Contents lists available at ScienceDirect

Electrochimica Acta

Scalable synthesis and electrochemical investigations of fluorine-doped lithium manganese spinel oxide

Hae Ri Lee [a,b], Boeun Lee [a], Kyung Yoon Chung [a], Byung Won Cho [a], Kwan-Young Lee [b], Si Hyoung Oh [a,*]

[a] Center for Energy Convergence Research, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Korea
[b] Department of Chemical and Biological Engineering, Korea University, 145, Anam-ro, Seongbuk-gu, Seoul 136-701, Korea

ARTICLE INFO

ABSTRACT

A scalable synthesis route for the preparation of fluorine-doped lithium manganese spinel was developed. The effect of 2.5% fluorine doping on the properties of aluminum-doped lithium manganese spinel was investigated by examining the electrochemical performance and structural changes. The electrochemical study indicates that the initial discharge capacity increases by about 5% while other properties, like the capacity retention and rate performance, remain almost unchanged. The structural studies indicate that no impurity phase was formed, along with only little morphological changes and a slight increase in the lattice parameter. The Mn K-edge absorption spectra clearly show that the average manganese oxidation state decreases as a result of fluorine doping and Mn $L_{II,III}$ -edge spectra indicate that the electronic structure of the fluorine-doped spinel changes significantly, which may alleviate the intrinsic structural instability of this material.

1. Introduction

For decades, lithium manganese spinel oxide ($LiMn_2O_4$) has been considered as a promising cathode material for medium and large-scale energy-storage systems needed for applications, such as hybrid electric vehicles and load leveling, due to its good electrochemical performance at a high current rate, high safety, and low material cost in spite of its relatively low theoretical capacity of 148 mAh/g [1–3]. Manganese is one of the most abundant elements of the Earth's crust, second only to iron among common heavy metals, and it is environmentally benign [4]. $LiMn_2O_4$ has the normal spinel structure with cubic space group *Fd-3m* and, during electrochemical cycling, lithium ions are located at the **8a** tetrahedral site inside of cubic closed-packed arrays of oxygen ions at the **32e** site, diffuse quickly through cross-linked 1×3 channels made of edge-sharing MnO_6 octahedra, thereby resulting in a good electrochemical performance at high current rate. However, this material shows a significant capacity fading during long-term electrochemical cycling, particularly at elevated temperatures ($\sim 60\,^\circ$C), mainly because of the enhanced manganese dissolution into the electrolyte caused by chemical and structural instabilities [5–7].

It is well known that the highly oxidizing conditions at the final stage of the charging process trigger the decomposition of some electrolyte systems containing $LiPF_6$ and, thereby, producing HF which in turn attacks and corrodes the cathodic surface in the presence of traces of water [5–7]. This series of processes results in protonated λ-MnO_2 where the proton is strongly bound to oxygen near Mn vacancies at the **16d** site, causing a significant discharge-capacity fading [6–8]. The kinetics of these processes can be strongly accelerated by increasing the temperature along with micro-stresses/strains developed by repeated volume changes (at a level of about 8%) during electrochemical cycling [9,10]. The inherent oxygen deficient character of lithium manganese spinel oxide synthesized above 800 °C also generates a large number of oxygen vacancies which contribute to the structural disorder [11–13]. In addition, the unstable Jahn-Teller ion Mn^{3+} is produced during the discharge process which may disproportionate into Mn^{2+} and Mn^{4+} ($2Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+}$), whereby Mn^{2+} can be dissolved into the electrolyte [14].

Many studies have been carried out during the last decade to find out effective measures to mitigate the problems mentioned above, including the simple reduction of the surface area to minimize the dissolution rate of manganese at elevated temperatures. One of the most popular and effective methods is doping of one or more of non-Jahn-Teller cations with a lower valence than Mn^{4+}, such as Li^+, Mg^{2+}, Al^{3+}, Ni^{2+}, Co^{3+}, and Cr^{3+} into the **16d** octahedral site of

manganese [15–17]. The principal effect of adding one or more of these dopants is the increase of the average oxidation state of manganese which improves the structural and chemical stability during cycling. The increase in the average manganese oxidation state reduces the fraction of unstable Mn^{3+} Jahn-Teller cations, and leads to smaller volume changes during cycling, although these favorable changes are accompanied by a decrease in the discharge capacity. For example, lithium-rich lithium manganese oxide $Li_{1.1}Mn_{1.9}O_4$ with the initial capacity of 103 mAh/g was reported to show a superb performance without significant degradation up to 80 cycles at elevated temperature (55 °C), where the average oxidation state of manganese is assumed to be +3.63. This implies that maintaining a high average oxidation state of manganese during cycling is one of the most important factors in achieving a good cyclic stability [18]. The approach of employing core-shell structures in which the outer region of the particle consists of chemically more stable materials was also developed to minimize the capacity decrease originating from doping of low-valent cations while maintaining the structural and chemical stability of the outer region where manganese dissolution into the electrolyte can occur [19]. Another interesting approach is to alter the anion chemistry slightly (such as by fluorine doping into the **32e** oxygen site) and, thereby, to break down the local octahedral symmetry of MnO_6, which can bring about stability to the spinel structure by reducing the Jahn-Teller effect and by the formation of a stable solid-electrolyte interface (SEI) film at the surface [20–22]. Previous reports indicate that fluorine can be doped into the spinel structure up to a level of 5% [22]. The additional fluorine doping of some metal-doped lithium manganese oxides leads to an excellent capacity retention at increased discharge capacity compared to the parent material without fluorine doping [22]. It is also well known that the fluorinated surface of metal oxides and SEI layers formed on lithium manganese spinel oxide is chemically more resistant against acidic corrosion by HF due to the strong chemical bond between fluorine and metal cation or oxygen [23,24]. In addition, the fluorine substitution can increase the discharge capacity by lowering the average oxidation state of manganese. In this work, we developed a simple and scalable method to prepare fluorine-doped lithium manganese spinel oxide and investigated the structural and electrochemical changes due to fluorine doping.

2. Materials and methods

Materials Synthesis: To prepare $Li[Li_{0.05}Al_{0.10}Mn_{1.85}]O_4$, a stoichiometric amount of lithium carbonate (Li_2CO_3), aluminum hydroxide ($Al(OH)_3$), and manganese oxide (Mn_3O_4) was ball-milled using a Pulverisette mill (300 rpm, 2 h). The mixture was then subjected to a heat-treatment at 800 °C for 12 h and a further treatment at 600 °C for 6 h in air. To perform fluorine doping, 1 g of NH_4F was uniformly mixed with 50 g of aluminum-doped lithium manganese oxide and put in a Teflon container with a hermetically sealed cap. The container was stored at 200 °C in an oven for 6 h. Afterwards, the mixture was transferred to a ceramic boat and heat treated at 500 °C for 6 h in air.

Materials Characterization: The crystallographic structure was investigated by powder X-ray diffraction (XRD) using Cu-$K_{\alpha 1}$ radiation (λ = 1.5405 Å, Rigaku D/MAX-2500/PC) and the GSAS program was used to refine the patterns. Morphological features were observed by field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4200). The samples for FE-SEM were sputter-coated with platinum before the measurements. X-ray absorption spectra (XAS) were collected in transmission mode on the beamlines 10D (for the Mn K-edge) and 1D (for the Mn $L_{II,III}$-edge and O K-edge) at the Pohang Accelerator Laboratory. The Mn K-edge was recorded from 6340 to 7510 eV in interval steps of 0.5 eV. The Mn $L_{II,III}$-edge and O

K-edge spectra were measured from 630 to 665 eV and from 520 to 580 eV in steps of 0.1 eV, respectively. Extended X-ray absorption fine structure (EXAFS) spectra from the Mn K-edge were analyzed by commercial software with the theoretical spectra being calculated using the FEFF6 code. To extract the EXAFS contribution from single-atom absorption spectra, the Lengeler-Eisenberger method was utilized within the frame of a polynomial approximation and cubic spline smoothing of the atomic background. Low ($R < 1$ Å) and high ($R > 7.8$ Å) frequency noise was removed by Fourier-back Fourier transform of the k-weighted EXAFS spectra with a Bessel-Kaiser window.

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 manufactured using a commercial mixer. The slurry was cast on aluminum foil with a loading of around 8 mg/cm^2 of active material. The electrochemical behavior of the $LiMn_2O_4$ electrodes was observed with 2032 coin cells using an electrolyte composed of 1.1 M lithium hexafluorophosphate ($LiPF_6$) dissolved in the 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 range of 3.0–4.3 V at a rate of C/10 for the initial cycle and, thereafter, at C/1 (1 C = 148 mA g^{-1} of active material). The electrochemical impedance spectroscopy was carried out for the cycled electrodes with the frequency ranging from 10^5 to 10^{-2} Hz using coin cells at open circuit potential. The half cells containing lithium manganese oxide cathode were cycled for 50 cycles at 60 °C and were cooled to room temperature before measurement.

3. Results and discussion

The synthesis process for the preparation of fluorine-doped (F-doped) lithium manganese spinel oxide is described in Fig. 1. Aluminum-doped (Al-doped) lithium manganese spinel oxide with excess Li according to a nominal composition of $Li[Li_{0.03}Al_{0.1}Mn_{0.87}]O_2$, which has a discharge capacity of 104 mAh/g, was utilized as parent material for the fluorine doping. This material was mixed with the cost-effective fluorine source NH_4F by using mortar and pestle and, subsequently, was subjected to a gentle heat treatment at 200 °C. At this temperature, NH_4F is decomposed into hydrogen fluoride and ammonia gas ($NH_4F \rightarrow NH_3 + HF$). The hydrogen-fluoride gas moves freely and reacts at the surface of lithium manganese oxide, resulting in a thick fluorine-doped surface layer. During an additional heat treatment at 500 °C for 6 h, fluorine of these thick fluorine-rich surface layers diffuses into the interior of the grains to form F-doped shells or an overall F-doped material. Since the fluorination of the surface is carried out by hydrogen fluoride gas originating from NH_4F that is initially present in form of a homogenous mixture, the overall process is simple and can be easily applied to commercial metal-doped lithium manganese spinel oxide to produce fluorine-doped material on a large scale. In this work, the typical fluorine content in Al-doped lithium manganese oxide is fixed to about 2.5% since the previous work showed that excessive fluorination is often detrimental to the electrochemical performance. Also fluorination of undoped spinel generally involves the formation of impurity phase such as Mn_5O_8 which lead to poor electrochemical properties [20–22].

Fig. 2 shows XRD patterns and FE-SEM images of undoped $LiMn_2O_4$, Al-doped $(Li[Li_{0.01}Al_{0.1}Mn_{1.89}]O_4)$, and (Al, F)-doped $(Li[Li_{0.01}Al_{0.1}Mn_{1.89}]O_{3.9}F_{0.1})$. $LiMn_2O_4$ has the normal spinel structure in which oxygen ions build up a cubic closed-packed array, Li ions occupy 1/8 of the total tetrahedral sites, and Mn ions occupy