



Manganese dissolution in lithium-ion positive electrode materials



M. Saulnier^a, A. Auclair^a, G. Liang^b, S.B. Schougaard^{a,*}

^a Université du Québec à Montréal, Case postale 8888, Succ. Centre-ville, Montréal, Québec H3C 3P8, Canada

^b Johnson Matthey Battery Materials Ltd., 280 Ave. Liberté, Candiac, Québec J5R 6X1, Canada

ARTICLE INFO

Article history:

Received 8 March 2016

Received in revised form 30 May 2016

Accepted 11 June 2016

Available online xxxx

JEL classification:

A8100X

Keywords:

Manganese dissolution

Lithium-ion battery

Hydrofluoric acid

Phospho-olivine

Lithium manganese oxide

ABSTRACT

Understanding the key factors that affects overall performances of a battery is crucial to the lithium-ion battery industry. To this end characterisation methods must be specific, reproducible and representative. As such, an interference free and reproducible analytical method with a low detection limit (50 ppb) to evaluate manganese dissolution from lithium-ion battery positive electrodes is presented. Two different electrolytes (1.0 M LiClO₄ and 1.0 M LiPF₆ in EC:DMC (1:1)), LiFePO₄, two nominally similar LiFe_{0.3}Mn_{0.7}PO₄ samples and spinel LiMn₂O₄ are used for proof of concept. Mn and Fe quantification is performed on material ageing in solely in electrolyte, as well as, in a battery system with and without forced oxidation. It is demonstrated that water and free acid content in the electrolyte, as well as, imposing an oxidative electrochemical potential has a profound effect on manganese based material dissolution and battery performance.

© 2016 Published by Elsevier B.V.

1. Introduction

To compete in the energy storage and transportation market, lithium-ion batteries needs to be safe, low cost, have high energy density, high efficiency and a long service life. [1–4] In this perspective, there is a growing interest for phospho-olivines and manganese based positive electrode materials. Specifically, lithium manganese spinel LiMn₂O₄ (LMO) and lithium iron phosphate LiFePO₄ (LFP) appears to be good replacements for commercial lithium cobalt oxide LiCoO₂. One of the major drawbacks of LiFePO₄ is the potential of the Fe²⁺/Fe³⁺ redox couple (~3.45 V vs Li/Li⁺) that affects the overall energy. Substituting iron for manganese improves the redox potential (~4.05 V vs Li/Li⁺) and at an equivalent theoretical capacity (~170 mAh g⁻¹) which should lead to a higher energy density than LiFePO₄. However, it was clearly demonstrated that LiMnPO₄ (LMP) has a lower experimental energy density due to slow (de)lithiation kinetics entailing large overpotentials and capacity loss at practical rates compared to LiFePO₄ [5–8]. The origin of the slower kinetics is still a matter of discussion, but structural differences related to the relative size of the transition metal ions in different oxidation states and the accompanying unit cell differences, the effect of Jahn-Teller distortions, and poor electronic conduction has been invoked as possible causes

[9–16]. Importantly however, it has been reported that the coexistence of Fe and Mn in the phospho-olivine structure LiFe_{1-x}Mn_xPO₄ (LFMP) minimize the capacity loss when $x < 0.8$. [5,17–20] These mixed iron-manganese phosphates are therefore more attractive than pure LiMnPO₄ for practical applications at this point in time.

Manganese dissolution in lithium-ion battery electrolyte is a well known problem and widely documented for the spinel LiMn₂O₄ [21–31], however studies of similar processes for LiFe_{1-x}Mn_xPO₄ are scarce [20,32,33]. Manganese dissolution is a major concern in part due to inter-particle connection being lost in the composite electrode. In addition manganese ions migrate towards the negative electrode and are reduced to manganese metal in the solid electrolyte interface causing electrolyte decomposition and self-discharge. [28,30] Therefore, even minute amount of manganese dissolution can affect energy density and the longevity the cell. This problem is of such importance that Mn trapping polymers coated separators have been developed to reduce the amount of Mn migrating to the negative electrode. [34].

In this paper, we report on the amount of manganese dissolution in lithium-ion battery electrolyte for LiFePO₄, two nominally similar LiFe_{0.3}Mn_{0.7}PO₄ samples and spinel LiMn₂O₄. Previous reports suggest that Mn dissolution occurs when the LiFe_{1-x}Mn_xPO₄ ages in the electrolyte. [20,32,33] Here a different approach is taken, in that Mn and Fe is quantified in two different electrolytes in the absence and in the presence of forced oxidation within a battery system. In addition, ageing in electrolytes is still performed for comparative purposes. Further, a FePO₄ (FP) counter/reference electrode is used due to the flat ~3.45 V vs Li potential, which avoids possible reduction of the Mn

* Corresponding author.

E-mail addresses: saulnier.mathieu@courrier.uqam.ca (M. Saulnier), Antoine_auclair_14@hotmail.com (A. Auclair), guoxian.liang@matthey.com (G. Liang), schougaard.steen@uqam.ca (S.B. Schougaard).

ions on the negative electrode, a factor that could reduce the amount of Mn in the electrolyte. Finally, the analytical technique used to quantify Mn content in the electrolyte is the Zeeman graphite furnace atomic absorption spectroscopy (Zeeman-GFAAS) couple with standard addition method, which provides a ppb range limit of detection, by overcoming the matrix effects due to the solvent and salt in the battery electrolyte.

2. Experimental

2.1. Materials

The positive electrode base materials were research grade carbon coated C-LiFe_{0.3}Mn_{0.7}PO₄ (LFMP-1 and LFMP-2, Johnson Matthey Battery Materials Ltd.), LiMn₂O₄ (MTI Corporation), and commercial C-LiFePO₄ (P2, Johnson Matthey Battery Materials Ltd.). The negative electrode base material was C-FePO₄ prepared from C-LiFePO₄ as describe by *Lepage et al.* [35] Phase purity of the research grade samples was confirmed using a Philips X'pert diffractometer ($2\theta = 15^\circ\text{--}75^\circ$) with a CuK α source. Electrolytes (BASF) were 1.0 M LiClO₄ in EC:DMC (1:1) (Electrolyte A) and 1.0 M LiPF₆ in EC:DMC (1:1) (Electrolyte B). Water content, 11.5 ± 2.1 ppm and 22.2 ± 3.7 ppm, electrolyte A and B respectively, was determined with a 785 DMP Titrino Potentiometric Titrator (Metrohm) using Aqualine™ Complete 5 single component Karl Fischer reagent (Fischer Scientific). All electrolytes samples were transferred *directly* from the argon filled glovebox to the titrator in a syringe to avoid exposure to ambient atmosphere. Free acid titration yielding 1.6 ± 0.6 ppm (mass of HClO₄ per mass of total electrolyte) and 18.8 ± 0.1 ppm (mass of HF per mass of total electrolyte) for electrolyte A and B respectively, was completed as describe by *Chen et al.* [36] with minor modifications: Titrations were performed on a slurry composed of 3 g of crushed ice, 1 mL of water, 5 drops of indicator (bromothymol blue 0.04%) and approximately 1 g of electrolyte (accurately weighted) using NaOH 0.005 N standardized with potassium biphtalate primary standard (Sigma-Aldrich). All titration were completed in <2 min and once the end point was reached the blue color did not revert to yellow for at least 1 min, indicating that acid formation was minimal during the titration.

2.2. Sample preparation

Suspension experiments were conducted with 250 mg of material (LFP; LMO; LFMP-1 and LFMP-2) place into closed polystyrene containers with 3 mL of electrolyte A or B and stirred for 7 days at room temperature, labeled Susp samples hereafter. All dissolution experiments were conducted in an argon atmosphere glovebox (water and O₂ content < 3 ppm).

Electrochemical cell experiments were based on electrodes prepared by mixing in a roller mill for 24 h active materials, SUPER P® Carbon Black (Imerys Graphite & Carbon) and polyvinylidene fluoride (PVDF, Kynar KF Polymer W#1100) 80:10:10% w/w in N-methylpyrrolidinone (NMP, Alfa Aesar) to produce an ink, which was coated onto an aluminium foil current collector using a doctor blade coater (4-sided film applicator p/n: 2021 from BYK).

The coatings were dried at 90 °C in air for 2 h, followed by 24 h in a vacuum at 65 °C. The electrodes had a geometrical surface area between 60 and 68 cm² with coating thicknesses between 60 and 90 μm, and active material loading between 1.3 and 2.7 mg cm⁻². A Celgard 2500 membrane was sandwiched between the positive and negative electrode, the assembly rolled and place into a high density polyethylene container before transfer to the glovebox. 3 mL of electrolyte was subsequently added to the cell, which was closed with a low density polyethylene lid, and let to settle for 24 h. Two different analyses were performed. In the first type, the sample was not submitted to electrochemical oxidation but allowed to rest with electrolyte for the same amount of time as required for electrochemical treatment (Labeled:

Cell samples). The second type of sample, labeled Ox, was subjected to galvanostatic oxidation at 0.05 C rate until a potential of 0.9 V vs FP (4.35 V vs Li) immediately followed by a potentiostatic step at 0.9 V vs FP (4.35 V vs Li) for a period of 72 h. Electrochemical measurements were performed with a VMP3 multi-channel potentiostat and EC-Lab software from BioLogic Science instrument. All electrochemical curves are available in the supporting information section. (Fig. S-1 and S-2) The experimental capacities were calculated from the mass of active material in the electrode, by integrating the current, applied or measured, as a function of time, combining both the galvanostatic and potentiostatic steps. The total capacity in % was calculated from the experimental values divided by their respective theoretical capacities. (i.e.: 170 mAh g⁻¹ for LFP, LFMP and 140 mAh g⁻¹ for LMO).

Samples for chemical quantification were obtained by transferring the electrolyte into a 10 mL polycarbonate syringe and rinsing 3 times for a total of 5 mL of anhydrous acetonitrile (Sigma-Aldrich). Subsequently the samples were filtered with 0.02 μm pore size filter (Whatman Anotop) inside the argon filled glove box. Samples were prepared in triplicates in Nalgene™ labware to avoid any side reaction with HF or metal leaching that could occur with glassware. All dissolution experiments were conducted at room temperature.

LFMP coin cell batteries were prepared using the same cathodes and separators as above, as well as, 0.75 mm thick metallic lithium (Sigma-Aldrich) which served as the negative electrode. The geometrical areas for the electrodes were 1.5 cm² and 2.0 cm² for the cathode and anode respectively.

Manganese and iron quantification: Standard solutions were prepared from 1000 ppm manganese and iron reference standard solution (Fischer Scientific and Spectro pure, respectively). All analytical measurements were performed in triplicates for all solutions on a Varian Spectra 220Z with coated graphite tube analyser (Agilent Technologies). Single element hollow cathode lamps were used for manganese (AtomaxPerkin Elmer; $\lambda = 279.5$ nm) and iron (SCP science; $\lambda = 248.3$ nm). All curves obtain for GFAAS have a regression coefficient higher than 0.990. All confidence intervals were calculated at a 95% confidence level, using Student-t statistics. For manganese, an instrumental detection limit of 0.5 ppb was calculated with respect to the signal equal to three times the standard deviation of the background. Since the minimum dilution factor for the sample preparations was 100 times, a 50 ppb detection limit was obtained for the overall analytical method.

Note that the results in ppm reported in Fig. 2 represent the mass of ions per mass of active material i.e. the proportion of the active material dissolved in the electrolytes. Since the value of active material varies between the different sample preparation and the electrolyte volume is always constant in our methodology, reporting the results in ppm of active material is more representative of the effects of electrolytes and oxidation occurring to the materials. The result in ppm i.e. mass of ions per mass of electrolyte is presented in the supplementary information section for ease of comparison with literature (Fig. S-3) [20,32,33].

3. Results and discussion

3.1. Method validation

The GFAAS technique was chosen to measure the manganese content because of two major advantages: 1) the limit of detection for manganese is one to three orders lower than other spectroscopy techniques. [37] The samples can as such be diluted further to yield a more reproducible matrix compared to other techniques. 2) Low temperature preheating of the graphite furnace removes the organic solvents, followed by a pyrolysis step to decompose organic materials in the sample before atomisation. Organic solvents have been shown to present interference in other spectrometric techniques that involves sample transport and droplet formation [38,39]. Validation of the analytical

Download English Version:

<https://daneshyari.com/en/article/7744911>

Download Persian Version:

<https://daneshyari.com/article/7744911>

[Daneshyari.com](https://daneshyari.com)