latter delivered a capacity of 234.7 mAh g$^{-1}$ between 0.1–1.4 V vs. Li/Li$^+$. Based on this, a quasi-symmetrical battery was fabricated, which used MoS$_2$ as a single active material for both the cathode and anode. This proof-of-concept full-cell cycled stably between 0.3–3.1 V and delivered a energy density of 97.6 Wh kg$^{-1}$.

This work should inspire further efforts in the rational modification of both active materials and energy-storage systems. For active materials, the different conversion-type metal compounds have been widely studied for use in the lithium ion battery [1]. However, poor kinetics is a common problem and restricts the practical use of conversion-type metal compounds. Electrochemical modification can provide an alternative way to use these high-energy materials. On the other hand, it is also able to solve the main problems of a sulfur-based cathode which has poor conductivity and a serious shuttling effect. By electrochemical modification, the MoS$_2$ can be transformed to a metal-sulfide matrix with uniform distribution of Li$_2$S and metal nanoparticles, which is difficult to obtain by materials engineering. The metal nanoparticles improve the electrical conductivity and catalyze the sulfur redox reactions, and the metal-sulfide matrix provides strong chemical bonding with polysulfides to improve the stability. For energy-storage systems, electrochemical modification also opens up a new way to build symmetrical batteries based on a variety of conversion-type metal compounds. This symmetrical configuration can simplify the production process for electrode materials.

5. Summary and perspective

In the future, we believe that electrochemical modification will play a key role in the commercialization of energy-storage devices and promote integrated research combining materials and devices (table 1). To achieve this goal, there is a need to further understand the basic mechanisms of different electrochemical reactions, and explore the relationships between the properties of active materials and their electrochemical behavior. It is also important to develop new modification techniques to achieve time-efficient and in-situ tuning after the electrodes have been assembled into cells.

It is estimated that studies are needed of the following aspects:

(a) For electrochemical coating, an effective modification for the cathode/electrolyte interface is a challenge but is needed. This is beneficial for promising electrode materials, e.g. sulfur, Ni-rich metal oxides and spinel metal oxides capable of withstanding high-voltage. An ideal coating layer may eliminate the shuttling effect and attack from electrolyte oxidation. Such advances will greatly promote the commercialization of lithium-sulfur and high-energy & high-voltage lithium ion batteries. In addition, a stable coating layer on porous carbon materials, especially for mesoporous carbon, is also helpful for electrochemical capacitors because it provides an alternative way to develop high-voltage electrochemical capacitors without using ionic-liquid electrolytes, which are expensive and have a low conductivity. We also believe that electrochemical coating is a potential way to construct quasi- or all-solid-state cells, in which the coating layer is formed in-situ and is directly used as an electrolyte to avoid a large interfacial resistance.
Table 1. Summary of three electrochemical modification strategies and their applications.

| Electrochemical coating | Capacitive-type charge injection | Battery-type charge injection |
|-------------------------|----------------------------------|------------------------------|
| • Modification of surface chemistry | • Modification of surface chemical structure | • Modification of structure and phase |

Current energy-storage applications

| Anode of Lithium ion battery (e.g. metal oxides\cite{1-10}, S\cite{11}, graphite\cite{11,12}) | High-energy supercapacitor (e.g. Porous carbon materials\cite{13}) | Activation of electrode materials (e.g. Li$_{2}$O, Li-rich metal oxides\cite{14}) |
|---------------------------------|-----------------|---------------------------------|
| Cathode of lithium-ion battery (e.g. Ni-rich metal oxide, high-voltage spinel metal oxide) | High-energy asymmetric capacitor (e.g. V_xC_y\cite{15}) | Long-cycle lithium ion capacitors (e.g. Superscap of lithium sources\cite{16,17}) |
| High-voltage supercapacitors (e.g. Porous carbon materials\cite{18-20}) | All-solid-state electrochemical energy-storage cells | Activity modulation of electrode materials (e.g. Conversion-type metal oxides\cite{21}) |
| Symmetrical secondary batteries (e.g. Conversion-type metal oxides\cite{21}) |

Future energy-storage applications

(b) For capacitive-type charge injection, it should be not only limited to electrochemical capacitors. With reducing size, the electrochemical behavior of a battery-type material changes to capacitive-type. At the same time, the charge profile plateau is replaced by a slope, which indicates that capacitive-type charge injection may play a key role to maximize the energy density of future nanomaterial-based secondary batteries.

(c) For battery-type charge injection, we must emphasize that the most suitable working conditions for an electrode material may not be when it is in the original state. By a preliminary reaction, the electrode material can be converted to an ideal intermediate phase and provide excellent electrochemical performance. Because some electrochemical redox reactions are less reversible, they cannot be used for energy-storage but can be used to activate the material.

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