Carbon materials in Lithium-Ion batteries

Systems for electrochemical energy storage convert chemical energy into electrical energy. To value the energy content of a system, terms of "energy density" (or "specific energy") and "power density" (or "specific power") are used. "Energy density" is expressed in watt-hours per liter (Wh L^{-1}) or in watt-hours per kilogram (Wh kg^{-1}) and "power density" is expressed in watts per liter (WL^{-1}) or in watts per kilogram (Wkg^{-1}). Among various energy-storage devices, it is clear that electrochemical capacitors (ECs) and supercapacitors can be considered as high power density systems with relatively low energy density, whereas lithium-ion batteries (LIBs) alone with high energy density show relatively low power characteristics. LIBs and ECs share some common features. They both consist of two electrodes that are in contact with the electrolyte. Requirements for electron and ion conduction in electrodes and electrolyte are valid for both systems. Furthermore, electron and ion transport are separated during the charge/discharge processes. On the other hand, historically, differences between LIBs and ECs do exist. For instance, compared to traditional ECs, the electrodes of which are composed of the same materials (activated carbons) and therefore exhibit the same electrochemical potential, an inherent potential difference exists between the electrode materials in LIBs. The potential difference between the two electrodes in LIBs, for example, a graphite anode and a lithium cobalt oxide cathode, is ideally constant through discharge or charge, but the working voltage of ECs linearly declines with the extent of charge. Furthermore, charge storage takes place by a faradic reaction (redox reactions) at the electrode in the case of LIBs. This is a diffusion-controlled slow-rate process and is also the origin of the low power density of LIBs. However, in the case of ECs, charges mainly form at the interface of the electrode and electrolyte by means of a non-faradic reaction through the formation of electrical double layers. Although this process exhibits a fast rate of ion diffusion to give rise to higher power density, the confinement of charges on the surface of the electrode leads to a low energy density for ECs [1].

Recently, LIBs and ECs have attracted attention from both industry and academia owing to the emergence of nanomaterials and nanotechnologies. Carbon-based materials including carbon nanotubes (CNTs), carbon nanofibers (CNFs), graphene, and their composites have been widely studied as electrode materials for both devices. Compared to traditional electrode materials, for example, graphite or activated carbons (ACs), these new types of carbon materials exhibit differences not only in dimensionality and morphology but also in the distribution of

chemical bonding, which allows mixtures of local electronic structures between sp^2 and sp^3. Therefore, the carrier-transport properties are different from classic carbon materials if they are in contact with the reactants. Novel carbon materials with high accessible surface areas and short diffusion lengths for ions open new perspectives for high energy and high power density devices. In this class, electrode performance of LIBs based on different carbon materials will be reviewed.

The working principles of LIBs

A LIB battery is made up of an anode, cathode, separator, electrolyte, and two current collectors (positive and negative). The anode and cathode store the lithium. The electrolyte carries positively charged lithium ions from the anode to the cathode and vice versa through the separator. The movement of the lithium ions creates free electrons in the anode, which creates a charge at the positive current collector. The electrical current then flows from the current collector through a device being powered (cell phone, computer, etc.) to the negative current collector. The separator blocks the flow of electrons inside the battery. While the battery is discharging and providing an electric current, the anode releases lithium ions to the cathode, generating a flow of electrons from one side to the other. When plugging in the device, the opposite happens: Lithium ions are released by the cathode and received by the anode. Fig. 1 shows the charging-discharging mechanism of Li ion secondary battery [2].
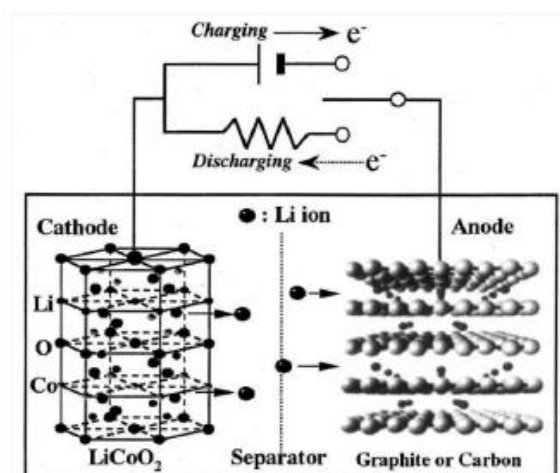

Fig. 1. Charging-discharging mechanism of Li ion secondary battery [3]

Mechanism

Intercalation is a simple, solid-state redox reaction in which ions are inserted into host materials. During intercalation, mobile guest ions such as Li+ , Na + , and K + in the electrolyte are inserted into a solid layered material but the primary structural features are maintained with only a minimal amount of volume expansion. Apart from protons, the smallest ion, Li+ , is considered to be one of the best ion candidates for the intercalation reaction. In electrochemical storage, the concept of "intercalation" was first applied to cathode materials for lithium-ion batteries by Whittingham in the 1970s. Transition metal oxides and chalcogenides with stable layered or tunnel structures were adopted as host materials. The redox reaction takes place only on the host lattice, whereas no faradaic changes occur in the guest ions. Later on, carbonaceous materials were widely used as anodes in lithium-ion batteries by forming graphitic intercalation compounds (GICs) with a wellknown configuration of Li_xC_n . During the charging process, positively charged lithium ions intercalate into negatively charged graphite layers; the ions maintain their ionic states rather than adopting their metallic states. The electrostatic force between the Li ions and graphite can provide the energy to overcome van der Waals forces between the graphene layers and thus the layer distance in graphite expands [1].

References

[1] ChemSusChem 2015, 8, 2284 – 2311

[2] https://www.energy.gov

[3] Carbon 38 (2000) 183–197