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Investigations on high energy lithium-ion batteries with aqueous binder

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ABSTRACT

An aqueous binder, fluorine acrylic hybrid latex (TRD 202A), is utilized as the binder to fabricate a cathode electrode using a lithium manganese rich composite (LMR-NMC) as the active material. The derived Li/LMR-NMC half cells have advantages of more than 240 mAh/g specific capacity and low impedance of less than 50 Ω cm^2. Differential Scanning Calorimeter (DSC) results indicate that the electrode with aqueous binder shows improved thermal stability compared with polyvinylidene difluoride (PVDF). Furthermore, the cathode electrode with aqueous binder is tested against the graphite electrodes with another aqueous binder, Styrene-Butadiene Rubber (SBR). The evaluation results of graphite/LMR-NMC full cells show that full cells with aqueous binders in both anodes and cathodes inherit almost all advantages of Li/LMR-NMC half cells, except the long cycle life.

1. Introduction

Binder is not an essential component but it plays a critical role in determining properties of electrodes applied in lithium-ion batteries [1] including mechanical [2] and electrochemical performances [3]. Among tremendous binders currently developed in lithium-ion battery technologies, poly(vinylidene fluoride) (PVDF) is the most popular binder that has been widely adopted in both the anode and cathode, due to its good electrochemical stability, high adhesion to electrode materials, and current collectors [4,5]. However, the utilization of PVDF as a binder preliminarily requires it to be dissolved in an organic solvent, such as N-methy-2-pyrrolidone (NMP), to fabricate appropriate slurries for electrodes. The employment of organic solvent generally brings out concerns involving the safety, environmental issues and cost [6,7]. Therefore, the exploration of polymers with low cost and environmental benignity as alternative binders in the electrodes' fabrication process is of practical significance to the development and application of battery technologies.

These concerns could be effectively alleviated as aqueous binders are utilized in the manufacturing process of electrodes. Currently, Styrene-Butadiene Rubber (SBR), together with the utilization of sodium carboxymethyl cellulose (CMC) [2,8–10], is becoming a well-adopted binder for graphite anode that provides great adhesion strength between electrode materials and the Cu substrate [9]. Compared to PVDF, a less amount of SBR is needed for the anode. The reduced amount of binder used in the electrodes affords batteries with potential advantages including more flexibility, higher capacity, and longer cycling life [3,11,12]. However, there are only quite a few research activities, which aim to find out the suitable aqueous binders for fabricating positive electrodes. For instance, the application of aqueous binders, including the gelatin binder, SBR-CMC mixture, polyacrylic acid (PAA), and water-soluble elastomer binder (WSB), has been investigated [13–17]. None of them has been widely applied and none aqueous binder can be used for all the different types of cathode materials because of their different morphologies, chemistries, and physical properties.

In this work, an aqueous binder, fluorine acrylic hybrid latex (TRD 202A, JSR), will be used in the lithium- and manganese-rich transition metal oxide cathode- (LMR-NMC) based positive electrode, which has been considered as the next generation high-energy cathode material for lithium-ion batteries due to its high capacity (>200 mAh/g) [5,18–22], low cost, and better thermal stability [23]. The effect of this aqueous binder on the electrochemical behaviors of the cathode will be investigated. Meanwhile, another aqueous binder, SBR, will be used in graphite-based electrodes. The electrochemical performances of graphite against lithium-manganese rich composite full cells with aqueous binders will be demonstrated.

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2. Experimental

2.1. Electrodes' fabrication

LMR-NMC electrode preparation includes CMC solution preparation, slurry making and casting, and drying. At first, a 1.5 wt.% solution of sodium carboxymethyl cellulose (CMC, MAC350, Nippon Paper chemicals) was prepared by dissolving CMC powders in deionized (DI) water. The active materials, lithium- and manganese-rich composite $0.49Li_2MnO_3 \cdot 0.51LiNi_{0.37}Mn_{0.39}Co_{0.24}Mn_{0.39}O_2$ (Toda HE5050, hereafter referred to as LMR-NMC), and carbon black were added into the CMC solution with continuous stirring to get solid particles well dispersed in the slurry. The TRD 202A water emulsion was added into the well-mixed slurry with stirring. The ultimately obtained slurry was casted onto Al foil. Then, the electrode was dried at 75 °C for 30 min, followed by being dried at 120 °C for another 30 min. The detailed procedure for making LMR-NMC cathode electrodes was provided by the aqueous binder provider – the JSR Corp. [24]. LMR-NMC electrodes with various TRD 202A were prepared. The final solid electrodes are composed of 2 wt.% CMC, 5 wt.% carbon black, 1–4 wt.% TRD 202A, and 92–89 wt.% active materials. The same procedure was used to prepare graphite-based electrodes except for replacing the TRD 202A with Styrene-Butadiene Rubber (SBR, TRD 2001, JSR). The composition of the finally solid electrodes was 98 wt.% graphite (CGP-A12, Phillips 66), 1 wt.% CMC, and 1 wt.% SBR. All electrodes were cut into disks of 1.6 cm^2, and then were assembled in 2032-type coin cells with lithium metal (referred to as half cell) or graphite (referred to as full cell) as negative electrodes.

For the sake of comparison, same graphite based anode with PVDF binder (composing of 89.8 wt.% active material, 4 wt.% carbon, 0.2 wt.% oxalic acid, and 6 wt.% PVDF binder), and same LMR-NMC based cathode with PVDF binder (composing 86 wt.% active material, 6 wt.% carbon, and 8 wt.% PVDF binder), were coated onto Cu and Al foil respectively. Both electrodes were cut into disks of 1.6 cm^2, and then were assembled into full cells. The electrolyte solution containing 1.2 mol/L $LiPF_6$ in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3/7 by weight) was used in all cells.

2.2. Characterizations

2.2.1. Electrochemical characterizations

Galvanostatic cycling tests of the Li/LMR-NMC electrode half-cells and graphite/LMR-NMC full cells were conducted on a Maccor series 4000 at a constant current of 0.1 C (0.25 mA) at 30 °C for 3 initial formation cycles before further electrochemical investigations. The voltage window applied to Li/LMR-NMC half cells was 2–4.6 V (vs. Li/Li^+), while 2–4.55 V for graphite/LMR-NMC full cells.

After 3 formation cycles, hybrid pulse power characterizations (HPPC)[25] were conducted, in which a 10 s 3 C discharge pulse and a 2 C regenerative charge pulse current were applied to the cells, respectively. There were 40 s rest between discharge and regen pulses. The pulse profile were conducted every 10% depth of discharge (DOD). The area specific impedance (ASI), as a function of the % of DOD, was established through calculating the voltage changes during pulses. Following the HPPC tests, the rate capability of cells was tested by varying the discharging current in the range of 0.2–2 C with a constant charging current of 0.3 C. At every rate, cells went through 3 cycles.

Finally, the cells were cycled with the following pattern: 1 cycle with low current charge at discharge (0.1 C); then, a constant charge/discharge current of 0.3 C (0.5 C for cells with PVDF as binders) was applied to the cells for 8 cycles; at last, the HPPC test was conducted using the same conditions as described previously. This pattern was repeated 5 times to complete total 50 cycle test of cells.

Electrochemical impedance spectroscopy (EIS) was collected using a frequency response analyzer (Solartron, model 1400) with a potential amplitude of 5 mV over the frequency range of 100 kHz–20 mHz. Before collecting EIS, all cells were charged to 4.0 V.

2.2.2. Differential scanning calorimetry

After 3 formation cycles, several Li/LMR-NMC half cells were fully charged to 4.6 V (vs. Li/Li^+) and disassembled in a glove box. The LMR-NMC electrodes were dried and then active materials were scratched from the substrate (Al foil). Differential scanning calorimetry (DSC) experiments were conducted on the fully lithiated LMR-NMC electrodes using a Perkin-Elmer Pyrius 1 instrument. Typically, 4 mg of LMR-NMC-based electrodes and 3 μL of electrolyte were mechanically sealed inside the stainless-steel high-pressure capsules to prevent leakage of the pressurized solvents and exposure of active materials to oxygen. The DSC data were collected between 50 °C and 400 °C at a heating rate of 10 °C/min with nitrogen purging. An empty stainless-steel capsule was used as a reference pan. To ensure reproducibility, at least three measurements were conducted for each data point.

2.2.3. Morphologies

After the cycle test, several cycled full cells were discharged to 2.0 V and opened in the glove box. The cycled electrodes were carefully rinsed by pure dimethyl carbonate (DMC). The morphology of electrodes was observed by scanning electron microscopy (SEM, Hitachi S-4700) with an accelerating voltage of 10 kV.

3. Results and discussion

The electrodes were visually inspected before cell fabrication. No cracks or delamination were observed on the surfaces and edges of all cut disks even as the percentage of TRD 202A in the electrodes was as low as 1 wt.%. During the formation, all lithium half cells presented the same voltage profiles, irrespective of the amount of TRD 202A used. Representatively, the performances of the cell with 4 wt.% TRD 202A are demonstrated in Fig. 1. As expected, the plateau-like feature at ~4.5 V (vs. Li/Li^+) could be observed on the initial charge curve and, it is replaced by slopes during the following discharge and charge cycles (Fig. 1a). Correspondingly, one sharp peak from the differential capacity plot (Fig. 1b) could be found at the voltage of ~4.5 V (vs. Li/Li^+) during the initial charge process and, two weak redox couples at ~3.7 V (vs. Li/Li^+) and 3.3 V (vs. Li/Li^+) during the following cycles. The identical electrochemical performance of the LMR-NMC electrode was observed, compared to the same electrode using PVDF as the binder[26]. This implies that, within the experimental operating potential range of 2–4.6 V (vs. Li/Li^+), TRD 202A possesses outstanding electrochemical stability. In addition, the calculated specific capacity delivered by the electrode with 4 wt.% TRD 202A is ~244 mAh/g, which is almost equal to that delivered by electrodes with 8% PVDF as a binder. Within the experimental range, the calculated specific capacity delivered by electrodes with different amount of TRD 202A varied within a narrow range of 236–244 mAh/g, which might result from the minor error of calculating the weight of active materials. Therefore, compared with PVDF binders, a less amount of TRD 202A enables the LMR-NMC electrodes with comparable energy without imparting the mechanical properties of electrodes. For the sake of clarification, the electrode with 4 wt.% TRD 202A is selected as a representative to demonstrate properties of electrodes with the TRD 202A binder.

Fig. 2 shows the cell's ASI changes as a function of the % DOD derived from the HPPC test on the Li/LMR-NMC cell. From Fig. 2, it is found that the ASI is below 50 Ω cm^2 and relatively stable when