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Improved electrochemical performance of $LiMn_2O_4$ surface-modified by a Mn^{4+}-rich phase for rechargeable lithium-ion batteries

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ABSTRACT

The surface of spinel $LiMn_2O_4$ is modified with different quantities of a Mn^{4+}-rich phase prepared by a facile sol-gel method to improve electrochemical properties at elevated temperatures. Impurity-free and uniform morphologies for the $LiMn_2O_4$ particles are demonstrated from the X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The Mn^{4+}-rich phase modified on the surface of the $LiMn_2O_4$ alleviates the dissolution of manganese in the electrolyte, thus improving the cycling performance and rate capability relative to the bare $LiMn_2O_4$. 1 wt.%-modified $LiMn_2O_4$ delivers a capacity retention of 92.7% and a discharge capacity of 113.5 mAh g^{-1} after 200 cycles at 1C and 25 °C, compared with that of 83.1%, and 100.8 mAh g^{-1} for the bare $LiMn_2O_4$. In addition, after 100 cycles, a capacity retention of 88.6% at 1C is achieved for 1 wt.%-modified $LiMn_2O_4$ at 55 °C, which is higher than the 76.0% for the bare $LiMn_2O_4$. Furthermore, this sample shows the best rate capability among all samples. The Mn^{4+}-rich phase is an appropriate candidate for modifying surfaces to suppress dissolution of manganese, thereby improving the electrochemical properties of $LiMn_2O_4$.

1. Introduction

Lithium manganese oxide, $LiMn_2O_4$, having a spinel structure is an attractive cathode material for rechargeable Li-ion batteries because of its low cost, environmental friendliness, natural abundance, and good safety compared with commercialized $LiCoO_2$ [1–3]. $LiMn_2O_4$ cathode materials undergo severe capacity fading during repeated cycling, particularly at elevated temperatures, which restricts its commercial usage for rechargeable Li-ion batteries [4]. Capacity fading in the 4-V (versus Li/Li^+) region is connected with the following factors: structural instability induced by the Jahn-Teller distortion and manganese dissolution via the Mn^{3+} disproportion reaction ($2Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+}$). The latter is caused by a trace of hydrofluoric acid present in the electrolyte, which is the most important cause of capacity fading [5–8].

Two mainstream strategies have been proposed by academic and industrial scientists to overcome the capacity fading issue. First, cationic doping of a small fraction at the manganese sites has been investigated to stabilize the spinel structure. Single-doping of Ni^{2+} [9], Al^{3+} [10], Cr^{3+} [11], Sm^{3+} [12], Ru^{4+} [13] has been reported. Co-doping with Ni-Cu [14], Cr-Fe [15], Mg-Si [16], and La-Bi [17] has also been carried out. The results have shown that these doped $LiMn_2O_4$ spinel materials display enhanced stabilization of their structure and improved cycling performance compared with non-doped $LiMn_2O_4$ materials. However, this doping method could not eliminate the irreversible capacity loss associated with the dissolution of manganese at the cathode/electrolyte interface, especially at elevated temperatures [18].

The second approach is surface modification, which can minimize direct contact between the cathode and electrolyte interfaces, thereby effectively suppressing the dissolution of manganese [7,19]. Recently, Huang et al. confirmed that the presence of Mn^{4+} on the surface of Mn-surface-modified $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, synthesized by an in situ oxidizing-coating method, could suppress capacity fading during charge-discharge cycles at room and elevated temperatures [20]. Jeong et al. pointed out that the average Mn oxidation of ~3.69 on the surface of $Li_{1.15}Co_{0.32}Mn_{1.53}O_4$-coated $LiMn_2O_4$ resulted in superior rate capability and improved capacity retention at 60 °C [21]. Kang et al. showed that Mn^{4+} in a MnO_2 coating layer could not only effectively suppress Mn dissolution, but also provide chemical

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stability, thereby improving storage and rate capability for MnO_2-coated $LiMn_2O_4$ [22]. Therefore, the presence of Mn^{4+} on the surface of $LiMn_2O_4$ particles can considerably lessen the dissolution of Mn, and maintain the stability of $LiMn_2O_4$, resulting in enhanced electrochemical performance. The Mn^{4+}-rich phase in this work is embodied in the form of Li_2MnO_3, which is based on the several factors. Monoclinic Li_2MnO_3, with its layered structure, acts as an indispensible component of the Li-rich layered $xLi_2MnO_3{\cdot}(1\text{-}x)LiMO_2$ (M = Mn, Ni, Co) cathode material because of its stabilization function [23,24]. The Li_2MnO_3 cathode material, where interslab octahedral sites are occupied by Li only, and the octahedral sites within the slabs are occupied by both Li and Mn in a ratio of 1:2 [25], supplies more mobile Li ions compared with others without Li ions in the structure. These mobile Li ions accessibly transport and permeate through the interslab channel into the electrolyte solution [26,27]. In addition, Li_2MnO_3 cathode material consisting of only Mn^{4+} shows a more stable structure resulting from the absence of the disproportion reaction of Mn^{3+} that occurs in $LiMn_2O_4$. Nanosized Li_2MnO_3 as the modification layer becomes active compared with its inactive status existing in micro-sized particles [28]. Xiong et al. [27] reported that Li_2MnO_3 as an impurity appeared in Li/F co-doped spinel $LiMn_2O_4$-based composites prepared by a solid state reaction, which Li_2MnO_3-impurity was detected at the surface of the composites in TEM images. These complicated composites exhibited excellent cycling performance and high rate capability, which results from eliminating the Jahn-Teller distortion by double-doping with Li and F, and suppressing the disproportion reaction of Mn^{3+} on the surface caused by the coated Li_2MnO_3 impurity. Given this, Mn^{4+}-rich phase is employed to modify the surface of $LiMn_2O_4$ particles to improve the electrochemical performance by decreasing the direct contact area at the cathode/electrolyte interface, thereby reducing the dissolution of manganese and stabilizing the structure.

In this work, a series of Mn^{4+}-rich phase-modified $LiMn_2O_4$ with weight ratios of 0 wt.%, 1 wt.%, 2 wt.%, and 4 wt.% were synthesized by a facile sol-gel method to ensure uniformity of the modified layers. The electrochemical properties at both 25 °C and 55 °C were investigated in detail.

2. Experimental

2.1. Preparation and characterization of Mn^{4+}-rich phase-modified $LiMn_2O_4$

$LiMn_2O_4$ powders were prepared by solution combustion synthesis (SCS) in combination with calcination [17,29,30]. Lithium nitrate ($LiNO_3$, 99.0%, Kishida Chemical Co., Ltd., Japan), lithium acetate (CH_3COOLi, 99.0%, Kishida Chemical Co., Ltd., Japan), manganese nitrate ($Mn(NO_3)_2$, 50% w/w aqueous solution, Alfa Aesar), and urea (NH_2CONH_2, 99.0%, Chameleon Reagent, Japan) were used as the raw materials without further purification. The oxidizers, $LiNO_3$ and $Mn(NO_3)_2$ (mole ratio of Li:Mn = 1.05:2), and reductant, NH_2CONH_2 (with $\phi = 0.5$, ϕ is the ratio of the total valence of reductants to the total valence of nitrate oxidizers), were dissolved in 5 ml of distilled water. After evaporating the water, the homogenous sol-gels were self-ignited in a homemade combustion apparatus. Following the SCS, the collected powders were further calcined at 800 °C at a rate of 5 °C/min in air for 24 h to obtain the $LiMn_2O_4$ powders.

A facile sol-gel method was employed to achieve the modification of a Mn^{4+}-rich phase. Stoichiometric amounts of CH_3COOLi and $Mn(NO_3)_2$, required to produce Li_2MnO_3, were homogenously dissolved in distilled water with stirring at room temperature. This solution was then added dropwise to a well-dispersed $LiMn_2O_4$ aqueous solution that had been subjected to ultrasonic treatment. After evaporating the water, the resulting powders were sintered at 600 °C for 3 h in air to obtain the final powders. The weight percent of Li_2MnO_3 to $LiMn_2O_4$ were 0 wt.%, 1 wt.%, 2 wt.%, and 4 wt.%. For simplicity, these samples are labeled as 0 wt.%, 1 wt.%, 2 wt.%, and 4 wt.%, respectively.

The phase structure of Mn^{4+}-rich phase-modified $LiMn_2O_4$ was characterized by powder XRD (Cu Kα, Rigaku Miniflex). The morphology and size of the powders were determined using SEM (JEOL, JSM-7001FA), and TEM (JEOL JEM-2010F). The surface composition of the samples was detected by X-ray photoelectron spectroscopy (XPS, JEOL Ltd., JPS-9200) using an Mg Kα X-ray source (1253.6 eV).

2.2. Cell assembly and electrochemical measurements

A Swagelock-type cell consisting of a working electrode and a lithium metal anode, was assembled in an Ar-filled glove box, as described in our previous reports [29,30]. The working electrode consisted of 80 wt.% active material, 10 wt.% binder (PVDF) dissolved in N-methyl-2-pyrrolidone (NMP), and 10 wt.% conductive carbon (acetylene black). The diameter of the working electrode was 10 mm and its thickness was 0.1 mm. A lithium metal disk was chosen as the counter and reference electrode. The electrolyte was a solution of 1 M lithium hexafluorophosphate ($LiPF_6$) in EC/DMC (1:1 in volume). The separator was a Celgard polypropylene membrane. Electrochemical measurements were galvanostatically carried out in the voltage range of 3.2–4.4 V at different current densities (a rate of 1C corresponding to a full charge/discharge of 150 mAh g^{-1} in 1 h) at 25 °C and 55 °C using a battery tester (Arbin Instruments, MSTAT4, USA). Cyclic voltammetry (CV) was performed by a potentiostat/galvanostat apparatus (Autolab, PGSTAT128N) in the voltage range of 3.2–4.4 V at a scan rate of 0.1 mV·s^{-1}, while the electrochemical impedance spectroscopy (EIS) was conducted by employing an Autolab instrument with the frequency response analyzer (FRA), in the frequency range from 1000 kHz to 0.01 Hz after the 5 cycles of CV measurement scanning at 0.3 mV·s^{-1}

3. Results and discussion

Fig. 1 shows XRD patterns of Mn^{4+}-rich phase-modified $LiMn_2O_4$ samples. All the diffraction peaks are consistent with the characteristic diffraction peaks of well-defined spinel $LiMn_2O_4$ with a space group of *Fd*3*m*. The absence of an impurity phase is noticed in the XRD patterns for all modified $LiMn_2O_4$ samples. This

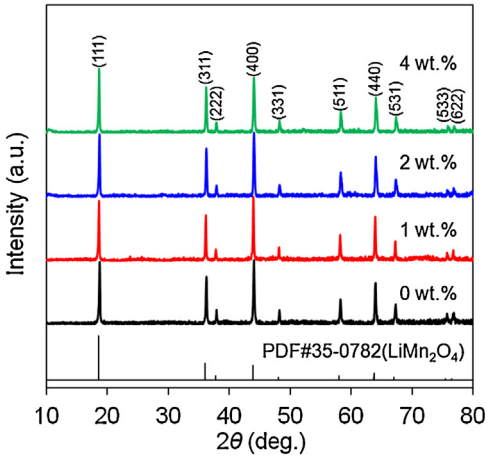

Fig. 1. XRD patterns of Mn^{4+}-rich phase-modified $LiMn_2O_4$ samples.