Spinel-structured surface layers for facile Li ion transport and improved chemical stability of lithium manganese oxide spinel

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ABSTRACT

Li-ion conducting spinel-structured oxide layer with a manganese oxidation state close to being tetravalent was prepared on aluminum-doped lithium manganese oxide spinel for improving the electrochemical performances at the elevated temperatures. This nanoscale surface layer provides a good ionic conduction path for lithium ion transport to the core and also serves as an excellent chemical barrier for protecting the high-capacity core material from manganese dissolution into the electrolyte. In this work, a simple wet process was employed to prepare thin $LiAlMnO_4$ and $LiMg_{0.5}Mn_{1.5}O_4$ layers on the surface of $LiAl_{0.1}Mn_{1.9}O_4$. X-ray absorption studies revealed an oxidation state close to tetravalent manganese on the surface layer of coated materials. Materials with these surface coating layers exhibited excellent capacity retentions superior to the bare material, without undermining the lithium ion transport characteristics and the high rate performances.

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1. Introduction

Spinel-type lithium manganese oxide ($LiMn_2O_4$) is a promising cathode material for Li-ion batteries in emerging commercial markets such as the power sources for electric vehicles (EV) and large-scale energy storage systems (ESS), which require high cost-competitiveness and reliable high-power performance at elevated temperatures [1–3]. This material has a normal spinel structure, $[Li]_T[Mn_2]_O O_4$ based on a cubic space group symmetry, *Fd-3m* (No. 227), where lithium occupies one eighth of total tetrahedral sites (8a) and manganese occupies half of the octahedral holes (16d) available on the face-centered cubic-closed packed arrays of oxygen (32e). Insertion and extraction of Li^+ ions from this material can be accomplished via three-dimensionally-interconnected 1×3 channels, which facilitates a fast Li^+ ion diffusion and results in good electrochemical performances at the high current rates. Recently, these properties related to high-rate performances were further improved through downsizing the material to nano-scale or realizing three-dimensional architectures [4–7]. However, $LiMn_2O_4$ spinel structure experiences inherent structural instability during the charge-discharge process due to the formation of Jahn-Teller cation, Mn^{3+}, which has a high-spin $d^4 (= t_{2g}{}^3 e_g{}^1)$ electronic configuration [8]. Furthermore, the electrochemical cycling of $LiMn_2O_4$ in the elevated temperature, i.e. ~50–60 °C, induces a significant manganese dissolution into the electrolyte system [9–11]. The chemical instability of Jahn-Teller cation promotes the disproportionation reaction, $2Mn^{3+}(s) \rightarrow Mn^{4+}(s) + Mn^{2+}$, to occur with trace amounts of hydrofluoric acid (HF) in the $LiPF_6$-containing electrolytes acting as the catalyst [9–12]. This not only leads to the structural degradation of the cathode material, but also induces a significant impedance growth on the electrode/electrolyte interface (SEI), leading to capacity fading of the cells in long-term cycling [9–12]. For the last decade, numerous sophisticated measures have been employed to tackle this problem. One of the most popular and effective approaches aimed at replacing a fraction of manganese ions in the octahedral sites by low-valent metal cations such as Li^+, Mg^{2+}, Ni^{2+}, Zn^{2+}, Co^{3+}, and Al^{3+} for increasing the average oxidation state of manganese over +3.5, simultaneously providing a surface coating with the corrosion-resistant metal oxides, e.g., Al_2O_3 and MgO [13–17]. However, due to heavy doping and increased average manganese oxidation state, practical discharge capacity of the material obtained using this approach was limited to approximately 100 mAh/g, which is only around 70% of its original theoretical capacity (148 mAh/g). Manufacturing of core/shell composite materials with corrosion-resistant layered oxide as the outer shell has also

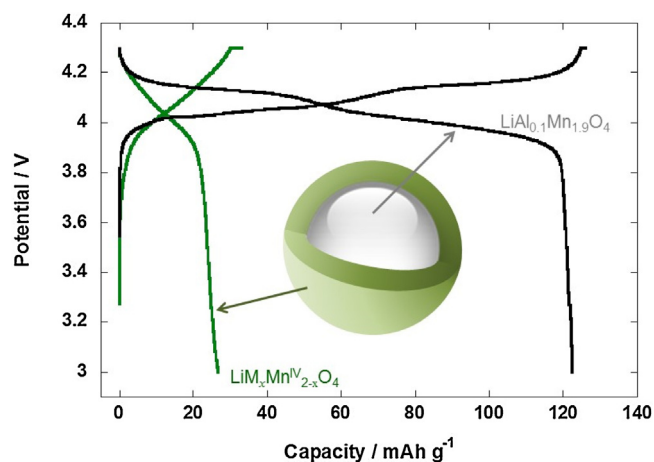**Fig. 1.** Schematic diagram of the coated lithium manganese oxide spinel consisting of $LiAl_{0.1}Mn_{1.9}O_4$ core and $LiM_xMn^{IV}_{2-x}O_4$ coating layer with their electrochemical characteristics.

been found to be an effective approach [18–20]. Oxygen arrays in the layered oxides with α-NaFeO$_2$ structure and spinel oxides share a common cubic closed packed arrangement that can be epitaxially connected at the interface smoothly, although the connectivity of Li$^+$ ion diffusion channels between these two structures was not precisely evaluated. Carbon-coating was also applied on the bulk surface for reducing the manganese dissolution rate at elevated temperatures as well as to improve the electrical conductivity [21].

In this work, we prepared a thin spinel-structured oxide layer ($LiM_xMn^{IV}_{2-x}O_4$) that can act as both an ionic conduction path for the Li$^+$ ion transport and a chemical barrier to protect the core from the attack of in-situ generated corrosive species such as HF from the electrolyte as described in Fig. 1. The outer coating layer is designed to have a chemically stable tetravalent manganese oxide in order to protect the core that delivers a high reversible capacity. The conventional material with a spinel core and a layered oxide shell has a similar anion array that can be coherently connected at the interface; however, the diffusion channels for Li$^+$ ion and the axis of lattice expansion/contraction between the core and the shell could be different, which might cause the development of a non-negligible stress at the interface during cycling. In our material, the thin coating layer barely contributes to the total capacity, but it acts only as a window for Li$^+$ ion to be transported to the core material and a chemical barrier to protect the bulk core from the corrosive species.

2. Material and methods

2.1. Materials synthesis

To synthesize the core material with a composition of $Li[Al_{0.1}Mn_{1.8}]O_4$, stoichiometric amounts of lithium carbonate (Li_2CO_3), aluminum hydroxide ($Al(OH)_3$), and manganese oxide (Mn_3O_4) were ball-milled using a Pulverisette mill (300 rpm, 2 h). The mixture was then heat-treated at 800 °C for 12 h and was further annealed at 600 °C for 6 h in air to react with oxygen. For preparing $LiAlMnO_4$-coated $Li[Al_{0.1}Mn_{1.8}]O_4$ spinel oxide, ethanolic solution containing appropriate amounts of lithium acetate ($LiCH_3COO\cdot2H_2O$), aluminum nitrate ($Al(NO_3)_3\cdot9H_2O$) (or magnesium acetate ($Mg(CH_3COO)_2\cdot4H_2O$) in the case of $LiMg_{0.5}Mn_{1.5}O_4$ coating), and manganese acetate ($Mn(CH_3COO)_2\cdot4H_2O$) was prepared and the core material was added and soaked for 12 h in a sealed container. The slurry obtained was then dried in an evaporating dish at room temperature. After drying, the powder was

collected and heat-treated in a furnace at 600 °C for 6 h, resulting in the formation of $LiAlMnO_4$-coated spinel oxide.

2.2. Materials characterization

Crystallographic structure of the sample was investigated by powder X-ray diffraction (XRD) using Cu-Kα radiation ($\lambda = 1.5405$ Å, Rigaku D/MAX-2500/PC) and the XRD patterns were refined using the GSAS program to calculate lattice parameters. Morphological features were examined using field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4200) and high-resolution transmission electron microscopy (HR-TEM, FEI Tecnai G2 operating at 200 keV). The samples for FE-SEM were sputter-coated with platinum prior to the measurements. X-ray absorption spectra (XAS) were collected in transmission mode at 10D (Mn K-edge) and 1D (Mn L$_{II,III}$-edge) beamlines at the Pohang Accelerator Laboratory. Mn K-edge was recorded from 6340 to 7510 eV with a step size of 0.5 eV. Mn L$_{II,III}$ −edge spectra were measured from 630 to 665 eV and 520 to 580 eV with a step size of 0.1 eV.

2.3. Electrochemical measurements

A slurry containing a homogeneous mixture of lithium manganese oxide powder, a conductive agent (super P), and polyvinylidene difluoride (PVdF) binder in the ratio of 87:8:5 in N-methyl-2-pyrrolidone was prepared using a commercial mixer. The slurry was cast on aluminum foil with a loading of active material around ∼7–8 mg/cm^2. Electrochemical behavior of the LiMn$_2$O$_4$ electrodes was measured with 2032 coin cells using an electrolyte composed of 1.15 M lithium hexafluorophosphate (LiPF$_6$) dissolved in 1:1 (v/v) co-solvent solution of dimethyl carbonate (DEC) and ethylene carbonate (EC). Electrochemical cycling was carried out in a temperature-controlled oven (25 °C or 60 °C) in the voltage range of 3.0–4.3 V at a rate of C/10 for the initial cycle and C/1 for the subsequent cycles (1C = 148 mA g^{-1} of active material). For the galvanostatic intermittent titration technique (GITT) measurements, rectangular current pulses were repeatedly applied to the cell until the first charge-discharge process was completed. The current pulse was applied for 10 min at a rate of 0.1C and the cell was then to relax for 1 h so that the voltage profile reaches equilibrium. Chemical diffusion coefficient of Li$^+$ ions passing through the cathode material was calculated based on the following equation [22,23].

$$D_{Li^+} \approx \frac{4}{\pi\tau}\left(\frac{mV_M}{MS}\right)^2\left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2 \tag{1}$$

,where m and M are the mass (g) and the molecular weight (g mol^{-1}) of the active material, respectively. V_M is the molar volume (cm^3 mol^{-1}) of LiMn$_2$O$_4$ and S is the effective surface area (cm^2) between the active material and the electrolyte. Surface areas of bare, LiAlMnO$_4$-coated, and LiMg$_{0.5}$Mn$_{1.5}$O$_4$-coated materials are measured to be 3.84, 4.56, and 3.87 m^2 g^{-1}, respectively using the Brunauer-Emmett-Teller surface area (S$_{BET}$) method. ΔE_s and ΔE_τ are the voltage changes measured during the resting period and the current pulse, respectively. Electrochemical impedance of the cells was measured at the fully discharged state using Biologic VMP3 in the frequency range of 10^6–10^{-2} Hz with a perturbation voltage of 7.1 mV at room temperature.

3. Results and discussion

3.1. Strategic design of surface layer chemistry

In this work, we strategically designed the chemical composition of the spinel-structured surface layer, $LiM_xMn_{2-x}O_4$, such that the manganese atoms in the coating layer maintains an oxidation