Journal of Power Sources 299 (2015) 231–240

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Contribution of the oxygen extracted from overlithiated layered oxides at high potential to the formation of the interphase

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HIGHLIGHTS

- Quantitative ^{7}Li and ^{19}F NMR allow describing the interphase of Li-rich materials.
- Extracted oxygen leads to exacerbated parasitic reactions with the electrolyte.
- Oxygen extraction at high potential strongly influence the interphase composition.
- Accumulation of fluorophosphates at the positive surface along cycling.

ARTICLE INFO

Article history:
Received 1 June 2015
Received in revised form
31 July 2015
Accepted 3 August 2015
Available online xxx

Keywords:
Li-ion battery
Surface
NMR
LiF
Parasitic reactions

ABSTRACT

Li-rich $(1-x)LiMO_2.xLi_2MnO_3$ layered oxides materials have been proposed recently as an attractive alternative to $LiCoO_2$ Their electrochemical performance is greatly improved by charging above the 4.5–4.6 V voltage plateau during the first oxidation. The associated reaction mechanism has been assigned to a transformation from layered to spinel, accompanied a partial oxygen removal process from the surface. Nevertheless, many questions are still unanswered concerning the influence of oxygen extraction and reaction on the chemical composition and evolution of the electrode/electrolyte interphase. Quantitative ^{7}Li, ^{19}F and ^{31}P MAS NMR shows that the partial oxygen extraction at the surface of the electrode material above 4.5 V has a strong influence on the composition/nature of the interphase and exacerbates reactions at the electrode/electrolyte interface. Oxygen reacts as soon as it is extracted from the structure of the positive electrode material to form fluorophosphates in much higher amount in the case of the overlithiated material compared to the stoichiometric material exposed to comparable potentials. The presented study indicates that the release of oxygen from the Li-rich layered oxides greatly influences the electrode/electrolyte interphasial chemistry.

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1. Introduction

Li-ion batteries suffer from parasitic reactions occurring at the electrode-electrolyte interface [1]. These reactions mainly concern the degradation of the lithium salt [2] and the solvents [3] from the electrolyte. They are responsible for the loss of electrons or lithium ions, leading to electrode capacity slippage [4,5], but also for the deposition of chemical products at the surface of active material grains, leading to increase in interphasial resistance [6]. It is then worth examining the link between the battery performance degradation, i.e. its capacity loss, and the surface chemistry, Li-rich $(1-x)LiMO_2.xLi_2MnO_3$ layered oxides materials have been proposed recently as an attractive alternative to $LiCoO_2$ [7–11]. Although this family of materials exhibits a very high specific capacity above 250mAh/g, their poor rate capability, their high irreversible capacity as well as the progressive voltage fading [12,13] upon cycling prevent their commercial application. The electrochemical performance of Li-rich layered oxides is greatly improved by charging above the 4.5–4.6 V voltage plateau during the first oxidation. The associated reaction mechanism has been extensively studied, by many groups [14–21] and has been assigned, at room temperature, to a change in the crystal structure close to the surface of the particles, from layered to spinel, accompanied by densification of the material [19] due to the reorganization and migration of transition metals (mostly manganese [20,22]) towards the core of the particles. This densification is also accompanied by a partial oxygen removal process [18,23] from the surface while oxygen is oxidized

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http://dx.doi.org/10.1016/j.jpowsour.2015.08.006
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within the bulk and participates to the redox process during the charge [19]. Previous HRTEM studies report the formation of cracks and nanosize domains after the initial charge, the former being ascribed to oxygen loss [24,25]. Oxygen gas is considered to be formed first as observed from mass spectrometry [18,23]. However, in other studies [24] no oxygen was observed by *ex situ* mass spectrometry measurements on the gases evolved from the battery, the oxygen presumably reacting with the electrolyte. Indeed, oxygen has been found to play a role in the formation of oxygen containing species upon reduction, such as lithium carbonate, accumulating on the electrode surface [21]. Nevertheless, many questions are still unanswered concerning the influence of oxygen extraction and reaction on the chemical composition and evolution of the electrode/electrolyte interphase.

Within this scope, our study of $LiNi_{1/2}Mn_{1/2}O_2$ electrode/electrolyte interphase [26–28] has been extended to overlithiated layered oxides, and the composition $Li[Li_{0.2}Ni_{0.4}Mn_{0.4}]O_2$, was selected owing to its position in the $LiNiO_2$–$LiMnO_2$–$LiMn_2O_3$ ternary system making it the Li-richest compound for which the lithium and oxygen extraction during the initial high potential plateau would theoretically result in the composition of $LiNi_{1/2}Mn_{1/2}O_2$. The differences between the Li-rich and stoichiometric materials, in terms of interphase chemistry and electrochemical performance, therefore would only lie in the initial particular charge process involving lithium and surface oxygen removal. The present paper aims at monitoring the evolution of interphase species, using multinuclear quantitative ^{7}Li, ^{19}F and ^{31}P MAS NMR as already developed in Refs. [28–30]. Studies are performed on $Li_{1.2}Ni_{0.4}Mn_{0.4}O_2$ and $LiNi_{0.5}Mn_{0.5}O_2$ in order to understand the formation and evolution of the active material/$LiPF_6$–based electrolyte interphase. In a first step, NMR and EELS are combined to study the simple immersion of two different Li-rich materials obtained by different synthesis routes as well as the stoichiometric $LiNi_{0.5}Mn_{0.5}O_2$, in order to analyse the influence of the initial oxidation state of Ni on the composition of the electrode/electrolyte interphase. The first electrochemical cycles are then investigated using different cycling protocols to understand the influence of the partial oxygen extraction upon the first oxidation on the interphase chemical composition.

2. Experimental methods

A combustion synthetic route is used here to obtain both stoichiometric and Li-rich materials [31]. This sol gel synthesis uses lithium, manganese and nickel nitrate precursors ($LiNO_3$, $Mn(NO_3)_2$, $4H_2O$ and $Ni(NO_3)_2$, $6H_2O$) in aqueous solution. The gel obtained at 80 °C through the addition of glycine (NH_2CH_2COOH) is then placed at 180 °C to fire the organic precursor, leaving the active precursors well dispersed and finely divided. Finally, the annealing of $LiNi_{0.5}Mn_{0.5}O_2$ is carried out at 850 °C for 7h under pure O_2 atmosphere in a dedicated tubular quartz oven transferable to the glovebox. This material will be refered to as LMN-st in the manuscript. In the case of the Li-rich material, a similar protocol was followed except that the annealing of $Li_{1.2}Ni_{0.4}Mn_{0.4}O_2$ was carried out at 900 °C for 62 h under air and ends with a quenching by liquid nitrogen. This lithium rich material will be refered to as LMN-Lir in the manuscript. The composition of both stoichiometric and overlithiated was estimated from XRD Rietveld refinement. A second Li-rich material was synthesized using the hydrothermal method developed by Cho et al. [32]. The first step consisted in the synthesis of $K_{0.32}MnO_2$ Birnessite: fumaric acid is added an aqueous solution containing of $KMnO_4$. The obtained brown gel is then annealed at 400 °C for 6 h and then at 700 °C for 12 h. The resultant dark black powder ($K_{0.32}MnO_2$ Birnessite) was washed with water three times and vacuum dried at 200 °C overnight. The second step consisted in the synthesis of $Ni_{0.45}Mn_{0.55}O_2$: $K_{0.32}MnO_2$ is mixed with $NiCl_2 \cdot 6H_2O$ with a weight ratio of 5:1 in distilled water and stirred for 5 days before being washed with water. The final step consisted in mixing $LiOH \cdot H_2O$ and $Ni_{0.45}Mn_{0.55}O_2$ with a 4:1 weight ratio. The mixture is then transferred to an autoclave where it was maintained at 200 °C for 24 h. The powders were rinsed with water and dried under vacuum at 120 °C. XRD Rietveld refinements (see next section) lead to a $Li_{1.16}Mn_{0.45}Ni_{0.29}O_2$, indicating a lower content of Ni in the material and the effective overlithiation. This material will referred to as LMN-LirH (Li-rich, Hydrothermal method) in the following.

XRD data were collected with a $\theta/2\theta$ BRUKER D5000 diffractometer ($\lambda_{CuK\alpha}$) equipped with a linear MOXTEK detector, using a scan step of 0.01° (2θ) for 10 s. The crystallite size has been obtained from the refinement of the XRD patterns using the TOPAS software with the method of the fundamental parameters profile fitting [33]. The crystallite size and microstrain contributions are correlated. In our case, considering the globally isotropic shape the grains, from microscopy imaging it was fixed to 0.1 (+/− 0.01).

Electrochemical studies were performed on a Biologic MPG2 using Swagelok-type cells. Electrodes were constituted of 80 wt% of active material, 10 wt% of ketjenblack and 10 wt% carboxymethylcellulose (CMC). Loadings of ~5 mg cm^{-2} were used for all experiments. $LiPF_6$ in EC/DMC (1:1) electrolyte and Li foil negative electrode were used. Cells were cycled between 2 and 4.5 V at C/20 regime or under potentiodynamic conditions (5 mV/h). *N,N*-diethylamino trimethylsilane was added to standard electrolyte up to 1 wt%.

MAS-NMR measurements were acquired on a BrukerAvance 500 spectrometer (B = 11.8 T, Larmor frequency of ^{7}Li, ^{19}F and ^{31}P are 194 MHz, 470 MHz and 202 MHz, respectively). The electrode was scraped off from the collector, then filled into a cylindrical 2.5 mm diameter zirconia rotor (sample preparation was made in argon filled glove-box). ^{7}Li NMR was performed at a spinning rate of 25 kHz with a single pulse sequence, a pre-scan delay of 50 ms and a recycle time of 60 s and for a spectral width of 2 MHz; ^{19}F NMR was performed at a spinning rate of 23.5 kHz with a Hahn echo sequence, a pre-scan delay of 5 ms and a recycle time of 60 s and for a spectral width of 0.5 MHz; these acquisition conditions were adapted from Dupré et al. [28], in order to detect surface species. The absolute quantification of detected species was performed using i) numerical fit and integration of each set of peaks corresponding to a chemical compound, ii) calibration of this integral using various LiF–electrode mixtures.

TEM-EELS analyses were performed with GATAN Digipeels 766 spectrometer attached to a JEOL 2010F microscope, operated at 200 kV. Samples were cooled down at liquid nitrogen temperature to avoid beam damages. Spectra were recorded in diffraction mode (image coupling) with a 2.0 eV energy resolution (given by the zero loss peak (ZLP) full width at half-maximum) with a dispersion of 0.5 eV/channel. Convergence and acceptance angles were, respectively, 7 and 14 mrad. All recordings were dark count and gain corrected and then processed using standard tools provided for quantification in Digital Micrograph. Samples were probed using TEM in order to ensure the representative character of the particles chosen for EELS analysis.

3. Results and discussion

3.1. Characterisation of pristine materials

The XRD pattern of pristine LMN-st is displayed in Fig. 1, and shows a perfect matching with the $R\overline{3}m$ space group characteristic of the AMO_2 layered oxides (A = Li, Na and M = Fe, Mn, Co, Ni). The lattice parameters deduced from Rietveld refinement, as well as

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