Recent Advances in Supercapacitors: Ultrafast Materials Make Innovations

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ABSTRACT

Electrical energy storage (EES) devices are at the core of the environmental technologies that are highly influential in advancing our life in a future society. Among different EES technologies, electric double layer capacitors (EDLCs) are considered as promising devices due to their high-power, safe and long-lived characteristics. One of the approaches to further enhance the cell voltage and energy density of EDLCs while maintaining their high power is to replace the activated carbon with ultrafast lithium ion battery materials. Increasing their cell voltage and energy density contribute to decrease a number of serial cell connection and a volumetric package, respectively. In this article, we introduce examples of the synthesis of several nanomaterials using our original ultracentrifugation process, allowing the in-situ growth of active materials onto carbon surface enables ultrafast electrochemical response for 2nd and 3rd generation supercapacitors.

Keywords : New Generation Capacitors, New Generation Batteries, Ultracentrifugation Treatment, Nano Composites

1. Introduction

The growing demand for fast charge-discharge electrical energy storage devices with long cycles lifetimes has led to the need for alternatives to current battery systems,3 which store energy via slow faradic reactions. The devices that may fit such demands are the electric double layer capacitors (EDLCs), which combine efficient charge/discharge characteristics with long life spans.2 However, the energy density of currently developed EDLCs is low due to limitations on capacity and operating voltage imposed by their charge-storage mechanism, which involves physisorption of ions on the surface of porous activated carbons (AC).3 The replacement of the carbon electrodes with pseudocapacitive/ultrafast battery-like materials results in devices, called asymmetric or hybrid supercapacitors, that we term “2nd generation (2nd gen.) supercapacitor” (Fig. 1), with the potential for higher energy storage capabilities compared to EDLCs.5

2. New Generation Supercapacitors: Nanohybrid Capacitors and SuperRedox Capacitors

One of the high-standard examples of the 2nd gen. supercapacitor is the NanoHybrid Capacitors (NHCs) which offer beside safety outstanding cycling performance (>10,000 cycles) and power density (6 kW L⁻¹ at charge/discharge), together with high energy densities (in the order of 30 Wh L⁻¹) three times higher than that of over EDLCs.3,6 The NHCs is composed of an AC positive electrode combined with a nano-sized Li4Ti5O12 (LTO) negative electrode which synthesized using our original “ultracentrifugation” process enables rate capabilities comparable to those of AC electrodes (>300 C-rate).7 Still, the low volumetric capacity of AC positive electrodes (<40 Ah L⁻¹) limits the volumetric energy density of such hybrid capacitors. To overcome this limitation, the replacement of also the AC positive electrode with battery-like material treated to facilitate ultra-high-rate operation is expected to drastically increase the cell voltage and energy density, contributing to decrease a number of serial cell connection and a volumetric package, respectively. Such cell configuration offers tantalizing possibilities for realizing a new generation of energy-storage devices—that we term SuperRedox Capacitors (SRCs) as the “3rd gen. supercapacitor” (Fig. 1)—that combine the high energy density of lithium-ion batteries with the high-rate charge/discharge capability of supercapacitors.8 As shown in Fig. 1, depending on the combination of active materials, SRCs can achieve different maximum cell voltages (2.8–3.5 V) and energy density (5.4–5.7 fold of EDLC). This

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headline introduces our recent works on the production of new ultrafast active materials for SRCs highlighting the generalization of our ultracentrifugation process to the synthesis of a broad range of lithium oxides/phosphates compounds exhibiting ultrahigh-rate performances, making them suitable as active materials for the SRC configuration.

3. Key Processing Technology: Ultracentrifugation

An in-situ material processing technology called “ultracentrifugation (UC)” has been used to prepare a novel ultrafast LTO nanocrystal electrode for NHC. The ultracentrifugation enables the preparation of nano-sized and dimension-controlled (1D to 2D) LTO, directly bounded on high-surface-area carbons such as carbon nanotubes (CNT). The ultracentrifugation process (Fig. 2a) involves first an ultracentrifugation at 75,000g which accelerates unbundling of the carbon matrix for maximum dispersion in order to obtain the contact with reactant species. Then an in-situ sol-gel reaction takes place and produces the nanoscale LTO precursors onto the carbon matrix. The mechanochemical sol-gel reaction is finally followed by a short heat-treatment process allowing completing the crystallization process of LTO spinel structure without crystal growth neither irreversible structure transformation during the lithiation reaction. This irreversible structure transformation includes ion migration and cation (Li⁺ and V⁴⁺) mixing, resulting in a cation-disordered LVO.

4. High Rate Negative Electrode: Li₃VO₄ (LVO)

For the design of the SRC, 3rd gen. supercapacitor, we identified a LVO as a replacement of the nano-LTO used in NHC, because of its lower reaction potential and larger capacity compared to LTO (1.55 V vs. Li/Li⁺, 175 mAh g⁻¹). The redox reactions of V⁵⁺/V⁴⁺ and V³⁺/V⁴⁺, lying in safe range from 0.4 to 1.3 V vs. Li/Li⁺, result in the reversible intercalation of two Li⁺ per formula unit (394 mAh g⁻¹) with excellent cyclability over 1,000 cycles. However, its low electronic conductivity (≈10⁻¹⁰ Ω⁻¹ cm⁻¹) and large voltage hysteresis (<500 mV) are detrimental in achieving high-power and high-efficient energy storage performances. We demonstrated that such LVO can be transformed into a pseudocapacitive/ultrafast materials by randomizing cationic arrangements in the intrinsic cation-ordered crystal structure of LVO (Fig. 3a and b). First, we have synthesized nanoparticles of LVO (size below 50 nm), highly-dispersed and entangled within the multi-walled CNT (MWCNT, 40 wt.%), via ultracentrifugation. The capacity of the uc-treated composite reached 330 mAh g⁻¹ when cycled in the potential range from 2.5 V down to 0.1 V vs. Li. This capacity corresponds to 95% of theoretical capacity of LVO (2Li) after 100 cycles.

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mechanism, the galvanostatic charge achieved at constant potential through a two-phase reaction composite shows different electrochemical signatures both with plateau and sloping (pseudocapacitive) regions (Fig. 4a inset). Three different electrochemical regions were observed: one plateau at a constant potential of 3.4 V corresponding to the crystalline LFP phase and two sloping profiles below and above 3.4 V corresponding to amorphous LFP containing Fe$^{3+}$ defects and graphitic carbon phases, respectively. Such unusual electrochemical signature originates from the peculiar structure of the LFP/graphitic carbon composite material, which contains single nanosized LFP crystals encapsulated within hollow-structured graphitic carbons (Fig. 4b). Evidenced by the combination of spectroscopic and X-ray diffraction characterization techniques, the LFP/graphitic carbon composite material has a core LFP (crystalline “core 1”)/graphitic carbon (shell) composite was evaluated using cavity microelectrode, which allows focusing on the kinetic properties of the material on a broad range of scan rate (Fig. 4c–d). The electrochemical analysis shows two different behaviors and kinetic regimes in the core LFP (amorphous and crystalline). A surface charge storage pseudocapacitive mechanism drives the kinetics in the amorphous LFP phase containing Fe$^{3+}$ defects, while the Li$^{+}$ intercalation in the core crystalline LFP phase is a diffusion-limited process at a high scan rate (>120 mV s$^{-1}$). These results propose new routes for designing high power materials to assemble high energy density SRCs.

5. High Rate Positive Electrode: LiFePO$_4$ (LFP)

As mentioned in the section 2, a replacement of the AC positive electrode with pseudocapacitive/ultrafast materials may lead to realize the SRC concept. We chose LFP as a candidate for SRC positive electrode materials because of its relatively high theoretical capacity of 170 mAh g$^{-1}$, low cost and high electrochemical and thermal stabilities. However, the slow diffusion kinetics of Li$^{+}$ at the LiFePO$_4$/FePO$_4$ interface along b-axis together with the poor electronic conductivity of the pristine olivine-LFP ($10^{-10}$–$10^{-7}$ Ω$^{-1}$ cm$^{-1}$) limit the power capability of the material. Using ultracentrifugation, we realized the pseudocapacitive/ultrafast performance of LFP by synthesizing a LFP/graphitic carbon composites. The synthesized LFP/graphitic carbon composites have an extremely high rate capability both in charge and discharge; 89, 60, 36, and 24 mAh g$^{-1}$ at 1, 100, 300, and 480 C, respectively (Fig. 4a). Such a linear relationship means that the composites can offer a high-power capability of the material in discharge as well as in charge, such as expected for the practical use of SRC. More interestingly, unlike conventional LFP where Li$^{+}$ intercalation is always achieved at constant potential through a two-phase reaction mechanism, the galvanostatic charge/discharge profile of the composite shows different electrochemical signatures both with plateau and sloping (pseudocapacitive) regions (Fig. 4a inset). Three various regions were observed: one plateau at a constant potential of 6. High Voltage Positive Electrode: LiCoPO$_4$ (LCP)

As shown in the sections above, the ultracentrifugation induces crystalline structure changes of battery materials, which led to ultrafast electrochemical characteristics. This synthesis technique can even bring about a stabilization of electrode/electrolyte interface at an extremely high voltage. A good example was demonstrated on LCP, that offers a tremendous advantages to conventional cathode
materials: high reaction potential of 4.8 V vs. Li/Li+, theoretical capacity of 167 mAh g$^{-1}$, and thermal stability thanks to the P-O covalent bonding. Hence, use of LCP may realize 5 V-class lithium-ion batteries (LIBs) which effectively reduce both a number of serial cell stacking and a volumetric cell space. However, a serious obstruction to practical utilization of LCP is its poor cyclability: LIBs with LCP cathodes exhibit a dramatic decrease in capacity within just a few 10 s of cycles. Mechanisms proposed to explain the poor capacity retention include instability of the ethylene carbonate-based electrolyte$^{1}$ and of the delithiated phase (Li$_{1-x}$CoPO$_4$, $x<1$).$^{22}$ We have been able to achieve stable cycle performance and to elucidate the influence of Fe$^{3+}$ substitution on the cyclability of LCP, taking into account both crystal structure and the electrode/electrolyte interface.$^{23}$ We have synthesized Fe$^{3+}$-substituted LCP nanoparticles (LCFP, 100 nm in average diameter) in highly dispersed MWCNT matrix prepared via ultracentrifugation. Surface analysis using X-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy suggest that Fe$^{3+}$ enrichment of the surface of LCP nanoparticles occurs through the oxidation of Fe$^{2+}$ into Fe$^{3+}$ along with the creation of vacancies at Co$^{2+}$ sites during air-annealing process (Fig. 5a). The Fe$^{3+}$-rich phase formed on the LCP surface play a significant role in yielding stable charge-discharge performance. The Fe$^{3+}$-rich phase on the surface stabilizes the delithiated phase of (Li$_{1-x}$Fe$_{0.11}$Co$_{0.76}$Fe$_{0.13}$O$_{2-x}$)CoPO$_4$ ($x<1$), preventing both the crystal structure degradation and continuous electrolyte decomposition on the LCPF nanoparticle surface. The phase stabilization yielded excellent cyclability, with 85% capacity retention over 5,000 cycles at 1 C and 96% capacity retention over 1,000 cycles even at a slow C-rate of 0.2 C (Fig. 5a and b).$^{23}$ The importance of Fe$^{3+}$ retention in the crystal structure, which required to prevent Fe$^{3+}$ reduction to Fe$^{2+}$ around 3.5 V vs. Li/Li+, was demonstrated by a combination of XRD and XAFS analysis on samples with and without operation-voltage extending below 3.5 V vs. Li. Meanwhile, different from previous reports,$^{14,23}$ it was found that the vacancies on Co/Fe sites improve the overall electrochemical performances such as the capacity and C-rate capability (100 C-rate with capacity of 45 mAh g$^{-1}$, Fig. 5c), thanks to the enhancement of Li$^+$ diffusivity within LCFP crystals. By demonstrating the existence of the Fe$^{3+}$-rich phase on LCFP nanoparticles and its critical impact on electrochemical performance, this example may open the way to the design of stable 5 V cathode materials via fine-tuning of surface phenomena.

7. Conclusions

The next generation supercapacitors such as SRCs, based on pseudocapacitive/ultrafast battery-like positive and negative electrode materials, have the possibility to drastically increase the energy density compared to EDLCs without sacrificing the high power density and prolonged cyclability. The ultra centrifugation-treated transition metal oxides/nanocarbon composites (LVO and LFP) described in this headline are excellent candidates as active materials for SRCs. This ultra centrifugation can be also applied for 5 V-class active materials (LCP) to stabilize its electrode/electrolyte interface with ultralong cycling performances over 5,000 cycles. Nanosized and rapid Li$^+$ diffusion-controlled materials directly bound on high-surface area conducting carbons synthesized via ultra centrifugation, contribute to achieve ultrafast and stable electrochemical performance which are needed to develop the next generation of supercapacitors and even batteries.

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Figure 4. (a) Plots of discharge capacity vs. charge capacity of LFP/graphitic carbon composite as a function of C-rate. Inset: Charge/discharge profiles at different charge C-rates from 1 to 480 C. (b) Schematic illustration of the core–shell nanostructure of the LFP/graphitic carbon composite, representing a minute structure consisting of an amorphous outer sphere of a LFP containing Fe^{3+} defects and an inner sphere of crystalline LFP. (c) Cyclic voltammogram of LFP/graphitic carbon for the crystalline LFP phase (green), amorphous LFP phase (red). (d) Plots of I_p/v^{1/2} vs. v^{1/2} for peak of the crystalline LFP phase and amorphous LFP obtained at 10 different scan rates ranged from 1 to 1,000 mV s^{-1}.

Figure 5. (a) Cycle performances, (b) Charge/discharge profile of a half-cell consisting of Li/1 M LiPF_6 EC:PC:DMC(vol. 1:1:3)/(air-annealed LCFP/MWCNT composite) between 4.3 and 5.0 V. (c) Rate performance for the composites over the range 2.5–5.0 V.