

## Cathode properties of amorphous and crystalline FePO<sub>4</sub>

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Available online 23 June 2005

### Abstract

FePO<sub>4</sub> is an attractive rare-metal-free cathode active material. Simple and inexpensive new synthesis routes obtained from solution were investigated. P<sub>2</sub>O<sub>5</sub> and Fe metal powders, both of which react in water at room temperature, were selected as inexpensive starting materials. Amorphous powders obtained through ball milling were annealed at various temperatures (100–650 °C) in air. IR spectra showed that PO<sub>4</sub> tetrahedra units existed even in the amorphous matrix. XRD peaks of the trigonal FePO<sub>4</sub> phase appeared above 500 °C. Reversible Fe<sup>3+</sup>/Fe<sup>2+</sup> redox reactions in the amorphous and crystalline FePO<sub>4</sub> were confirmed by <sup>57</sup>Fe Mössbauer spectroscopy. The heating temperature dependence of the cathode properties is reported.

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**Keywords:** Olivine; Iron-phosphate; Amorphous

### 1. Introduction

Recently, two remarkable developments have emerged in cathode research: a high-voltage cathode with a 4.5–5 V plateau and an iron-based eco-friendly cathode for EV use. LiMPO<sub>4</sub>-type phospho-olivine cathodes played an important role in both developments, for example, LiCoPO<sub>4</sub> as a 5 V cathode and LiFePO<sub>4</sub> as a rare-metal-free cathode [1,2]. However, divalent iron starting materials such as FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O and (CH<sub>3</sub>COO)<sub>2</sub>Fe are expensive and toxic. In addition, the calcination process should be performed in an inert atmosphere. In order to keep production costs down, we changed the synthesis target from lithium iron(II) phosphate to iron(III) phosphate [3–7], which can be synthesized in air as shown in Table 1. Moreover, P<sub>2</sub>O<sub>5</sub> and metallic iron powder were selected as inexpensive starting materials.

In this research, the cathode characteristics of the synthesized amorphous and crystalline trigonal FePO<sub>4</sub> are investigated using coin-type cells.

### 2. Experimental

We identified all the synthesized materials by XRD (Rigaku RINT2100HLR/PC) and FT-IR (JASCO 680 plus). In addition, we used TG-DSC (Rigaku Thermo Plus TG8110), GC/MS (Shimadzu), SEM (JEOL JSM-6060LA), and <sup>57</sup>Fe Mössbauer spectroscopy (Laboratory Equipment Corp.) where needed.

To improve the rate capability, the cathode powders (70 w/o) were dry ball milled with 25 w/o AB. Cathode pellets were then fabricated by mixing the powder with a 5 w/o PTFE Teflon binder (Polyflon TFE F-103, Daikin Industry Ltd.). We evaluated the electrochemical cathode performance in coin-type Li cells using a nonaqueous electrolyte (Mitsubishi Chemical Co. and Tomiyama Pure Chemicals Co.) and a polypropylene separator (Celgard 3501) against a Li metal anode.

### 3. Result and discussion

The P<sub>2</sub>O<sub>5</sub> and metallic iron powders were reacted in water at room temperature. The precursor solution was mixed for 24 h by a planetary ball mill (200 rpm) and annealed at various

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Table 1  
Synthesis conditions of FePO<sub>4</sub> (P321) according to the current literature

Starting material		Atmosphere	Temperature (°C), time (h)	Reference
Fe source	P source			
Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	Air	650, 24	[3]
Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	Air	400, 4	[4]
Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	K <sub>2</sub> HPO <sub>4</sub>	Air	650, 24	[5]
FeCl <sub>3</sub>	Na <sub>3</sub> PO <sub>4</sub>	Air	350, 10	[6]
Fe	P <sub>2</sub> O <sub>5</sub>	Air	650, 12	This work

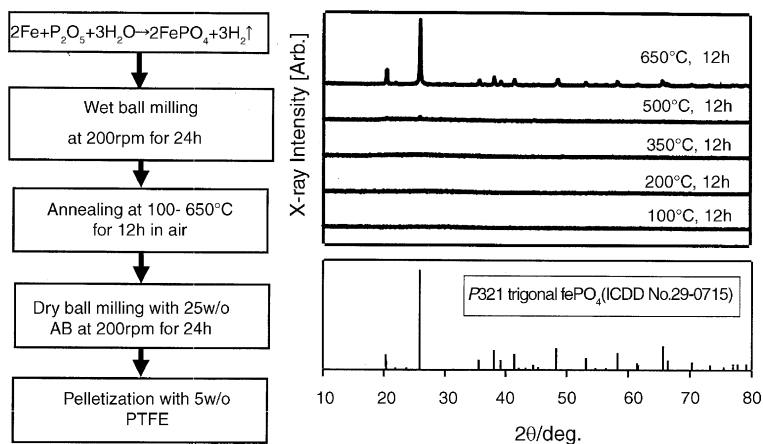


Fig. 1. Cathode assembly procedure and XRD profiles of obtained FePO<sub>4</sub> powders.

temperatures (100–650 °C) for 12 h in air. The XRD profiles shown in Fig. 1 indicate that the crystallization to the trigonal FePO<sub>4</sub> phase started above 500 °C. The crystalline phase annealed at 650 °C was identified as trigonal FePO<sub>4</sub> with a P321 space group (ICDD29-0715). The difference between delithiated orthorhombic phase from olivine LiFePO<sub>4</sub> and trigonal FePO<sub>4</sub> is shown in Fig. 2. The trigonal FePO<sub>4</sub> has the FeO<sub>4</sub> tetrahedra instead of the FeO<sub>6</sub> octahedra, and it consists of a corner-sharing framework with the FeO<sub>4</sub> and PO<sub>4</sub> tetrahedra.

On the other hand, the FT-IR spectra (Fig. 3) showed that PO<sub>4</sub> tetrahedral units existed even in amorphous samples. An IR absorption peak around 1600 cm<sup>-1</sup>, attributed to the H–O–H bending mode of crystal water, was detected in all samples except the crystalline sample. The TG-MS profile of Fig. 4 shows that outgas during annealing between 100 and 700 °C was water almost entirely. The crystal water content of each amorphous sample annealed at 100 °C can be roughly estimated by the weight loss in Fig. 5 as FePO<sub>4</sub>·H<sub>2</sub>O.

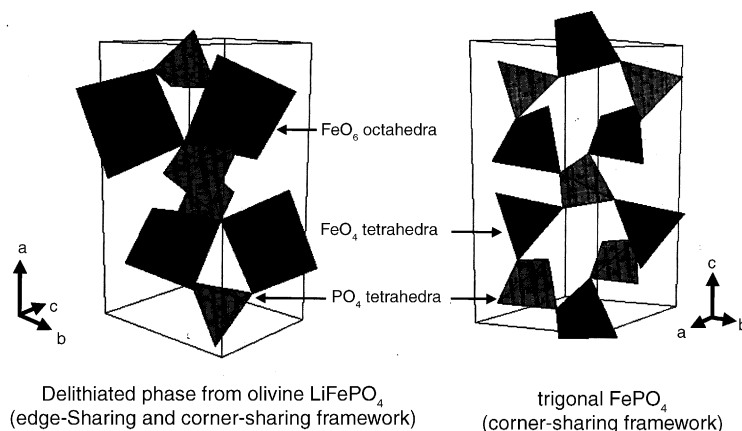


Fig. 2. Crystal structures of orthorhombic and trigonal FePO<sub>4</sub>.

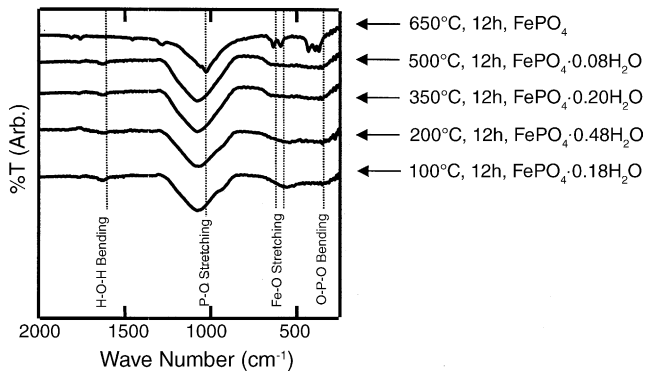


Fig. 3. FT-IR spectra of trigonal FePO<sub>4</sub> samples.

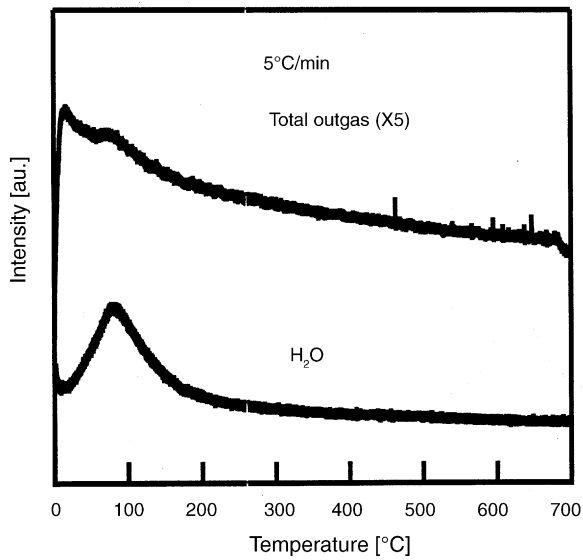


Fig. 4. TG-MS profiles of outgas from a-FePO<sub>4</sub>.

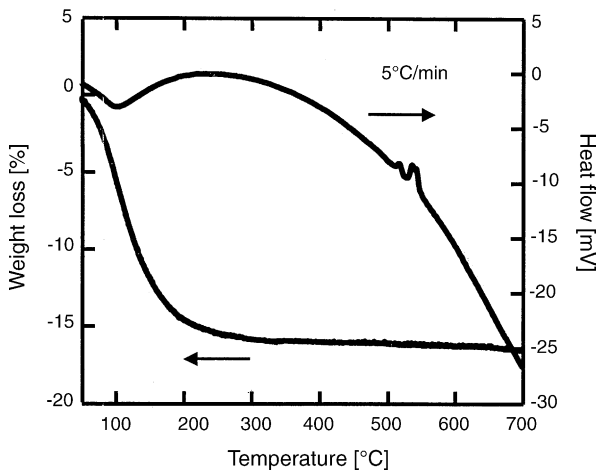


Fig. 5. TG-DTA profiles of a-FePO<sub>4</sub>.

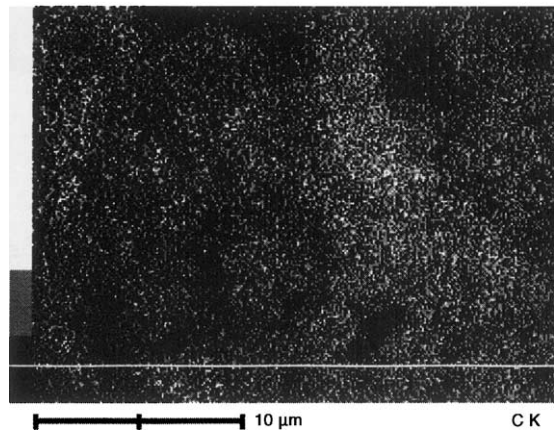
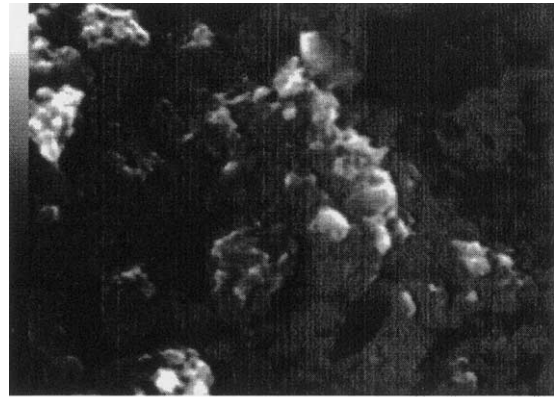


Fig. 6. SEM and EDS mapping image of carbon on FePO<sub>4</sub> cathode pellet.

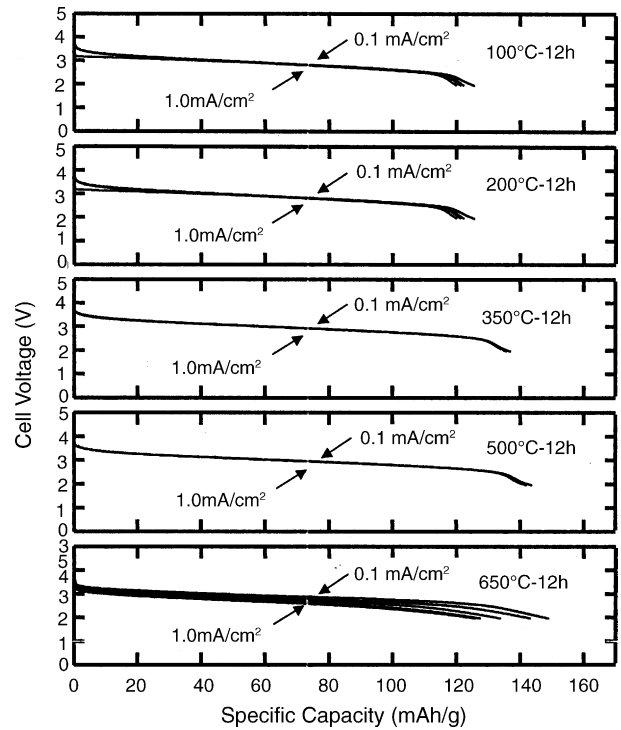


Fig. 7. Rate capability of a-FePO<sub>4</sub> and c-FePO<sub>4</sub>.

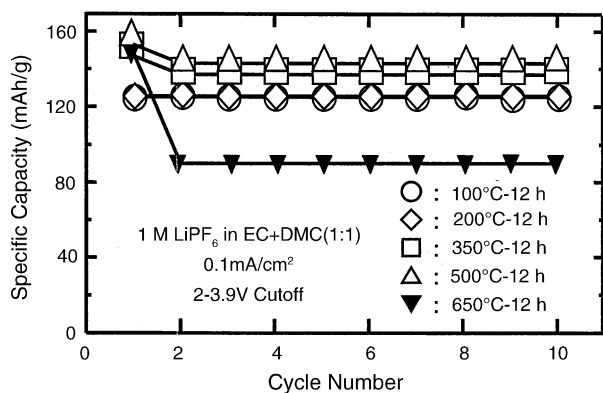


Fig. 8. Cyclability of a-FePO<sub>4</sub> and c-FePO<sub>4</sub> at a rate of 0.1 mA cm<sup>-2</sup> between 2 and 3.9 V.

Uniform carbon distribution on the FePO<sub>4</sub> particle after 24 h dry ball milling (200 rpm) was confirmed by SEM and energy-dispersive spectroscopy (EDS) mapping image of carbon (Fig. 6). Actually, the specific capacity was maximally improved 35% by dry ball milling. The rate capability and

cyclability of the improved FePO<sub>4</sub> cathode are shown in Figs. 7 and 8, respectively. Both the amorphous (a) and crystalline (c) FePO<sub>4</sub> cathodes show a monotonically decreasing charge–discharge profile; in contrast, the olivine LiFePO<sub>4</sub> has a 3.4 V flat voltage plateau.

As mentioned above, the amorphous sample included crystal water in the matrix. Nevertheless, the amorphous sample was more reversible than the crystalline. In both samples, the highest reversible capacity was 153 mAh g<sup>-1</sup>, which was obtained by annealing at 500 °C. In the cycling voltage range of 2–3.9 V, crystal water must be stable against the decomposition with H<sub>2</sub> and O<sub>2</sub> gas generation.

The <sup>57</sup>Fe Mössbauer spectra of the amorphous FePO<sub>4</sub> annealed at 100 °C and that of the crystalline one indicated that the matrixes of both samples had high-spin Fe(III) at the tetrahedral sites in their initial states (Fig. 9). In the fully charged state, it changed to Fe(II) in the octahedral site and returned to Fe(III) in the tetrahedral site again for the amorphous sample as shown in Fig. 10. However, in the crystalline sample, the Fe(II) state remained even in the fully recharged state. This must be a result of insufficient reversibility as shown in Fig. 8.

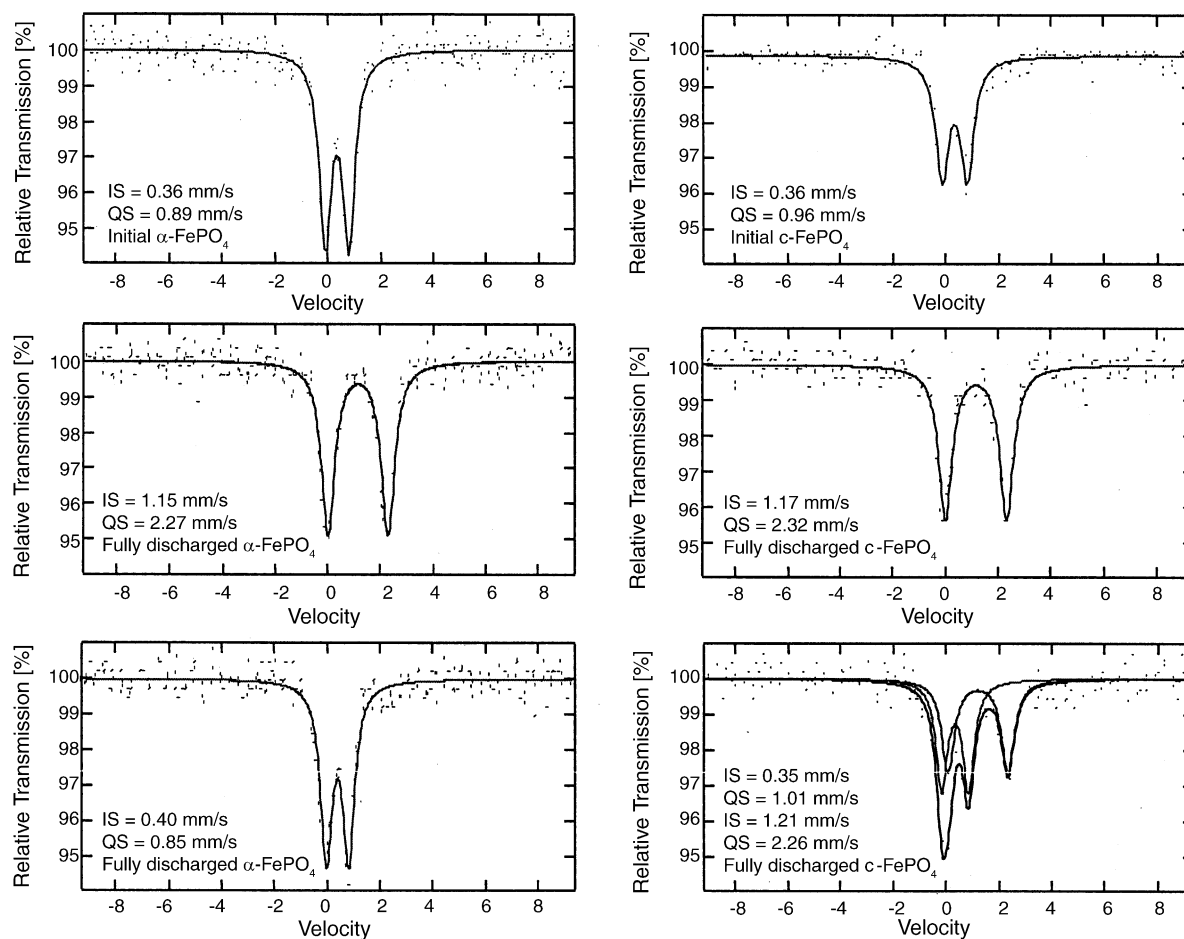


Fig. 9. <sup>57</sup>Fe Mössbauer spectra of a-FePO<sub>4</sub> and c-FePO<sub>4</sub> cathode pellets on the first cycle.

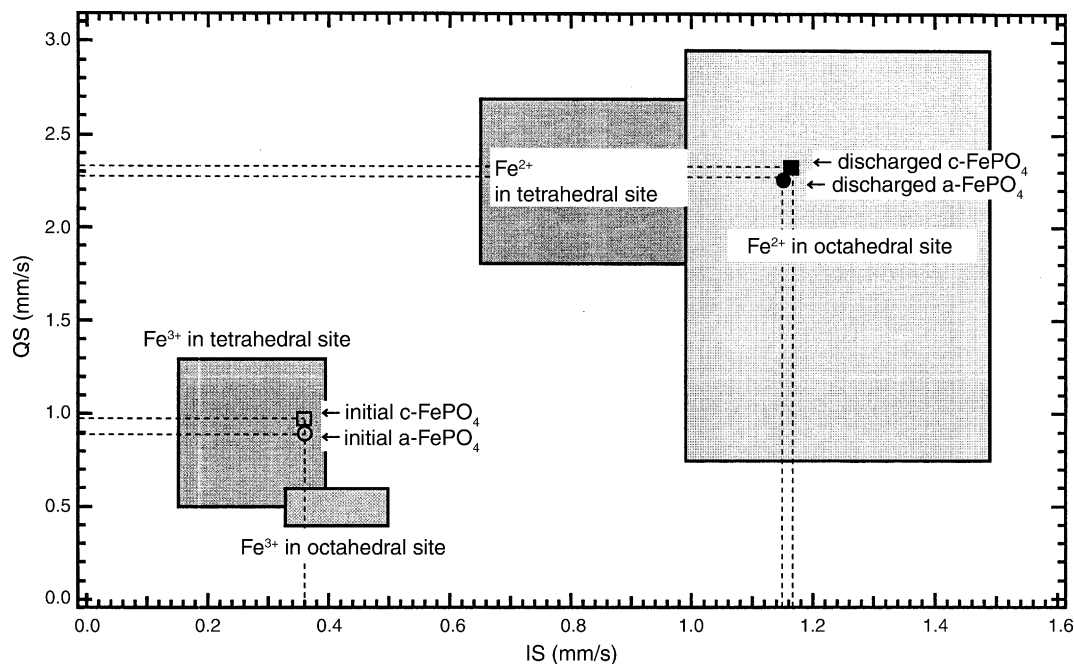


Fig. 10. Iron valence states in a-FePO<sub>4</sub> and c-FePO<sub>4</sub> matrix.

#### 4. Conclusion

A new low-cost low-temperature synthesis route using P<sub>2</sub>O<sub>5</sub> and Fe powders in air was proposed for FePO<sub>4</sub>. TG-DSC and FT-IR spectra proved that amorphous FePO<sub>4</sub> included some crystal water in the matrix. Nevertheless, the reversible capacity of the a-FePO<sub>4</sub> exceeded that of c-FePO<sub>4</sub>. Fe<sup>3+</sup>/Fe<sup>2+</sup> redox reactions during cycling were confirmed in both a- and c-FePO<sub>4</sub> by <sup>57</sup>Fe Mössbauer spectrometry.

#### Acknowledgement

The present work was financially supported by the Japan Science and Technology Agency.

#### References

- [1] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1188.
- [2] A.K. Padhi, K.S. Nanjundaswamy, C. Masquelier, S. Okada, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1609.
- [3] P.P. Prosini, M. Lisi, S. Scaccia, M. Carewska, F. Cardellini, M. Pasquali, *J. Electrochem. Soc.* 149 (3) (2002) A297.
- [4] A. Hammouche, R.W. De Doncker, A. Kahoul, L. Telli, *LiBD* 2003 (9) (2003).
- [5] S. Scaccia, M. Carewska, A.D. Bartolomeo, P.P. Prosini, *Thermochim. Acta* 383 (2002) 145.
- [6] Y. Song, S. Yang, P.Y. Zavalij, M.S. Whittingham, *Mater. Res. Bull.* 37 (2002) 1249.
- [7] C. Masquelier, P. Reale, C. Wurm, M. Morcrette, L. Dupont, D. Larcher, *J. Electrochem. Soc.* 149 (2002) A1037.