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Review

The roles of graphene in advanced Li-ion hybrid supercapacitors

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ABSTRACT

Lithium-ion hybrid supercapacitors (LIHSs), also called Li-ion capacitors, are electrochemical energy storage devices that combining the advantages of high power density of supercapacitor and high energy density of Li-ion battery. However, high power density and long cycle life are still challenges for the current LIHSs due to the imbalance of charge-storage capacity and electrode kinetics between capacitor-type cathode and battery-type anode. Therefore, great efforts have been made on designing novel cathode materials with high storage capacity and anode material with enhanced kinetic behavior for LIHSs. With unique two-dimensional form and numerous appealing properties, for the past several years, the rational designed graphene and its composites materials exhibit greatly improved electrochemical performance as cathode or anode for LIHSs. Here, we summarized and discussed the latest advances of the state-of-art graphene-based materials for LIHSs applications. The major roles of graphene are highlighted as (1) a superior active material, (2) ultrathin 2D flexible support to remedy the sluggish reaction of the metal compound anode, and (3) good 2D building blocks for constructing macroscopic 3D porous carbon/graphene hybrids. In addition, some high performance aqueous LIHSs using graphene as electrode were also summarized. Finally, the perspectives and challenges are also proposed for further development of more advanced graphene-based LIHSs.

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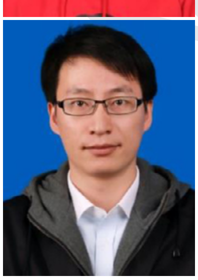

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1. Introduction

With the rapid development of world economy and sharp growth of the world population, the global environmental pollution and energy crisis are becoming more and more serious, and human are facing a great threat to existence. Therefore, it is urgent to look for clean, efficient and renewable green energy to replace traditional fossil energy. Electrochemical energy storage device is an important part of the energy system which we have used for a long time. Among the numerous energy storage devices, electric double layer capacitors (EDLCs) [1–5] and lithium-ion batteries (LIBs) [6–8] are currently considered to be the most promising energy-storage devices. EDLCs using carbon based active materials, show the prominent advantages in fast charging and discharging performance, thus it can delivers the essential high power density (10 kW/kg) and long cycle life (more than 10^5 cycles) through formation of an electric double layer at the electrode-electrolyte interface. However, EDLCs suffer from low energy density (5–10 Wh/kg), unless the specific surface area of the active carbon is sufficiently high to allow high energy and power densities simultaneously [9–12]. In comparison with supercapacitor, LIBs can provide higher energy densities (150–200 Wh/kg) because of faradaic reactions derived from the intercalation of lithium ions into the electrodes, but their power densities are relatively low (below 1 kW/kg) and their cycle life is quite poor (usually less than 1000 cycles) due to intrinsically sluggish solid-state lithium ions diffusion in the bulk and the accompanying volumetric strain [13–15]. In view of the above characteristics, even though these two systems possess independent merits, the conventional EDLCs alone cannot satisfy the maximum peak energy or LIBs alone cannot satisfy the maximum peak power required by the hybrid electric vehicles and all-electric vehicles system. Therefore, there is an urgent need to develop energy-storage devices with both high energy and power density to meet the requirements of the current special application areas.

The approach to overcome the energy density limitation of the EDLCs and the power density limitation of the LIBs is to develop hybrid capacitors like lithium-ion hybrid supercapacitors (LIHSs), in which the respective advantages of LIBs and EDLCs are well combined [16–19]. The LIHSs generally employ a battery-type (faradic) electrode in combination with a capacitor-type (non-faradic) electrode in an electrolyte containing Li ions in a single device. The electrochemical reaction mechanisms of EDLCs, LIHSs and LIBs are shown in Fig. 1. EDLCs adopt an electrostatic, non-Faradaic, double-layer charge-discharge mechanism, that store energy physically by the electrostatic attraction of electrolyte ions on the surface of

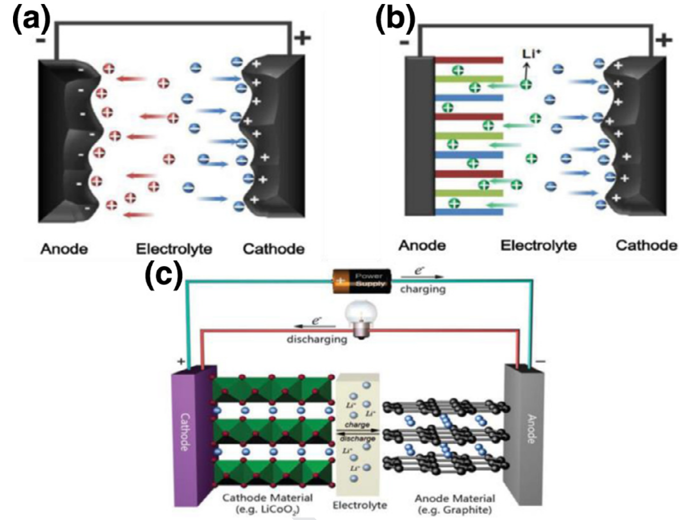

Fig. 1. Electrochemical reaction mechanisms of (a) EDLCs [20], (b) LIHSs [20] and (c) LIBs [21].

active materials; LIBs are called "rocking chair batteries" since lithium ions reversibly intercalate/de-intercalate between two electrodes along with the removal and addition of electrons; LIHSs work with anions adsorbing/desorbing onto/from the capacitor-type electrode surface and Li^+ ions intercalating/de-intercalating into/from the bulk of the battery-type electrode simultaneously [20–22]. Since the cathode and anode work reversibly in distinct voltage regions, LIHSs can potentially achieve a higher cell voltage compared to conventional ELDCs. Moreover, benefiting from the high specific capacity of the battery-type electrode and the excellent rate capability of the capacitor-type electrode, LIHSs could deliver high energy density, high power density and long durability [23–26]. Under the circumstances, LIHSs have attracted considerable attention and provides a new strategy for the development of hybrid electric vehicles and all-electric vehicles system. Up to now, the commonly used capacitor-type electrode materials for LIHSs are carbonaceous materials (activated carbon (AC) [23,24,27], carbon nanotube (CNT) [28,29] and graphene [13] etc.). AC is the most widely used due to its high specific surface area (SSA), relatively good electrical conductivity and low cost. It should be noted that AC can be employed as either a positive or a negative electrode, depending on the relative potential of the counter electrode [30]. The battery-type electrode materials used for LIHSs are insertion-type anode materials including pre-lithiated carbonaceous (graphite [31–34], soft carbon [35], hard carbon [36–40]), metal compounds [41] and lithium titanate (LTO) [42–46] anode materials, and lithium compounds [47,48] cathode materials. Among them, graphite-based materials and LTO are two mainly types of commercial LIB anode materials, and the combination of AC and graphite, or AC and LTO are most typical for LIHSs. There are two types of electrolytes for LIHSs: aqueous and non-aqueous electrolyte that containing Li ions. From the operating voltage point of view, the most commonly used electrolyte is $LiPF_6$ dissolved in an organic solvent (e.g. ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC)) [49]. From the cost and safety issues point of view, most researchers are ongoing for developing and utilizing aqueous electrolyte for LIHSs [47,50–52].

However, throughout the research reports in recent years, we find that the obtained performance of these devices are still not satisfactory, although their energy density have been greatly improved compared to EDLCs, the power and energy performances are not decoupled, the rate performance, especially the long-term

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