

LiFePO₄ storage at room and elevated temperatures

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Abstract

The stabilities of olivine LiFePO₄ and spinel LiMn₂O₄ in a LiPF₆-based electrolyte were investigated by means of atomic absorption spectroscopy. At 85 °C a significant increase in Mn/Fe dissolution was observed in comparison to 60 °C stored cathode materials. However, the comparison indicates a much lower solubility of the LiFePO₄ versus LiMn₂O₄. This result shows a new advantage of LiFePO₄ as a promising alternative cathode.

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1. Introduction

Olivine LiFePO₄ has become a very attractive cathode material for rechargeable lithium batteries for EV applications following Padhi's publication [1] which showed that it has 3.4 V OCV in lithium cells and a 120 mAh/g reversible capacity. LiFePO₄ has the following distinctive advantages: it is environmentally benign, inexpensive, has a 170 mAh/g theoretical capacity with a flat charge/discharge curve, long cycleability due to small volume contractions (6.8%), and an acceptable true density (3.6 g/cm³, higher than other iron phosphates such as Li₃Fe₂(PO₄)₃ and LiFeP₂O₇ [2], however, lower than the LiCoO₂ density).

The main disadvantage of LiFePO₄ is its poor rate capability. By reducing the discharge current, capacity is restored, indicating a diffusion control within a single grain [3]. A. Yamada [4] identified the undesired particle growth over 600 °C and the presence of a residual Fe³⁺ phase below 500 °C as two extrinsic obstacles for achieving optimum charge/discharge performance. Takahashi [5] reported that LiFePO₄ prepared at 675 °C showed a higher capacity when compared to samples synthesized at higher temperatures. He [5] related this result to the relatively small particle size and to the rough surface morphology of the samples prepared at low temperature.

Recent publications suggest that the initially reported low rate capability problem of LiFePO₄ can be overcome by

carbon coating [6–8], the addition of 1% Ag or Cu [9], 1 atom % substitutional doping for Fe [10], and low temperature liquid phase synthesis [11]. Specifically it has been reported that at 5C, the capacity increases on initial cycling to reach a maximum at ~120 mAh/g, with ~8% loss over 800 cycle [7]. Although the good thermal stability for LiFePO₄ has been reported [4,12], there is a absence of published reports regarding the solubility of LiFePO₄ in electrolyte.

In the present paper, the stabilities of olivine LiFePO₄ and spinel LiMn₂O₄ in a LiPF₆-based electrolyte were compared by means of atomic absorption spectroscopy.

2. Experimental

A LiFePO₄ sample was prepared by a solution route; CH₃COOLi·2H₂O, Fe(CH₃COO)₂ and H₃PO₄ were mixed in a molar ratio of Li:Fe:P = 1.05:1:1 in *N,N*-dimethylformamide. The solvent was evaporated at 150 °C in air. The solid dry residue was pre-heated at 350 °C for 2 h and final synthesis was performed at 700–800 °C for 10 h in an Ar + 5% H₂ atmosphere. LiMn₂O₄ powder was obtained from the Tosoh Corporation.

Powder samples were identified using a powder X-ray diffractometer (Rigaku RINT2100HLR/PC) with monochromatized Cu K α radiation. Morphological observations were done using a SEM (Hitachi S-2100B). Cyclic voltammetry was performed in a flooded three-electrode cell at room temperature. The working electrode was prepared

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by pressing a 1:1 w/o LiFePO_4 :teflonized acetylene black (TAB-2, Hosen Corp.) cathode mix onto an aluminum X-met current collector. Counter and reference electrodes were lithium metal. Cathode properties were tested galvanostatically in 2032 coin cells. A LiFePO_4 , acetylene black and PTFE cathode mix in a 70:25:5 w/o ratio was used.

Prior to storage tests, both LiMn_2O_4 and LiFePO_4 powders were dried at 200 °C for 2 h under a vacuum in a furnace directly connected to a dry box. LiFePO_4 and LiMn_2O_4 powders containing 5% PTFE were rolled into 0.8–1.0 mm-thick sheets. From these sheets, constant weight pellets (0.27 ± 0.005 g) were cut and were stored in a 1 M LiPF_6 EC:DMC (1:1) electrolyte for 4 days at room and elevated temperatures.

The cathode pellet weight to electrolyte ratio was kept exactly the same as that described in Okada's LiMn_2O_4 study (3.5 cm^3) [13]. Storage was performed in sealed vials filled with dry Ar gas at RT, 60 °C, and 85 °C for different durations. Iron and manganese concentrations in the electrolyte were analyzed using a Z-5310 Polarized Zeeman atomic absorption spectrophotometer (Hitachi).

3. Results and discussion

The X-ray diffraction pattern of LiFePO_4 obtained from the liquid phase is shown in Fig. 1. LiFePO_4 material, obtained from the liquid phase reaction, is a single-phase with an ordered olivine structure indexed to the orthorhombic $Pnmb$ space group. The SEM image of the LiFePO_4 sample in Fig. 2 shows that the particle sizes, ϕ , are ca. 5 μm . The cyclic voltammetry profile is shown in Fig. 3. The

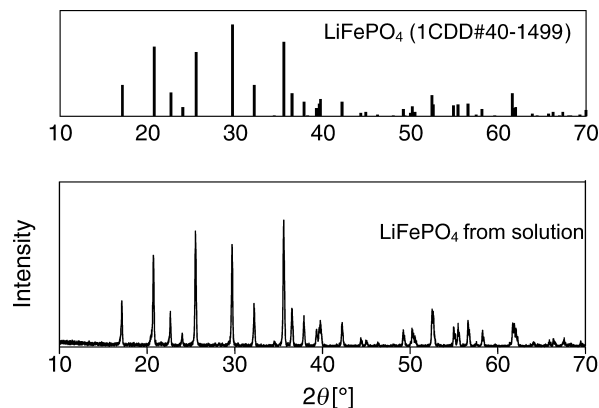


Fig. 1. XRD profiles of the LiFePO_4 sample obtained from a liquid phase.

cathodic and the anodic peak of LiFePO_4 are located at 3.2 V and 3.6 V, respectively. The charge/discharge profile shown in Fig. 4 and the rate capabilities in Fig. 5 demonstrate that the LiFePO_4 powder sample obtained by the solution route shows sufficiently high cathode performance.

Mn and Fe concentrations in 1M LiPF_6 EC:DMC (1:1) electrolyte after 4 days RT storage of LiMn_2O_4 and LiFePO_4 , are presented in Fig. 6. The LiFePO_4 sample shows lower solubility, in comparison to LiMn_2O_4 . In Fig. 6, Mn concentration in the electrolyte is close to the one reported by Okada et al. [13]. In consideration of these properties, the effect of temperature on material stability was tested and is summarised in Figs. 7 and 8. It is recognized from Figs. 6–8, that for the LiFePO_4 samples, stored at RT, 60 and 85 °C, the Fe concentrations in the electrolyte are significantly lower in comparison to Mn concentration from

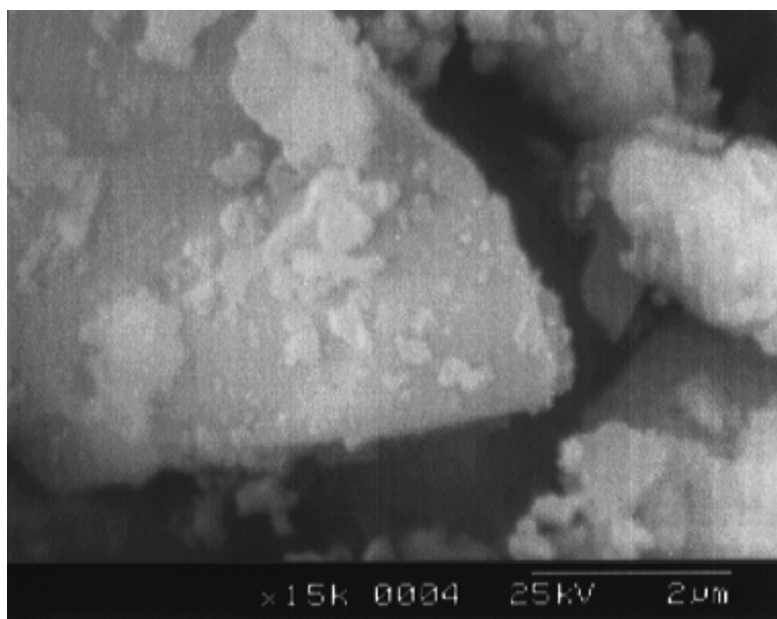


Fig. 2. SEM image of the LiFePO_4 sample. The scale bar indicates 2 μm .

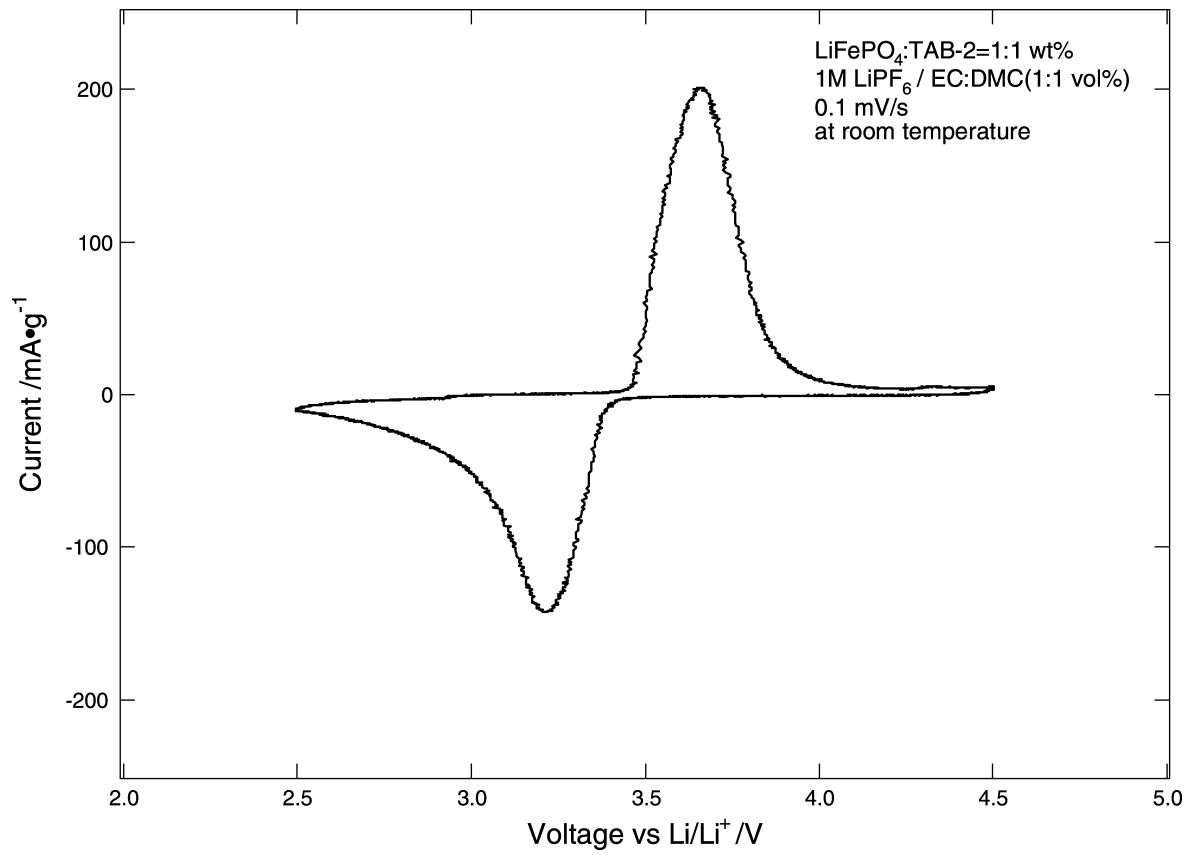


Fig. 3. First cycle voltammetric profiles of the LiFePO₄ sample obtained at a 0.1 mV/s sweep rate.

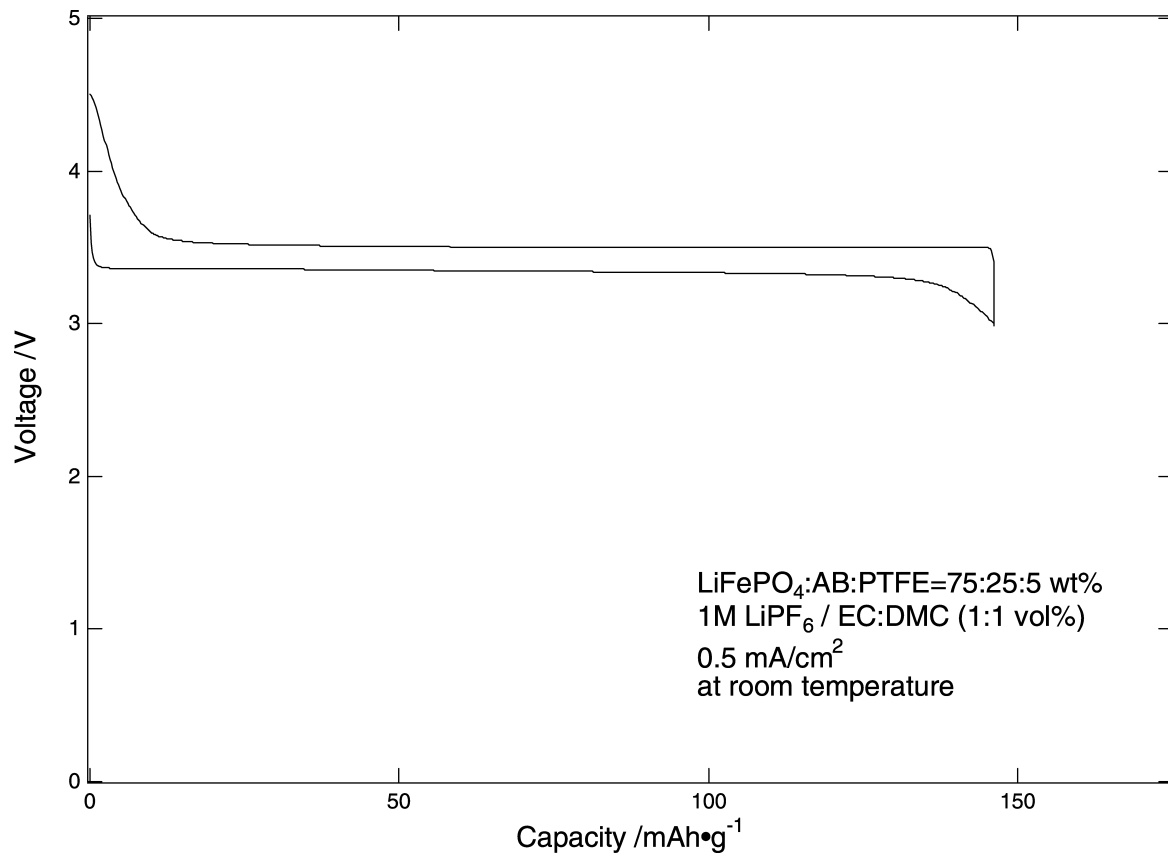


Fig. 4. First discharge and second charge profiles of the LiFePO₄ sample obtained at a 0.5 mA/cm² rate.

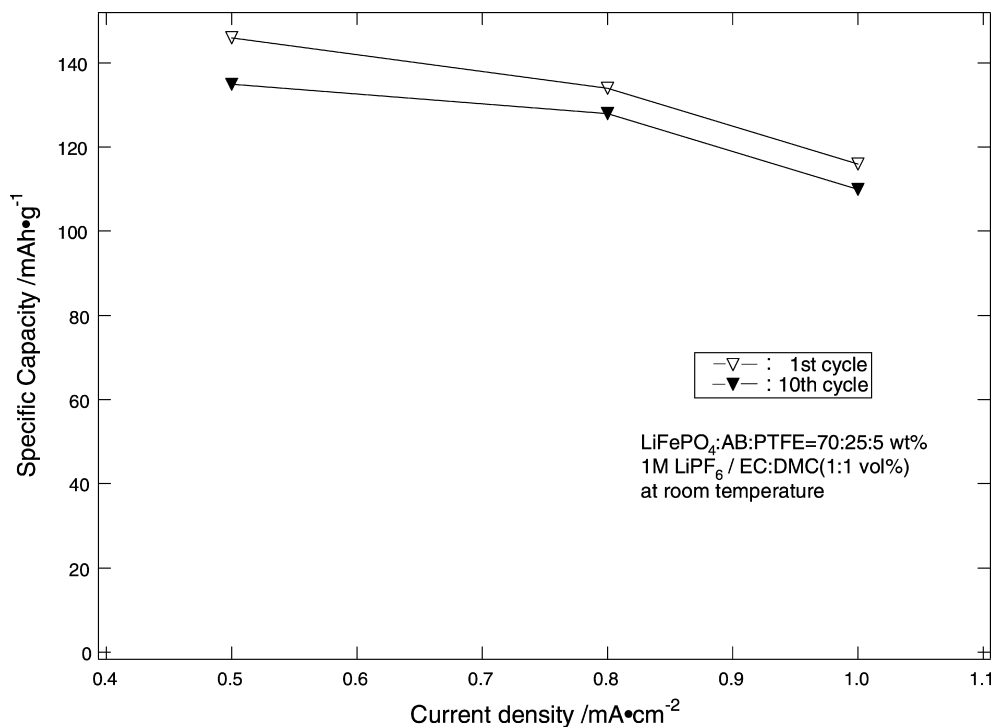


Fig. 5. First and 10th cycle rate capability of the LiFePO₄ sample in the 3.0–4.5 V voltage window.

the LiMn₂O₄ material. In all storage experiments, LiFePO₄ was less soluble in the electrolyte.

Finally, in order to check the influence of moisture on LiMn₂O₄ and LiFePO₄ stability, storage experiments in air were

performed at 60 °C. In this experiment, Mn dissolution increased by two orders of magnitude, and Fe dissolution at four orders of magnitude. These results suggest that the ionic compound LiFePO₄ is more sensitive to moisture than LiMn₂O₄.

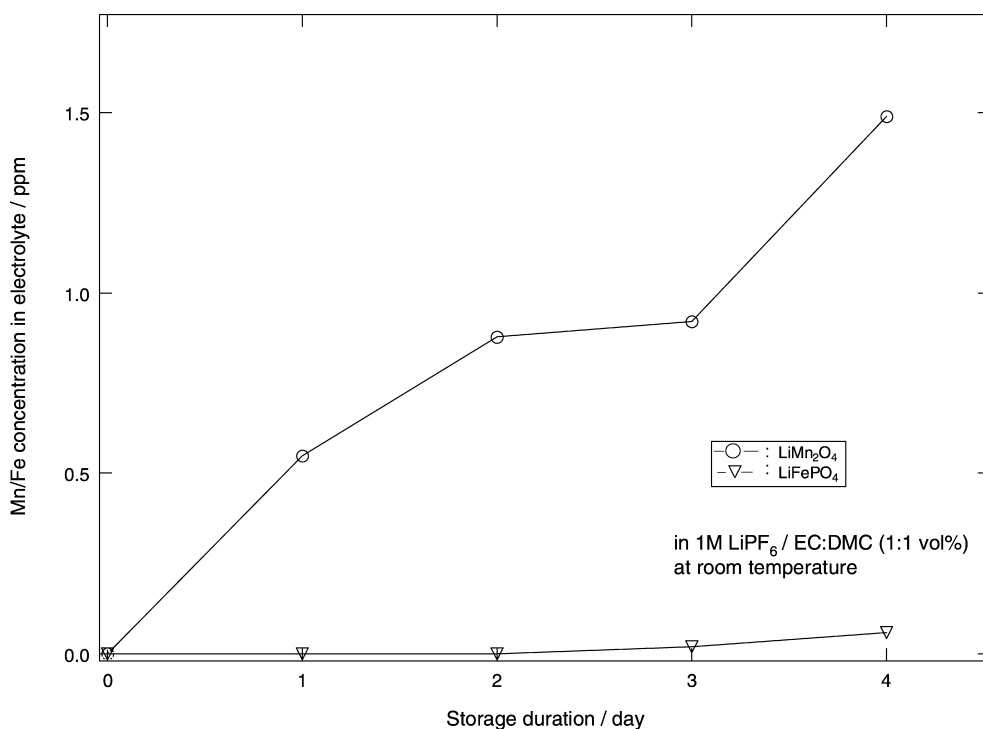


Fig. 6. Mn and Fe dissolution from LiMn₂O₄ and LiFePO₄ pellets stored in 1 M LiPF₆ EC:DMC (1:1) electrolyte at RT for 4 days.

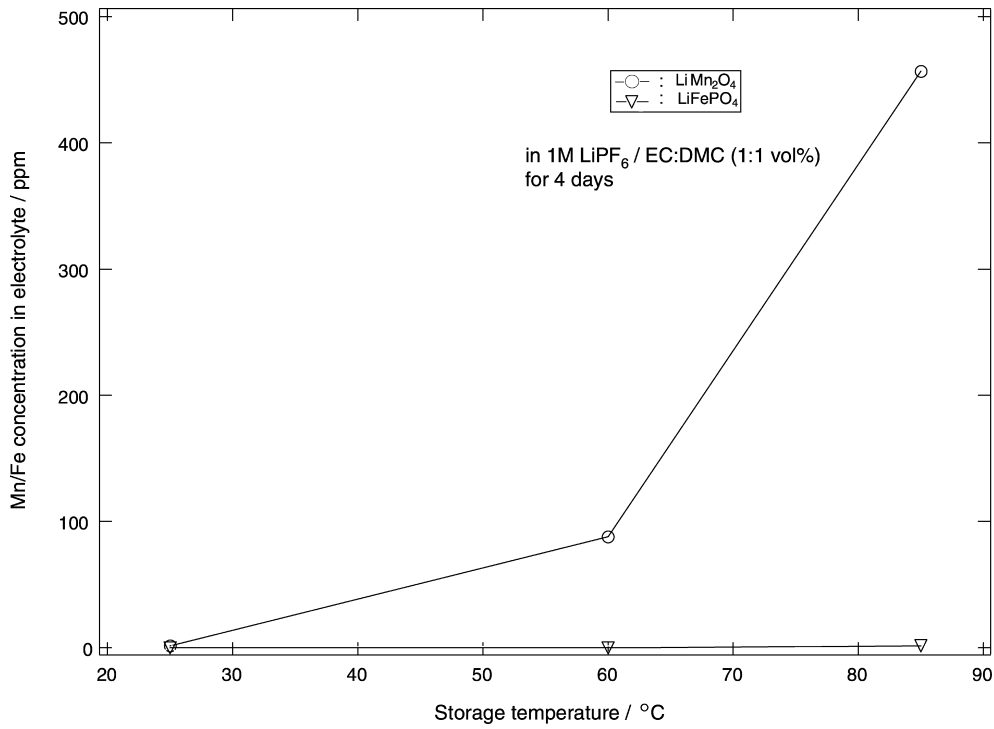


Fig. 7. Effect of storage temperature on Mn/Fe dissolution from LiMn₂O₄ and LiFePO₄ pellets, stored in 1 M LiPF₆ EC:DMC (1:1) electrolyte for 4 days.

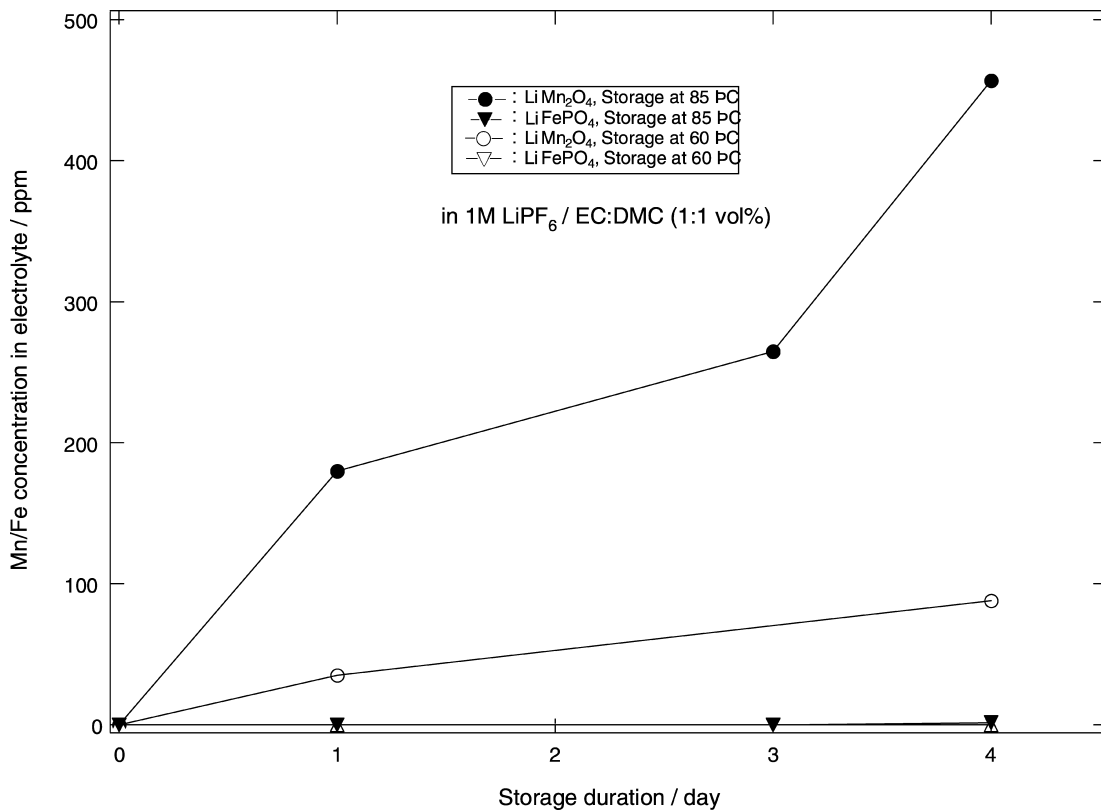


Fig. 8. Effect of storage duration on Mn/Fe dissolution from LiMn₂O₄ and LiFePO₄ pellets stored at 60 and 85 °C.

4. Conclusion

LiFePO₄ obtained through a liquid synthesis route shows relatively good cathode performance. Moreover, LiFePO₄ shows superior storage characteristics to LiMn₂O₄ in dry LiPF₆-based electrolytes at ambient and elevated temperatures as a result of lower Fe/Mn stability. However, traces of moisture in the LiFePO₄ prepared by the liquid route could be detrimental to the long term storage of such a material.

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