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Nano-assembled Na₂FePO₄F/carbon nanotube multi-layered cathodes for Na-ion batteries



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ABSTRACT

The electrochemical performance of multi-layered cathodes containing alternately arranged Na₂FePO₄F nanoparticles and amino-functionalized carbon nanotubes (CNTs) for Na-ion batteries has been investigated. The Na₂FePO₄F/CNT multi-layered cathodes are fabricated using a layer-by-layer (LbL) nano-assembly technique, which leads to a three-dimensional porous structure that may contribute to fast Na-ion transport. The highly intertwined CNT layers serve as an electrical conductive network and the abundant pores serve as ionic conductive pathways. Evidences of enhanced electric and ionic transport are provided by impedance spectroscopy data, which show a significantly decreased resistance compared to traditional batteries. The unique multi-layered Naion cathodes are found to deliver 100 mA hg⁻¹ reversible capacity at a rate of 0.4 C and 80 mA hg⁻¹ at 0.8 C, and to maintain 60% of capacity at 2 C. After 400 cycles at 0.4 C, the cells still provide 77.8 mA hg⁻¹ capacity, corresponding to 74% capacity retention.

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1. Introduction

Na-ion battery is a promising alternative to the widely studied Li-ion battery for large-scale electrical energy storage [1–3]. In particular, iron based phosphate Na-ion batteries [4] have received considerable interest, and Na₂FePO₄F is a promising and interesting cathode material due to its two-dimensional layered structure, its small change in unit cell volume upon oxidation and reduction, and its room temperature solid solution behavior [5–8]. However, the large size of Na-ion (102 pm vs. 76 pm of Li⁺) makes it difficult to allow reversible and rapid Na-ion insertion/extraction. Carbon coating and particle size reduction [9-13] are the most common strategies to enhance the cycling stability and rate performance of Na₂FePO₄F. However, Na₂FePO₄F delivered only 50 mA hg⁻¹ capacity at 1 C and could only sustain the charge/discharge processes for 20 cycles even though the particle size was reduced to 30-200 nm and the particles were coated with carbon [11]. Manipulation of materials on the nano-meter scale is a viable method for optimizing material properties and a well-designed cathode structure could be an effective way to enhance Na-ion diffusion in cathodes.

Here, we report on the layer-by-layer (LbL) nano-assembly, which we have previously used for the development of multifunctional coatings [14–17], of Na₂FePO₄F/carbon nanotube (CNT) multi-layered cathodes for Na-ion batteries. The LbL technique [18], based on physical adsorption of positively-charged CNTs and negatively-charged Na₂FePO₄F nanoparticles, was chosen due to its possibility of finely

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tuning the interface between Na₂FePO₄F nanoparticles and CNTs. As shown in Scheme 1, the interconnected CNT layers served as highefficient conductive agents for efficient use of Na₂FePO₄F, and the pores served as reservoirs for liquid electrolytes capable of fast Na-ion conduction in cathodes. The porous CNT layers also accommodated volume change and corresponding strains accumulated in cathodes during charge/discharge processes [19,20].

2. Experimental procedure

 Na_2FePO_4F samples were synthesized using the sol-gel method: 1739 mg Fe(CH₃COO)₂, 820 mg NaCH₃COO (99%), 420 mg NaF (99%), and 1153 mg H₃PO₄ (concentration: 85%) were mixed together and then added and stirred in 20 ml dimethoxyethane solution for 12 h. Next, the solvents were evaporated in a vacuum oven. The formed gel was heated at 300 °C in argon for 2 h, and the obtained powder was further heated at 600 °C for 6 h. The reaction process is shown in Eq. (1).

 $Fe(CH_3COO)_2 + NaCH_3COO + NaF + H_3PO_4 \rightarrow Na_2FePO_4F + 3CH_3COOH (1)$

Na₂FePO₄F/CNT multi-layered cathodes were fabricated on copper current collectors by alternate adsorption of negatively-charged Na₂FePO₄F nanoparticles and positively-charged amino-functionalized CNTs. Procedures for the preparation of amino-functionalized CNTs were described in detail elsewhere [21]. The copper current collector was attached to a glass plate and only one side of the copper current collector was available for material deposition. Na₂FePO₄F nanoparticles and CNTs were sonicated for 6 h in deionized water separately to form



Scheme 1. LbL nano-assembly process for the formation of Na₂FePO₄F/CNT multi-layered cathodes.

uniform dispersions; the concentrations of both materials were 4 mg ml⁻¹ and their pH values were adjusted to 5.0. First, the copper substrate was treated with NaOH solution (4 M) for 5 min. The treated substrate was rinsed with deionized water and incubated in the Na₂FePO₄F suspension for 3 min followed by washing with deionized

water for 30 s. Next, the substrate was placed into the CNT suspension for 3 min and washed for 30 s. These steps were repeated until the desired number of layers was achieved. The assembly of a layer of Na₂FePO₄F nanoparticles followed by a layer of CNT was called a bilayer. In the present study, 45 bilayers were assembled to obtain Na₂FePO₄F/



Fig. 1. Characterization of Na₂FePO₄F/CNT multi-layered cathodes and related materials. (a) XRD pattern of Na₂FePO₄F nanoparticles. SEM image of (b) Na₂FePO₄F nanoparticles and (c) amino-functionalized CNTs. Inset is XPS characterization. (d) Na₂FePO₄F/CNT multi-layered films on a copper substrate. (e) Cross-section image and (f) TGA analysis of Na₂FePO₄F/CNT multi-layered cathodes. The tests were performed in air atmosphere with a heating rate of 5 °C min⁻¹.

CNT multi-layered cathodes, which, after LbL nano-assembly, were dried in air and treated at 100 °C in a vacuum oven for 5 h. The cathodes were then used to assemble cells.

The structures, morphologies, and thickness of the Na₂FePO₄F/CNT multi-layered cathodes were characterized by X-ray diffractometry (XRD) and scanning electron microscopy (SEM). The weight percent of Na₂FePO₄F in the multi-layered cathodes was determined by thermo gravimetric analysis (TGA). CR2032-type coin cells were used as testing cells, in which sodium foils were used as anodes, 1 M NaClO₄ in ethylene carbonate and dimethyl carbonate (1:1 by volume) as electrolytes, and Cellgard 2400 microporous membranes as separators. The cells were assembled in an argon-filled glove box. Electrochemical measurements were performed galvanostatically between 2.0 and 4.0 V at current densities of 0.4, 0.8, 1.2, and 2 C (with 1 C = 126.5 mAg^{-1}). The capacity was calculated based on the weight of Na₂FePO₄F in the cathodes. Cyclic voltammetry (CV) experiments were conducted using a NOVA potentiostat at a scan rate of 0.1 mVs⁻¹. Electrochemical impedance spectra (EIS) measurements were carried out using a NOVA electrochemical workstation at a frequency range between 100 kHz and 100 mHz at a potentiostatic signal amplitude of 5 mV. Kratos Axis Ultra X-ray photoelectron spectroscopy (XPS) (Kratos Analytical) with a monochromatized Al Ka X-ray source was used to analyze the surface chemistry of the functionalized CNTs.

3. Results and discussion

Typical XRD patterns of Na_2FePO_4F collected on a Panalytical diffractometer using Cu K ∂ radiation were shown in Fig. 1a. The main Bragg peaks were fully indexed, which was consistent with a previous report [5]. The XRD peaks could be indexed in a Pbcn space group with a =5.2226(5) Å, b = 13.8538(7) Å, c = 11.7802(5) Å. Fig. 1b shows the typical morphology of Na₂FePO₄F nanoparticles after annealing in argon at 600 °C for 6 h. The particle size was approximately 500 nm on average. The amino-functionalized CNTs synthesized tended to aggregate and seemed to be relatively flexible (Fig. 1c). XPS characterization (Fig. 1c) revealed that there was a significant amount of ammonium within the CNTs. Large-size samples were successfully prepared using the LbL nano-assembly method and the obtained Na₂FePO₄F/CNT multilayered cathodes had a robust structure, due to the high surface area and high mechanical properties of CNTs, and exhibited great flexibility without the use of binders like polyvinylidene fluoride or PVDF (Fig. 1d). CNTs and Na₂FePO₄F nanoparticles were well distributed throughout the multi-layered cathodes (Fig. 1e) and formed a threedimensional integrated skeleton that provided a highly reactive surface. The weight percent of Na₂FePO₄F in the multi-layered cathodes was found to be 79 wt.% (Fig. 1f), and the thickness of the multi-layered cathodes (45 bilayers) was determined to be ~20 µm based on SEM images.

The CV curves of the cells made with Na₂FePO₄F/CNT multi-layered cathodes (Fig. 2a) were tested in the voltage range of 2.0–4.0 V vs. Na⁺/Na at a scanning rate of 0.1 mV s⁻¹. In the high voltage range, the oxidation (Na extraction) peak could be separated into two continuous peaks located at 3.40 and 3.55 V, and the reduction (Na insertion) peak was located at 2.9 V. The average voltage was 3.2 V vs. Na⁺/Na, which was close to the equilibrium voltage of Fe^{3+/}Fe²⁺ redox couple. In addition, both the reduction and oxidation peaks had no obvious shifts within 20 cycles, indicating good reversibility for Na extraction and insertion in the multi-layered cathodes. These cells presented two charge



Fig. 2. Electrochemical performance of Na–Na₂FePO₄F cells made of Na₂FePO₄F/CNT multi-layered cathodes. (a) CV curves at first 20 cycles. 1st–5th cycles were tested with the fresh battery, and the 10th and 20th curves were tested after the 10th and 20th discharging, respectively. (b) Initial discharge/charge voltage profiles during 2.0–4.0 V at 0.4 C. (c) Discharge/charge voltage profiles at various current rates. (d) ElS analysis before cycling and after the 50th discharge. Both the Na₂FePO₄F/CNT multi-layered cathodes and the cathodes made using traditional slurry-coating had a thickness of ~20 µm and had the same weight percent of Na₂FePO₄F and CNTs.

plateaus and one discharge plateau (Fig. 2b), which were consistent with the CV data (Fig. 2a). The cells also exhibited high rate capability and delivered an initial capacity of 78.4 mA hg^{-1} even at a high discharge rate of 2 C (Fig. 2C). The high rate performance was probably attributed to the low resistance of the Na₂FePO₄F/CNT multi-layered cathodes, in which the CNT network may lead to high electrical conductivity. The inter-connected pores within the multi-layered cathodes may act as reservoirs for liquid electrolytes and facilitate fast Na-ion conduction.

To detect the interface barrier of the Na₂FePO₄F/CNT multi-layered cathodes, impedance analysis was performed to compare cells made of Na₂FePO₄F/CNT multi-layered cathodes with cells made of traditional slurry-coated cathodes. The real axis intercepting at high frequency represented the electrolyte resistance. The impedance located in the high-frequency semicircle region was regarded as the SEI layer resistance, corresponding to the charge transfer resistance of the cell. One can see that the Na₂FePO₄F/CNT multi-layered cathodes had a small impedance semi-circle and the charge transfer resistance increased only ~20% after 50 cycles compared to the 1st cycle (Fig. 2d); this indicated a relatively low interface barrier and good charge-transfer capability in the Na₂FePO₄F/CNT multi-layered cathodes. By contrast, in the cathodes made of traditional slurry-coating, a much higher charge transfer resistance was observed (Fig. 2d), probably due to the blockage of electrolyte penetration and ion diffusion by the PVDF used.

The improved charge-transfer property of Na₂FePO₄F/CNT multilayered cathodes was verified by the rate capability over multiple cycles. The initial discharge capacity (Fig. 3a) of Na-ion cells made of Na₂FePO₄F/CNT multi-layered cathodes reached 103.5 mA hg⁻¹ at 0.4 C, which was 82% of the theoretical value (126 mA hg⁻¹), and a reversible capacity of 97.9 mA hg⁻¹ was obtained after 100 cycles, corresponding to 94.6% capacity retention. With increasing current density in the range of 0.4–2.0 C, the discharge capacity decreased, probably due to the polarization effect, and at a rate of 2 C, the cell capacity was ~40 mA hg^{-1} after 100 cycles. Meanwhile, Na-ion cells made of Na₂FePO₄F/CNT multi-layered cathodes showed good cycling stability (Fig. 3b). At 0.4 C, a reversible capacity of 77.8 mA hg^{-1} was obtained after 400 cycles, corresponding to 74% capacity retention. At 0.8 C, 58.6 mA hg⁻¹ capacity was obtained after 330 cycles, corresponding to 61% capacity retention. These results indicated that Na-ion cells made of Na₂FePO₄F/CNT multi-layered cathodes had high cell operation properties over multiple cycles with good reversibility and fast kinetics. This good electrochemical performance of Na-ion cells made of Na₂FePO₄F/CNT multi-layered cathodes was probably due to the unique material compositions and microstructures of the Na₂FePO₄F/CNT multi-layered cathodes. As shown in Fig. 3c, the Na₂FePO₄F/CNT multi-layered cathodes had a porous structure favoring Na-ion transport and an interconnected CNT network providing excellent electrical conductivity and mechanical support. In fact, no destructive structural damage was observed on the Na₂FePO₄F/CNT multi-layered cathode even after 100 cycles (Fig. 3d). The capacity utilization of multilayered cathodes at 0.4 C was approximately 15% higher than that of Na₂FePO₄F cathodes recently reported in the literature [9,11], which had similar Na₂FePO₄F particle sizes.

4. Conclusion

In summary, large-size samples of Na₂FePO₄F/CNT multi-layered cathodes were successfully developed using LbL nano-assembly and the obtained multi-layered cathodes exhibited great flexibility without the use of binders like PVDF. The Na₂FePO₄F/CNT multi-layered



Fig. 3. Cycle performance and SEM characterizations of Na–Na₂FePO₄F cells made of Na₂FePO₄F/CNT multi-layered cathodes. (a) Rate performance over 100 cycles. (b) Multiple cycle performance at 0.4 and 0.8 C. Top surface characterizations of Na₂FePO₄F/CNT multi-layered cathodes (c) before cycling and (d) after 100 discharge/charge cycles.

cathodes had a porous structure and well distributed Na₂FePO₄F nanoparticles and CNTs. These Na₂FePO₄F/CNT multi-layered cathodes presented high cycling stability and rate capability, good reversibility, and fast kinetics, probably due to the unique multi-layered porous structures, which may provide adequate electron/ion conductive pathways and a strong affinity of Na₂FePO₄F nanoparticles without detaching from the conductive CNTs during discharge/charge processes.

Conflict of interest

The authors have no conflict of interest to declare.

Acknowledgments

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