Conformal poly(ethyl α-cyanoacrylate) nano-coating for improving the interface stability of LiNi0.5Mn1.5O4

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ABSTRACT

Undesired interfacial reaction between the high voltage spinel LiNi0.5Mn1.5O4 and commercial organic electrolyte is one of the most essential obstacles for the application of cathode material LiNi0.5Mn1.5O4 in lithium-ion batteries (LIBs). Here, to amend the high voltage cathode/electrolyte interface of LiNi0.5Mn1.5O4, we proposed a conformal nano-coating strategy by in-situ polymerization of poly(ethyl α-cyanoacrylate) (PECA) on its surface. The electrochemical measurement results demonstrated that the conformal PECA nano-coating film, acting as high voltage polymer electrolyte, transition metallic ions blocking layer, and buffer layer against electrolyte erosion and particle cracks, can successfully decrease polarization and enhance capacity retention during cycling of LiNi0.5Mn1.5O4. This work will inspire extensive and intensive research on the interface modification of LIBs.

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1. Introduction

As the primary power supply of portable equipment, lithium-ion batteries (LIBs) have recently attracted great attention for applications in electric vehicles and large-scale energy storage systems [1–4]. In order to satisfy the demands of these applications, it is urgently required to further improve energy and power densities and resolve the issues of safety and lifetime. As the energy density of a battery is defined by its capacity and voltage, enhancement in voltage is the appropriate approach to increasing the cell energy density [5–11]. Although 4 V-class cathodes (LiMn2O4, LiCoO2, LiFePO4) have been successfully used in commercial LIBs, a strong demand to improve their energy densities is awaiting the realization of the “next-generation” batteries operating at high voltage [12]. Spinel LiNi0.5Mn1.5O4 (LNMO) has a better prospect as high energy density cathode material compared with currently used 4 V-class cathodes due to its high voltage plateau (ca. 4.7 V vs. Li+/Li) and theoretical capacity (148 mAh g\textsuperscript{-1}) arising from the operation of Ni\textsuperscript{3+/4+} redox couples.

Nevertheless, the high operating potential of LiNi0.5Mn1.5O4 also leads to critical interface issues, such as electrolyte decomposition, high surface reactivity between the electrolyte and electrode, and gradual dissolution of Ni and Mn ions from the host structure. Especially, the dissolved transition metal ions can migrate through the electrolyte, which deposit on the surface of graphite and result in gradually decreased reversible capacity [6–10,13–18]. To solve this problem, extensive studies have been carried out to surface modification of cathode active materials with coating layer, including carbon materials, metals, oxides, phosphates, lithium compounds, polymers [19,20]. The coating layer could suppress the dissolution of Ni and Mn ions and decrease the oxidative decomposition of electrolyte on the surface of LiNi0.5Mn1.5O4. However, the inorganic coating materials [21–27] (e.g. Al2O3 and ZrO2) are usually not Li ion conductors, which will hinder Li ion diffusion between cathode active material and electrolyte. Furthermore, as the morphology of LiNi0.5Mn1.5O4 is usually octahedron, the inorganic coating layer tends to be discontinuously deposited on the surface. Also, the complicated and high temperature treatment makes the coating process cost-effective and susceptible to ions interdiffusion between the inorganic coating layer and LiNi0.5Mn1.5O4. In sharp contrast, the simple and low-cost polymer electrolyte conformal coating layer...
contributes to highly continuous surface coverage and fast Li ion transport [28–32]. These unique properties of polymer electrolyte coating will benefit for the enhanced LiNi0.5Mn1.5O4/electrolyte interface stability and capacity retention during long cycling.

In our previous study, a poly(ethyl α-cyanoacrylate) (PECA, formula as (CH2C(CN)COOC2H5)n) based composite gel electrolyte was synthesized through an in-situ polymerization approach to improve the electrochemical performance of LiMn2O4/graphite battery [33]. Owing to the strong interaction between cyano/ester groups of PECA and Li+, the dissociation of LiPF6 was increased. As a result, the PECA gel electrolyte exhibited enhanced ionic conductivity in conventional organic electrolyte. On the other hand, the strong interaction energy of Mn2+ with cyano/ester groups made the PECA based electrolyte effectively suppress transition metallic ions transfer from the cathode to the counter graphite electrode, thus benefiting for the capacity retention during cycling. Moreover, the cyano-based polymer electrolyte exhibited high stability when it was applied in high potential LiNi0.5Mn1.5O4/Li batteries [34,35].

In this paper, PECA was explored for to modify the surface of spinel LiNi0.5Mn1.5O4 particles via in-situ polymerization of ethyl α-cyanoacrylate (ECA). The conformal PECA polymer nano-coating layer could provide continuous surface coverage and lithium ion transport channel, which can guarantee the LiNi0.5Mn1.5O4/electrolyte interfacial stability and decrease the interface impedance. Moreover, the strong interaction energy of multivalent cations and PECA will suppress the dissolution of Ni and Mn ions from the host structure of LiNi0.5Mn1.5O4 and avoid their deposition on the surface of anode. Therefore, in comparison to the pristine LiNi0.5Mn1.5O4, the PECA-coated LiNi0.5Mn1.5O4 exhibited superior cycling stability.

2. Experimental

2.1. Synthesis of PECA-coated LiNi0.5Mn1.5O4

LiNi0.5Mn1.5O4 was coated by PECA via an in-situ polymerization method. Firstly, diluted 8 mg of ethyl α-cyanoacrylate with 5 mL of anhydrous acetone. Secondly, 0.2 g of LiNi0.5Mn1.5O4 commercial powder was dispersed in 30 mL of anhydrous acetone under continuous stirring and sonicated for 15 minutes. The diluted solution of ethyl α-cyanoacrylate was added dropwise to the LiNi0.5Mn1.5O4 dispersion under magnetic stirring for approximately 1 hour in air. The moisture in air initiated the polymerization of ethyl α-cyanoacrylate on the surface of LiNi0.5Mn1.5O4 particles. After sufficient polymerization reaction, the residual acetone was removed by rotary evaporation. Finally, the resulting powder of PECA-coated LiNi0.5Mn1.5O4 was dried at 80 °C. The PECA-coated LiNi0.5Mn1.5O4 was abbreviated to PECA-coated LNMO.

2.2. Samples characterization

The surface morphology and structure of the obtained materials were observed by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and high resolution transmission electron microscopy (HRTEM, JEOL) with the magnifications from 10 k to 500 k. The crystallinity of pristine LNMO and PECA-LNMO powders was verified by X-ray diffraction (XRD, ADVANCED D8) in the range of 2-theta from 10° to 80°. Transmission Fourier transform infrared spectroscopy (FTIR) spectra were carried out using EO-SXB IR spectrometer in the wave number range of 400–2000 cm⁻¹. The resolution used in FTIR was 4 cm⁻¹.

2.3. Electrochemical evaluation

The electrode was made by mixing 90 wt.% active material, 5 wt. % PVDF and 5 wt.% carbon black onto a Al current collector. All coin cells were assembled in an argon-filled glove box using Li metal as anode, Celgard 2300 as the separator, and 1.0 mol L⁻¹ LiPF6 dissolved in ethylene carbonate/dimethyl carbonate (EC:DMC = 1:1 v/v) as the electrolyte. The galvanostatic charge/discharge curves were tested on a LAND battery test system at varied C (1C = 140 mAh⁻¹) rates in the potential range of 3.5–5.0 V vs. Li/Li⁺ at 25 °C. The cyclic voltammetry (CV) curves were performed using a CHI 440A instrument (CHI Instrument Inc.) with LiNi0.5Mn1.5O4 or PECA-coated LiNi0.5Mn1.5O4 as the working electrode and lithium metal as the counter and reference electrode in the potential range of 3.5–5.0 V vs. Li/Li⁺.

3. Results and discussion

The resultant products were characterized by XRD and FTIR to identify the crystal structure and composition, respectively. Fig. 1a shows the XRD patterns of the pristine and PECA-coated LiNi0.5Mn1.5O4 powders. All patterns can be assigned to well-crystallized cubic spinel LiNi0.5Mn1.5O4 (JCPDS Card No.: 80-2162, space group: Fd-3m), in which lithium ions occupy the tetrahedral (8a) sites and the transition metal ions (Mn and Ni) statistically reside at the octahedral (16d) site. The LiNi0.5Mn1.5O4 powder coated with polymer molecule showed similar XRD patterns to that of pristine LiNi0.5Mn1.5O4, indicating the polymer layer coating process did not alter the crystal structure of the LiNi0.5Mn1.5O4 cathode [28]. The FTIR peaks (Fig. 1b) at about 1745 cm⁻¹ (vs, C=O) and 1250 cm⁻¹ (vs, C-O) could be attributed to the characteristic

![Fig. 1. (a) XRD patterns of the pristine and PECA-coated LiNi0.5Mn1.5O4 powders. (b) FTIR spectra of the pristine LiNi0.5Mn1.5O4 powder, PECA-coated LiNi0.5Mn1.5O4 powder, PECA polymer, and ECA monomer.](image-url)
absorption of PECA [36]. Compared with the FTIR spectrum of ECA monomer, the disappeared strong peak at 1618 cm$^{-1}$ (s, C=C) of PECA polymer indicated the complete polymerization reaction initiated by moisture in air. In addition, the similar characteristic absorption peaks of PECA in pure PECA polymer and PECA-coated LiNi$_{0.5}$Mn$_{1.5}$O$_4$ suggested the PECA absorbed on the surface of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ through surface hydrogen bonding. Furthermore, the peaks assigned to Mn-O (619 and 557 cm$^{-1}$) and Ni-O (588 and 496 cm$^{-1}$) showed no significant changes, demonstrating no distortion of the intrinsic lattice structure of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ after PECA coating [37].

The surface morphology of the pristine and PECA-coated LiNi$_{0.5}$Mn$_{1.5}$O$_4$ was observed by SEM and HRTEM imaging. As shown in Fig. 2a and 2b, the pristine LiNi$_{0.5}$Mn$_{1.5}$O$_4$ particles exhibited a fine particulate morphology with smooth planes and well-defined edges. The average size of the pristine particles was ~100 nm. The morphology and size of the PECA-coated LiNi$_{0.5}$Mn$_{1.5}$O$_4$ particles (Fig. 2d and 2e) were consistent with that of the pristine sample. The HRTEM images (Fig. 2c and 2f) of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and PECA-coated LiNi$_{0.5}$Mn$_{1.5}$O$_4$ showed clear lattice fringes. The interplanar spacing was about 0.484 nm, which corresponded to the (111) crystal plane of LiNi$_{0.5}$Mn$_{1.5}$O$_4$. This result was consistent with the XRD analyses and further confirmed no distortion of the intrinsic lattice structure after PECA coating. In addition, the HRTEM images also demonstrated the uniform and conformal coating of PECA layer on the surface of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ particle with a thickness of approximately 10 nm, which was more uniform and continuous compared with conventional inorganic coatings [38]. The conformal coating layer can be favorable for protecting the whole LiNi$_{0.5}$Mn$_{1.5}$O$_4$ particle from electrolyte erosion during high voltage charging. As a result, the PECA coating layer is expected to enhance the electrochemical performance of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ by providing a stable ionic conductive path and suppressing the interfacial decomposition reactions between electrolyte and electrode.

To investigate the cycling performance of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ materials, LiNi$_{0.5}$Mn$_{1.5}$O$_4$/Li half cells with 1.0 molL$^{-1}$ LiPF$_6$ EC/DMC (1:1 v/v) electrolyte without any additives were tested in the potential range of 3.5-5.0 V. The charge/discharge profiles and capacity retention were shown in Fig. 3a and 3b. The long distinct plateau at around 4.7 V was corresponded to the Ni$^{2+/4+}$ redox couple of spinel LiNi$_{0.5}$Mn$_{1.5}$O$_4$, which agreed well with the pair of
redox peaks in the cyclic voltammetry (CV) curves of LiNi0.5Mn1.5O4 (Fig. 3c). The initial Coulombic efficiency of PECA-coated LiNi0.5Mn1.5O4 was 95.4%, while that of the pristine LiNi0.5Mn1.5O4 was only 85.3%. The larger capacity loss suggested worse interface side reactions happened in LiNi0.5Mn1.5O4/Li compared with the PECA-coated LiNi0.5Mn1.5O4/Li during the first charging and discharging. Furthermore, coating has been demonstrated as an effective strategy to reduce the polarization of LiNi0.5Mn1.5O4 during cycling process, such as carbon coating reported by Yang et al. [19]. Here, for PECA-coated LiNi0.5Mn1.5O4, there was little potential separation of charging-discharging plateaus and capacity fading between the initial cycle and the 100th cycle. By comparison, the pristine LiNi0.5Mn1.5O4 exhibited larger variation in potential gap and severe capacity fading with the increasing cycling number, indicating the high polarization and poor cycle performance in LiNi0.5Mn1.5O4/Li cell. This result was consistent with CV curves of the pristine and PECA-coated LiNi0.5Mn1.5O4 after the 2nd and 100th cycles (Fig. 3c and 3d). With cycle number increasing, the potential distance of peaks between anodic and cathodic (ΔV) increased, wherein a larger ΔV represents stronger electrode polarization. In the pristine LiNi0.5Mn1.5O4/Li cell, ΔV increased from 0.20 V to 0.33 V after the 100th cycle. In sharp comparison, the augment ΔV was considerably retarded during cycling of the PECA-coated LiNi0.5Mn1.5O4/Li cell, where the corresponding ΔV varied from 0.20 V to 0.25 V. In addition, the peak area in the CV curves of LiNi0.5Mn1.5O4 decreased much more seriously than that of PECA-coated LiNi0.5Mn1.5O4. It is known that liquid electrolytes are highly prone to electrochemical oxidation on the LiNi0.5Mn1.5O4 surface at high voltage conditions, which has a detrimental influence on cycle performance. The significantly suppressed growth of ΔV as well as the retention of peak area in the PECA-coated LiNi0.5Mn1.5O4/Li cell confirmed the effectiveness of the PECA layer in preventing the formation of cathode-electrolyte interface layer, which hindered the charge transport at the LiNi0.5Mn1.5O4/electrolyte interface.

C-rate capability was also compared between the pristine and PECA-coated LiNi0.5Mn1.5O4 with the charge-discharge current densities from 0.2C to 5.0C shown in Fig. 4a and 4b. Both electrodes exhibited the similar capacity from 0.2C to 5.0C. The capacity of PECA-coated LiNi0.5Mn1.5O4 reached 70 mAh g⁻¹, which was slightly higher than that of the pristine LiNi0.5Mn1.5O4. In our previous report [33], PECA was developed as gel polymer electrolyte, which exhibited high ionic conductivity of 0.33 mS cm⁻¹. This high ionic conductivity allowed for the fast ionic transport through the layer during high rate charging and discharging. The kinetic behavior of the cell based on pristine LiNi0.5Mn1.5O4 and PECA-coated LiNi0.5Mn1.5O4 was also investigated by CV techniques (Fig. 4c and 4d). The value of the apparent D₀ for PECA-coated LiNi0.5Mn1.5O4 was calculated to be 1.27 × 10⁻¹¹ cm² s⁻¹ according to the square root relationship between the peak current and the scan rate, as explained in previous report [39]. The value was the same order of magnitudes compared with that of the pristine LiNi0.5Mn1.5O4 (1.37 × 10⁻¹¹ cm² s⁻¹). This result demonstrates that the PECA coating layer did not hamper the
fast Li$^+$ insertion/extraction between LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and electrolyte during the cycling.

To further explain how the PECA coating layer ameliorates the cycling performance and restrains polarization of LiNi$_{0.5}$Mn$_{1.5}$O$_4$, the morphology changes of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ electrodes after cycling were characterized. Fig. 5 showed the typical SEM images of the PECA-coated and uncoated LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode electrodes after 100 charging and discharging cycles. For the uncoated LiNi$_{0.5}$Mn$_{1.5}$O$_4$, there were some cracks on the surface of active material particles, which could be explained by the well-known instability between naked LiNi$_{0.5}$Mn$_{1.5}$O$_4$ particles and organic electrolytes, as shown in Fig. 6. Though the cracks increased the contact area with the electrolyte and could have a beneficial effect on the Li$^+$ ions transfer between active materials and electrolyte, their destructions on the electron conduction between active materials was much severe to battery performance. These cracks destroyed the electronic contact among LiNi$_{0.5}$Mn$_{1.5}$O$_4$ particles and led to active LiNi$_{0.5}$Mn$_{1.5}$O$_4$ loss, which resulted in increasing interface impedance and capacity fading during battery cycling. Therefore, these cracks in LiNi$_{0.5}$Mn$_{1.5}$O$_4$ particles seem to be an incentive to bring about serious polarization and poor cycling performance. On the contrary, the PECA-coated LiNi$_{0.5}$Mn$_{1.5}$O$_4$ particles after 100 cycles showed a smooth surface similar to that prior to battery cycling, meaning that the influence of interface side reaction on the surface integrity was negligible. This unique property should be unambiguously ascribed to the protection of the conformal and highly continuous surface coverage by PECA nano-coating layer, which effectively suppressed the unexpected

![Fig. 4. Rate performance of the (a) pristine and (b) PECA-coated LiNi$_{0.5}$Mn$_{1.5}$O$_4$/Li cells. CV curves of the (c) pristine and (d) PECA-coated LiNi$_{0.5}$Mn$_{1.5}$O$_4$/Li cells at a series of sweep rates. Insets are the corresponding relationship between the peak current and the square root of sweep rate.](image)

![Fig. 5. Typical SEM images of the (a) pristine and (b) PECA-coated LiNi$_{0.5}$Mn$_{1.5}$O$_4$ electrodes after 100 cycles.](image)
side reaction between LiNi_{0.5}Mn_{1.5}O_{4} particles and organic electrolytes. As a result, the particle integrity was maintained during cycling consequently enhanced capacity retention in PECA-coated LiNi_{0.5}Mn_{1.5}O_{4}/Li cell.

4. Conclusions

The conformal nano-coating of PECA polymer electrolyte with the thickness of about 10 nm was explored to modify the high voltage interface stability of spinel LiNi_{0.5}Mn_{1.5}O_{4} particles via in-situ polymerization of ethyl α-cyanoacrylate. The PECA coating layer with continuous coverage can provide facile ion transport and effectively suppress the unexpected side reaction at the interface between LiNi_{0.5}Mn_{1.5}O_{4} and electrolyte. Therefore, in comparison to the pristine LiNi_{0.5}Mn_{1.5}O_{4}, the PECA-coated LiNi_{0.5}Mn_{1.5}O_{4} showed remarkably decreased polarization and improved cycling performance. This work will shed light on the interface modification of LiNi_{0.5}Mn_{1.5}O_{4} by reasonable application of high voltage polymer electrolyte materials in conventional LIBs.

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