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The Contradiction Between the Half-Cell and Full-Battery Evaluations on the Tungsten-Coating $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ Cathode

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ABSTRACT

A one-step synthesis method is developed to prepare the $Li[Ni_{0.5}Co_{0.2}Mn_{0.3}]O_2$ (NCM 523) cathode with uniform tungsten-coating layer for lithium-ion battery. Such modified material shows similar properties with the bare NCM 523 in terms of the primary particles, secondary structure, and specific capacity. With W coating layer, the NCM 523 gives remarkable improvement in the long-term capacity retention in the half-cell testing, which is sharply inconsistent with the result from the full-battery tests, indicating a contradiction between the half-cell and full-battery tests in some case. After further investigations, such conflict between the half-cell and full-cell tests in evaluating the W-coating strategy is attributed to the dissolution of Li_2WO_4 layer in the electrolyte, which probably destroys the solid electrolyte interface (SEI) on the graphite anode and irreversibly consumes the active lithium ions for renovating SEI in full-cell testing. These results will benefit researchers in the area of lithium-ion batteries to fully understand the differences between the half-cell and full-cell testing, and develop the effective strategies for cathode modifications.

1. Introduction

Fossil fuel crisis and global warming prompt the increasing demand and development of clean and sustainable energy [1]. The rechargeable lithium-ion batteries (LIBs) have been considered as one of the most promising alternatives to meet such challenges [2–4]. Since Dahn's and Ohzuku's groups first reported the structure and electrochemical performance of the mixed transition metal oxides $Li[Ni_xMn_xCo_{1-2x}]O_2$ with either $x \approx 1/3$ or $x = 1/3$, [5,6] the $Li[Ni_xMn_yCo_{1-x-y}]O_2$ (NCM, $0 < x < 1$; $0 < y < 1$) cathodes for advanced lithium-ion batteries have attracted intensive concerns over the past one and a half decades. Compared to the commercial $LiCoO_2$, less amount of Co element in NCMs provides these materials a reduced raw material cost and improved safety [7], also making them more promising in the power source applications, especially for electrical vehicles (EVs). Recently, the representative NCM material, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrode has been successfully industrialized and commercialized in Li-ion batteries for both EVs and grid energy storage systems, and the $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ is facing the same opportunity of growing market demand.

Although the increase of Ni content in $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ undisputedly rises the practical capacity compared to $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, the cycle and safety performances are both whittled down [8,9]. The $Li[Ni_xCo_yMn_{1-x-y}]O_2$ materials, as we know, are a complex system, whose capacity degradation mechanism during cycling is still controversial and needs further understanding [10,11]. The key fade reasons for these materials are generally ascribed to be the organic electrolyte decomposition induced by the active transition metals, structural evolution at highly charged state, along with the transition-metal dissolution [12,10,11,13]. In the case of such a complex fade mechanisms, the coating [14,13] and doping approaches [15–18] have been widely performed, in order to optimize the cycleability. For stabilizing the solid electrolyte interface (SEI), improving the electrochemical reaction resistance, as well as suppressing transition-metal dissolution, various attempts about surface coatings techniques [19–21] have been applied, and have realized remarkable progresses in improving their cycleability [22,23]. Yet, such improvements achieved from the half-cell testing system are more or less flimsy, because the active lithium in the half-cell using lithium foil as anode is infinite, dissimilar from the practical

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applications using the graphite anode. Therefore, in some special case, some incomplete results from half cell testing may be possibly achieved, misleading us.

In this study, we develop a one-step method to synthesize the W-coating NCM 523 secondary particles with uniform Li_2WO_4-coating layer. Interestingly, it is found that, compared to the bare NCM 523, the W-coating NCM 523 show remarkable improvement in the capacity retention in half cells, but suffered more dramatic capacity decline in full cells. Such inconsistent phenomenon between the half-cell and full-battery tests is analyzed and discussed in this paper, and the reasons are thought to be attributed to the side reaction with organic electrolyte and the dissolution of Li_2WO_4 layer, which consumes the active lithium ions on the graphite anode during the cycling process. This research obtaining indicates that the half cell testing method may have some boundedness, and can't consistently reveal the practical situations in practical Li-ion electrodes.

2. Experimental

2.1. Cathode Preparation

The precursor of $(Ni_{0.5}Co_{0.2}Mn_{0.3})OH_2$ was purchased from Bump company. The Li_2CO_3 (99.75%) was obtained from Alfa-Aesar. The W precursor ($(NH_4)_6H_2W_{12}O_{40}$) was bought from Aladdin. All precursors were directly used without further treatment. Before preparing the W-coating NCM 523, the $(Ni_{0.5}Co_{0.2}Mn_{0.3})OH_2$, Li_2CO_3 and W precursor (7000 ppm W-element) with the metal/Li ratio of 1:1.06 were well mixed in a 3-dimensional mixing machine for about 6 hours. After that, the high-temperature solid reaction was carried out in air at 930 °C for 10 h and cooled down to room temperature naturally. The W-element in the final product is about 6800 ppm. For comparison, the mixture without W precursor was prepared and heated following the same processes for W-coating NCM 523 sample. After the reaction, the samples were well milled in the mortar and sieved through a 300 mesh opening stainless steel sieve for following electrochemical testing and characterizations.

2.2. Cathode Characterization

The XRD patterns of these powder samples were collected with from the Bruker D8 Advance equipped with a Cu target X-ray tube and a diffracted beam monochromator. The morphology and element distribution were analyzed using a scanning electron microscope (SEM, Hitachi S-4800) equipped with an energy dispersive spectrometer (EDS, Horiba, EX-250). The X-ray photoelectron spectroscopy (XPS) data of W-coating NCM 523 was collected from an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al Kα radiation (225 W, 15 mA, 15 kV). Binding energies (BE) were corrected using C 1s hydrocarbon peak at 284.80 eV.

2.3. Electrochemical Performance

Coin cells (2032) were used for testing the electrochemical performance of the bare NCM 523 and W-coating NCM 523. Before the positive electrodes preparation, the slurry containing the NCM 523, carbon black, and PVDF with the weight ratio of 90:5:5 was stirred overnight in appropriate amount of NMP. After the thorough mix process, the slurry was coated on the cleaned Al foil and dried overnight in an vacuum oven at 120 °C. The as-prepared electrode was cut into small circle ones (0.95 cm^2) with the mass loading of the active material about 10 mg. In the half cell, the lithium metal foil was used as the counter electrode, Celgard 2400 microporous film as the separator and 1 M $LiPF_6$ in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:2,v/v) as the electrolyte. The cells were assembled in the argon-filled glovebox.

For assembling the full cells (Fig. S1), the graphite (FSN-1) was served as the anode, which was loaded on the cleaned Cu foil from the aqueous slurry containing graphite (FSN-1, 91.5%), binder (LA-132, 7.5%), and Super P carbon black (1%). The capacity ratio of

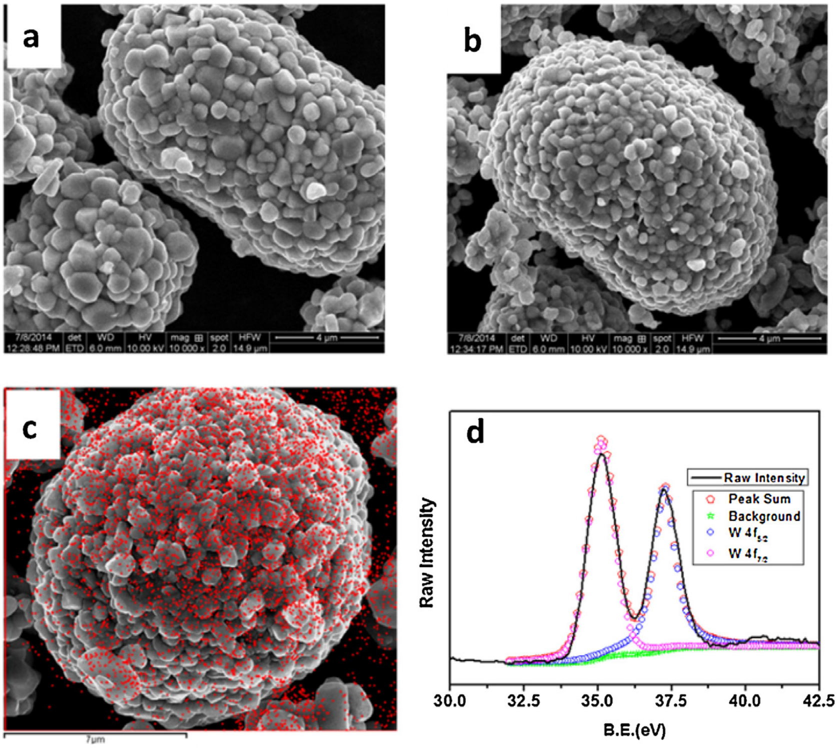

Fig. 1. (a) SEM images of the bare NCM523 and (b) W-coating NCM 523, (c) W-element mapping image and (d) XPS spectra of the W-coating NCM 523.