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Spinel-$Li_{3.5\,+\,x}Ti_5O_{12}$ coated $LiMn_2O_4$ with high surface Mn valence for an enhanced cycling performance at high temperature

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ABSTRACT

$Li_{3.5\,+\,x}Ti_5O_{12}$ and $Li_4Ti_5O_{12}$ layers coated $LiMn_2O_4$ were prepared via sol–gel route, with subsequent annealing at 750 °C. XRD studies showed coating did not change the structure of $LiMn_2O_4$. TEM studies showed coating layers were formed around $LiMn_2O_4$ particles, both corresponding spinel LiTiO phase. XPS studies showed the valence of surface Mn for the $Li_{3.5}Ti_5O_{12}$-coated-$LiMn_2O_4$ increased after annealing. This sample also demonstrated a favorable cycling performance.

1. Introduction

At the origin of capacity fading mechanism in $LiMn_2O_4$ cathodes is the well-established Jahn–Teller effect of high spin Mn^{3+} [1]. As a result, during the (de)lithiation process, the average valence of Mn atoms, particularly at the surface, would be easily reduced to less than +3.5, due to the accumulation of Li^+ [2], thus causing local structural damage leading to unfavorable cycling performance. Therefore, a higher oxidation state of surface Mn would be crucial to maintain the stability for the $LiMn_2O_4$. Another approach that has been explored is surface coating by using oxides, e.g. ZrO_2, SiO_2, and Al_2O_3 via a sol–gel method as previously reported [3,4]. $Li_4Ti_5O_{12}$ is a potentially competitive coating candidate, as it possesses a higher chemical diffusion coefficient (10^{-6} cm^2 s^{-1}) than that of $LiMn_2O_4$ (10^{-10}–10^{-12} cm^2 s^{-1}), and shares the same spinel structure making it structurally compatible with the targeting $LiMn_2O_4$. $Li_4Ti_5O_{12}$ is a zero-strain material during the insertion/extraction of lithium ions. $Li_4Ti_5O_{12}$ also has a high thermodynamic stability [5]. And therefore, the successful combination of abovementioned two advantages would greatly improve the cycling ability of $LiMn_2O_4$. However, no report on producing spinel LiTiO coated $LiMn_2O_4$ with high surface Mn valence was found.

Herein we report a novel in-situ strategy to prepare a spinel LiTiO coated $LiMn_2O_4$, where Mn atoms at the surface possess a higher formal oxidation state than +3.5. To realize this, we used a Li deficient spinel $Li_{3.5}Ti_5O_{12}$ (rather than $Li_4Ti_5O_{12}$) to coat the $LiMn_2O_4$. With an appropriate annealing treatment (which is also a necessary step to form LiTiO coating), Li^+ ions at surface of $LiMn_2O_4$ may diffuse from Li saturated region (of $LiMn_2O_4$) into the relatively Li unsaturated region of $Li_{3.5}Ti_5O_{12}$. Such Li diffusion would not likely occur for the Li saturated $Li_4Ti_5O_{12}$ coated $LiMn_2O_4$. As a result, the oxidation state of Mn at the surface of the spinel manganese is increased due to the departure of Li ions. Using this strategy, we could obtain a spinel LiTiO coated $LiMn_2O_4$ with higher oxidation state for the surface Mn atoms, and both factors contributed greatly to the improved high temperature cycling performance.

2. Experiment section

2.1. Sample preparation

$LiMn_2O_4$ powder was synthesized via the solid-state reaction of MnO_2 and Li_2CO_3 [6]. To coat $LiMn_2O_4$ with $Li_4Ti_5O_{12}$ and $Li_{3.5}Ti_5O_{12}$, $LiCH_3COOLi\cdot 2H_2O$ and $Ti(C_4H_9O)_4$ with a stoichiometric cationic ratio (e.g. 4:5 and 3.5:5) were dissolved in a solution contained ethanol and distilled water to form a clear solution. Then citric acid was added into the solution with stirring to obtain a sol. Then the as-prepared $LiMn_2O_4$ was homogeneously dispersed into coordinated solution. After hydrolyzing for 5 h, the resulting precipitate was filtered, washed several times with distilled water and dried at 120 °C for 2 h. Finally, the powder product was annealed in nitrogen at 750 °C for 5 h. For comparison, pristine $LiMn_2O_4$ was also heated at 750 °C for 5 h, and sample obtained is denoted as SA-1. The $Li_4Ti_5O_{12}$ coated sample is denoted as SA-2 and $Li_{3.5}Ti_5O_{12}$ coated sample is denoted as SA-3.

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2.2. Characterization

The phase compositions of the samples were identified by powder X-ray diffraction (XRD, PANalytical, X'Pert Pro) using Cu Kα radiation (λ = 1.5408 Å). The microstructure and morphology of products were investigated by scanning electronic microscopy (SEM, Hitachi S-4700) and transmission electronic microscopy (TEM, Tecnai G2 F30 S-Twin). X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD) was employed to probe the surface for Mn and Ti species and to determine their oxidation states. Energy-dispersive X-ray spectroscopy (EDS) was used in conjunction with TEM to determine the elemental composition of products from both area and point scans.

2.3. Electrochemical testing

The as-prepared materials were evaluated in a CR2032-type coin cell assembled in an argon filled glove box. The active materials, acetylene black and polyvinylidene fluoride (PVDF) were ground in 1-methyl-2-pyrrolidinone (NMP) solution in a weight ratio of 80:12:8 to form slurry, which was then casted onto an aluminum foil current collector and dried at 120 °C for 10 h under vacuum. The thickness of electrode composite is ca. 60 μm. The separator is Celgard 2400. Li metal as the counter electrode and an electrolyte of 1 mol L^{-1} $LiPF_6$ in a solvent mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethylmethyl carbonate (EMC) (1:1:1, v/v/v) were used. Galvanostatic charge–discharge tests were performed over a voltage range of 3.3–4.3 V (vs. Li/Li^+) with a Land CT2001A battery test system at 55 °C. Electrochemical impedance spectroscopy (EIS) was recorded with a Solartron Impedance/gain phase analyzer (model SI 1260) coupled to a potentiostat (SI 1287) over a frequency range from 10^{-2} Hz to 10^5 Hz at the open circuit voltage at room temperature.

3. Results and discussion

HRTEM studies of the prepared samples revealed that layers with a thickness of ca. 3 nm were coated onto the bare surface of $LiMn_2O_4$ (Fig. 1A). For both coated samples, the bulk $LiMn_2O_4$ material component shows good crystallinity with lattice fringes extending to the grain boundary. For instance, the distances between the neighboring lattice fringes are approximately 0.4767 nm and 0.2505 nm which correspond to the d-spacings for the (111) and (311) planes respectively in the Li–Mn–O spinel phase. EDX results for SA-2 and 3 from selected areas indicate that the Ti to Mn ratio is about 2:98. The coated layer in SA-3 exhibits lattice fringes with spacings of 0.251 nm and 0.212 nm, corresponding well to the d-spacings for the (311) and (400) planes respectively for a LiTiO spinel phase (Fig. 1A).

All of the diffraction peaks corresponded to a spinel structure (space group Fd-3m (no. 227)) and in good agreement with ICSD PDF card no. 35-0782. No LiTiO phase was detected indicating that there is no structural change of surface-modified $LiMn_2O_4$. As shown in the inset of Fig. 1B, the $LiMn_2O_4$ spinel phase diffraction peaks exhibit a discernible shift to lower 2θ following the annealing process at 750 °C, indicating the increase in the cubic lattice parameter. Rietveld refinement using the Reflex module of Materials Studio found the sample SA-3 is with the largest *a* value of 8.2653(3) Å. Indeed, Xia et al. found that the lattice

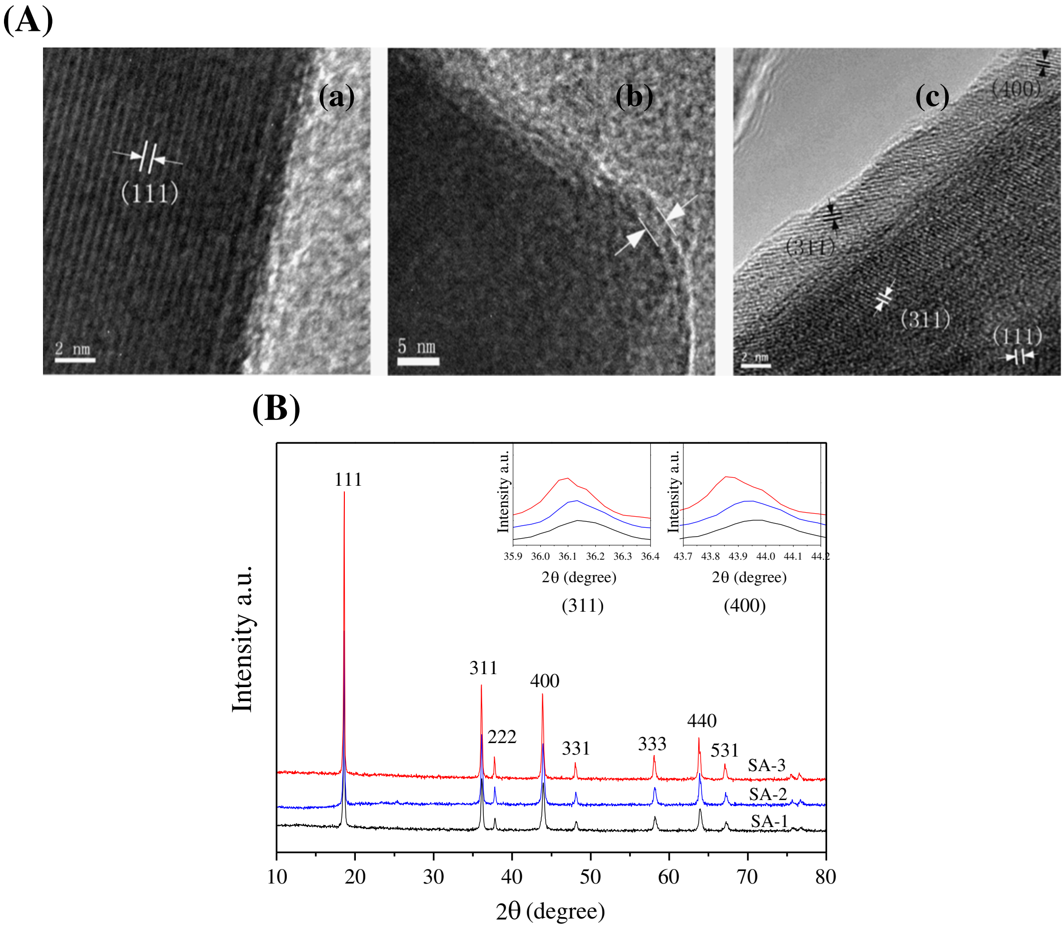

Fig. 1. (A) HRTEM images of (a) SA-1, (b) SA-2 and (c) SA-3. (B) Powder XRD patterns of the pristine (SA-1) and coated (SA-2, SA-3) $LiMn_2O_4$ samples.