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Journal of Power Sources 97–98 (2001) 433–436

JOURNAL OF
POWER
SOURCES

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$\text{Li}_{1+\delta}\text{Mn}_{2-\delta}\text{O}_4$ performance measured by leaching

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Received 23 June 2000; received in revised form 4 January 2001; accepted 13 January 2001

Abstract

Li–Mn–O spinel materials for Li-ion batteries were characterised by redox titration, controlled chemical de-lithiation and pH measurements in order to derive the capacity, rate performance and stability. These methods are shown to be fast and accurate. Furthermore, it is shown that the material with the composition of $\text{Li}_{1.04}\text{Mn}_{1.96}\text{O}_4$ reveals the highest practical capacity and the lowest dissolution in water. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: LiMn_2O_4 ; Spinel; Leaching

1. Introduction

In principle, LiMn_2O_4 (space group $Fd3m$) has manganese on octahedral sites and lithium on tetrahedral sites, but it was reported recently that part of the lithium resides on 16c octahedral sites [1]. Furthermore, the Mn_2O_4 framework provides room for lithium-ion transport, maintaining its structure over the compositional range $\text{Li}_x\text{Mn}_2\text{O}_4$, with usually $0 < x < 1$. Consequently, a gradual increase in the average Mn valency occurs, i.e. from 3.5 to 4.0, respectively. Upon Li extraction, Mn^{3+} is oxidised to Mn^{4+} , and only Mn^{3+} ions contribute to the capacity at 4 V. However, it was found that lithium ions cannot be extracted at 4 V anymore, if the lithium content $x < 0.25$ [2], reflected by a strong increase in the open-circuit voltage (OCV). Hence, this leads to a capacity reduction of the spinel material compared to the theoretical capacity, i.e. 148 mAh/g, giving a practical capacity of about 120 mAh/g. In addition, the exact composition LiMn_2O_4 seems to be unstable in the current Li-ion battery systems [3]. In order to stabilise the spinel for improved electrochemical performance, extra lithium was added during synthesis, usually resulting in $\text{Li}[\text{Li}_\delta\text{Mn}_{2-\delta}]\text{O}_4$ ($0 < \delta < 0.33$), with the ions between square brackets occupying 16d sites. Here, the average Mn valency varies from 3.5 at $\delta = 0$ to 4 at $\delta = 0.33$, and thus the maximum amount of lithium ions that can be extracted theoretically is $1 - 3\delta$. It is believed that the

regime reflecting the reduced capacity in LiMn_2O_4 , i.e. between $x = 0.0$ and 0.25, can substantially be reduced by adding small amounts of extra lithium; small δ -values keep the number of Mn^{3+} acceptable. Here, we report on the performance of $\text{Li}[\text{Li}_\delta\text{Mn}_{2-\delta}]\text{O}_4$ derived via redox titration [4] and a redox disproportionation reaction according to Hunter's method [5] and pH measurements.

2. Experimental

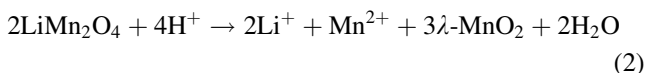
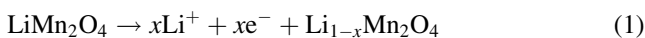
Various tests were carried out to derive the performance of the spinel material. These are listed below.

- The pH measurements were done in water by adding 4 g powder in 1 l of water (or smaller amounts but equal ratios). The pH was measured with a Metrohm pH meter using an Ag/AgCl (3 M KCl) electrode.
- Redox titration was done in order to derive the stoichiometry, i.e. the Mn valency and the Mn content. The Li–Mn–O material was dissolved in an acidic Fe^{2+} solution to form Fe^{3+} and Mn^{2+} with the latter going into solution. Mn^{2+} was titrated with KMnO_4 to form Mn^{3+} . Subsequently, the solution was saturated with sodium pyrophosphate for stabilisation of Fe^{2+} , and the titration resumed to form Mn^{4+} . From the equivalence points, both the Mn valence as well as the Mn content can be calculated.
- De-lithiation was carried out via the following methods.
 - Electrochemical (coulombic) titration (reaction (1)) measurements were done in a CR2320 coin cell

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(Hohsen Corp.). The electrodes were punched out of coatings made by doctor blading the active materials (typically 14 mm diameter, 90% active material, PVdF binder and Al substrate). The counter electrode was a 0.3 mm lithium ribbon (Chemetall Foote Corp.). The electrolyte was 1 M LiPF₆ in EC/EMC 1:2 (Mitsubishi Chemical). The charge/discharge curves were recorded on a MACCOR S4000 battery tester.

- o Chemical de-lithiation was done on 4 g powder in 75 ml water and subsequently titrating the mixture with sulphuric acid (1 M) with a Metrohm 716 DMS Titrino. The total amount of added sulphuric acid was chosen twice the required amount according to reaction (2) [5]. The pH (mV) was monitored with an Ag/AgCl (3 M KCl) electrode. Various powders were analysed, and the dosing rate of the sulphuric acid was varied also.



3. Results

The de-lithiated samples were analysed by redox titration, and it was found that they agree with a composition Li_x-[Li_δMn_{2-δ}]O₄, indicating that δ remains unaffected upon leaching. Thus, the stoichiometry was calculated according to evolution of reaction (3), where x and y are directly related, but not further specified for simplicity here.



In Fig. 1, both the discharge capacity and pH of various Li[Li_δMn_{2-δ}]O₄ materials are plotted. The capacity was taken from the third discharge curve recorded at a C/20 rate.

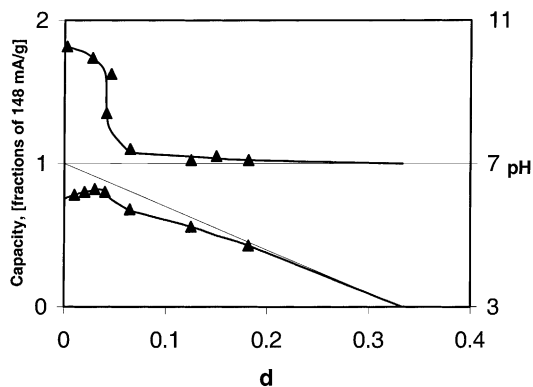


Fig. 1. Capacity (lower panel, primary axis) and pH (upper panel, secondary axis) as a function of the δ parameter in Li[Li_δMn_{2-δ}]O₄.

It can be seen that for δ = 0–0.04, the capacity increases, whereas at higher δ parameters the capacity drops, and finally reaches the theoretical curve, i.e. 1 – 3δ. Exactly near this optimum, a sharp drop in the measured pH was observed. The suggested reaction that accounts for this pH behaviour is similar as given in reaction (3), but with water as the proton donor rather than H⁺.



It is stressed that the dissolution reaction of the Li[Li_δMn_{2-δ}]O₄ materials is more complex in terms of stoichiometry, however the ratio of Li/Mn formed in solution becomes 2(2 + δ)/(2 – δ). This means that the Li/Mn ratio in solution was already in favour for high δ parameter, however this cannot explain the sharp drop of the pH near δ = 0.04. It seems that for higher δ parameter, the material becomes significantly more stable, which therefore leads to improved capacity. Furthermore, it seems that the pH at low δ parameter levels off to just above 10. This is explained by the solubility of Mn(OH)₂ that may be precipitated, as it has a very low solubility product S [6], i.e.

$$S = [\text{OH}^-]^2[\text{Mn}^{2+}] \sim 2 \times 10^{-13} \text{ M}^3 \quad (5)$$

According to reaction (4), at pH 10, [OH⁻] = 10⁻⁴ and [Mn²⁺] = 2.5 × 10⁻⁵, the product [OH⁻]²[Mn²⁺] > S, thus leading to precipitation of Mn(OH)₂. For accurate calculations however, we should include the δ parameter and activities rather than concentrations. Furthermore, S itself depends on the ionic strength of the solution [7].

With respect to these results, we will report in a forthcoming paper on a similar pH and solubility behaviour of the Li–Mn–O materials, which will be dispersed in various electrolyte systems in order to derive the stability. In addition, the measurements will be done at different temperatures, i.e. up to 100°C.

Fig. 2 shows chemical de-lithiation at various sulphuric acid dosing rates, i.e. ranging from total experiment time of 0.5–4 h. A similar profile is observed as in electrochemical cells. At very high sulphuric acid additions, the potential does not increase much anymore. At this concentration, the acid is not able to extract more lithium from the host material. In fact, the curve merely goes to the equilibrium situation determined by the second dissociation step [6] of sulphuric acid.



The de-lithiation for various materials having different δ parameters will, by careful analysis of the profile, reveal certain points of inflection which reflect the various phase transitions present in the parent materials as would be observed in a charge/discharge profile.

At low sulphuric acid dosing rates, it is possible to derive the practical capacity, by taking reactions (4) and (6) and the

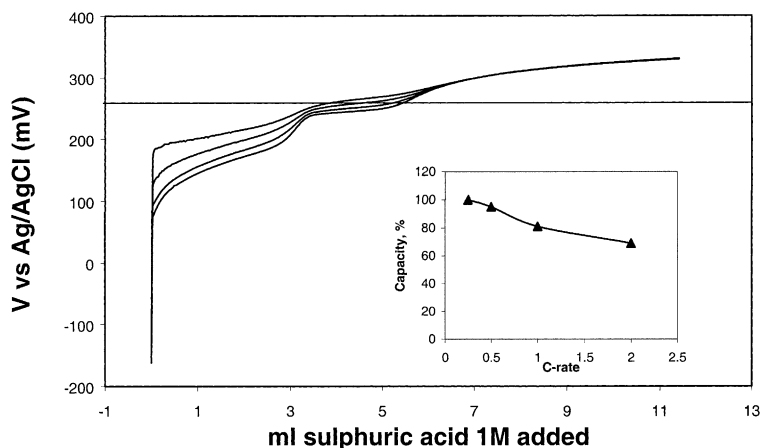


Fig. 2. De-lithiation of $\text{Li}_{1.04}\text{Mn}_{1.96}\text{O}_4$ at various sulphuric acid dosing rates (ml/h). From bottom to top: 4, 2, 1 and 0.5 h. The inset shows the capacity derived from the parent curves at a cut-off voltage of 260 mV. The capacity is relative to the 4 h measurement.

actual δ parameter into account. Fig. 3 shows the calculated capacity of $\text{Li}_{1.04}\text{Mn}_{1.96}\text{O}_4$ for both chemical as well as electrochemical titration. The capacity was found to be about 130 mAh/g. It is however stressed that the accuracy here is strongly influenced by K_{eq} and thus the temperature, and here too we have to use activities rather than concentrations for the calculations.

The curves recorded at different sulphuric acid dosing rates were performed in such a way that they match relevant C -rates, and thus reflecting the Li-ion transport in the insertion compound. By defining proper cut-off voltages, in the figure 260 mV was taken, it is possible to derive the practical capacity of the material. Clearly, the capacity drops on increased sulphuric acid dosing rates, as is presented in the inset in Fig. 2. Hence, the method is useful to verify the rate capability in terms of C -rates.

An interesting application of the above de-lithiation method is obtaining diffusion coefficients of Li in the

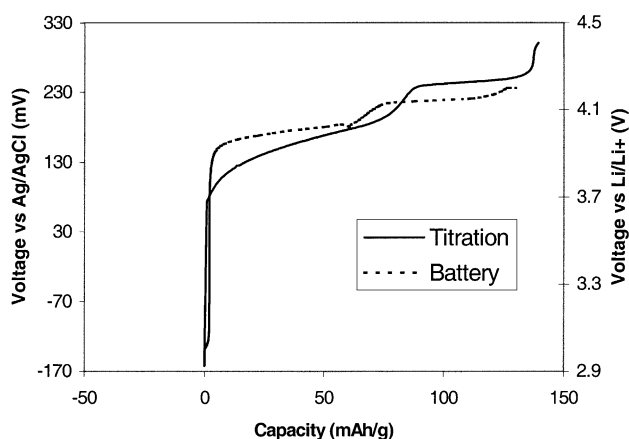


Fig. 3. De-lithiation profile ($C/2$, primary axis) and third discharge curve ($C/20$, secondary axis).

Li–Mn–O materials. By monitoring the rate of the process, i.e. $d(\text{pH})/dt$, the diffusion coefficient can be calculated, and this is a substantial advantage of this method over other electrochemical analysis methods for the determination of the diffusion coefficient. Here, the surface dissolves constantly giving a fresh surface any time.

4. Conclusions

Pure LiMn_2O_4 is very sensitive to partly dissolution in proton-donating solvents such as water. By analysing the pH (say 1 g spinel powder in 250 ml water), the stability of the spinel can be derived. In order to stabilise the spinel, small additions of extra lithium is necessary to form $\text{Li}_{1+\delta}\text{Mn}_{2+\delta}\text{O}_4$. The spinel with composition $\text{Li}_{1.04}\text{Mn}_{1.96}\text{O}_4$ ($\delta = 0.04$) was found to have the highest practical capacity and show almost no dissolution in water.

By analysing the pH evolution during titration of $\text{Li}_{1+\delta}\text{Mn}_{2+\delta}\text{O}_4$ with sulphuric acid, the chemical de-lithiation behaviour can be studied and related to the electrochemical behaviour in a galvanic cell. By varying the titration dosing rate, rate capability tests can be simulated, the chemical de-lithiation (via a modified method according to Hunter) and the performance of the spinel material can be characterised.

Acknowledgements

This work was carried out partly under a contract of NWO-CW and STW. DSM SoluTech and Shell IEP are acknowledged for their significant financial support. Honeywell (Riedel de Haen) is thanked for providing Li–Mn–O materials with different compositions. The authors thank Ms. Liping He, Dr. Hong Huang, and D.R. Simon for useful discussions and useful experimental help.

References

- [1] H. Berg, E.M. Kelder, J.O. Thomas, *J. Mater. Chem.* 9 (1999) 427.
- [2] T. Ohzuku, M. Kitagawa, T. Hirai, *J. Electrochem. Soc.* 137 (1990) 769.
- [3] P. Arora, R.E. White, M. Doyle, *J. Electrochem. Soc.* 145 (1998) 3647.
- [4] E.M. Kelder, M.J.G. Jak, J. Schoonman, M.T. Hardgrave, S. Yde-Andersen, *J. Power Sources* 68 (1997) 590.
- [5] J.C. Hunter, *J. Solid State Chem.* 39 (1981) 142.
- [6] *CRC Handbook of Chemistry and Physics* (D.R. Lide, Ed.i.c.), CRC Press, Boca Raton, Ed. 75 (1995), 8-58.
- [7] R. Nasanen, *Zeitschrift Physikalische Chemie (A)* 191 (1942) 54.