



Kinetics of electrochemical insertion of lithium ion into LiFePO_4 from aqueous 2 M Li_2SO_4 solution studied by potentiostatic intermittent titration technique

H. Manjunatha^a, T.V. Venkatesha^b, G.S. Suresh^{a,*}

^a Chemistry Research Centre, S. S. M. R. V. Degree College, Jayanagar, Bangalore 560041, India

^b Department of Chemistry, Kuvempu University, Jnanasahyadri, Shankaraghatta 577451, Shimoga, India

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ABSTRACT

Potentiostatic intermittent titration technique (PITT) has been used to study the lithium ion insertion into LiFePO_4 from aqueous 2 M Li_2SO_4 electrolyte along with cyclic voltammetry and electrochemical impedance spectroscopy (EIS) techniques. The current–time response to an applied potential step has been discussed for lithium insertion into LiFePO_4 from aqueous electrolyte and it is compared with that obtained with an organic electrolyte. The PITT technique is very useful in describing the whole intercalation mechanism. The effects of ohmic potential drops and charge-transfer resistances have been taken into account while predicting the current transients obtained with aqueous electrolyte and non-aqueous electrolyte. The deviation of current transients from ideal Cottrell behavior has been discussed in aqueous electrolyte and it is compared with that in presence of non-aqueous electrolyte. The characteristic diffusion time constant (t^0) in 2 M Li_2SO_4 is found to be 4.71 s and that in non-aqueous $\text{LiAsF}_6/\text{EC}–\text{DMC}$ electrolyte is 248 s. The chemical diffusion coefficient (D), an important kinetic parameter, calculated from PITT during intercalation process is found to be varying between 10^{-12} and 10^{-14} $\text{cm}^2 \text{s}^{-1}$ in aqueous electrolyte and between 10^{-13} and 10^{-15} $\text{cm}^2 \text{s}^{-1}$ in non-aqueous electrolyte.

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1. Introduction

LiFePO_4 has been receiving much attention as a next generation cathode material for rechargeable lithium ion batteries due to its superior thermal stability, less toxicity and low cost [1,2]. The electrochemical behavior of this material in non-aqueous lithium electrolytes is widely reported in the literature [3–7]. In aqueous electrolytes, the electrochemical behavior of LiFePO_4 has been reported by few authors [8–10]. LiFePO_4 undergoes partially reversible oxidation/reduction via lithium insertion/extraction mechanism due to the formation of FePO_4 during extraction process [8]. Since the rechargeable batteries with aqueous electrolytes have several potential advantages over non-aqueous electrolytes like low cost, safety, performance and environmental friendliness, a detailed study of the lithium ion insertion and de-insertion processes at LiFePO_4 cathode material and its comparison with that in non-aqueous electrolytes is necessary in realizing high power applications [11].

A comparative study of the electrochemical behavior of LiFePO_4 cathode material in aqueous (1 M $\text{LiNO}_3/\text{H}_2\text{O}$) and in non-aqueous (1 M $\text{LiClO}_4/\text{EC}–\text{DMC}$) electrolytes has been reported by Tarascon

et al. [12,13] using cyclic voltammetry. The CV profile obtained for LiFePO_4 in 1 M $\text{LiNO}_3/\text{H}_2\text{O}$ electrolyte exhibits a narrow redox peaks compared to that obtained in 1 M $\text{LiClO}_4/\text{EC}–\text{DMC}$ organic electrolyte indicating a fast reaction kinetic in the aqueous electrolyte. From CV profiles, a plot of capacity of LiFePO_4 as a function of scan rate shows that the capacity fading in 1 M $\text{LiNO}_3/\text{H}_2\text{O}$ was found to be low (24% of initial capacity) compared to that (61.8% of initial capacity) in 1 M $\text{LiClO}_4/\text{EC}–\text{DMC}$ electrolyte. A plot of current density vs. $\Delta E_p/2$ (ΔE_p is the peak potential difference and $\Delta E_p/2$ – equal to polarization of the cell) gave a linear evolution indicating ohmic behavior. The calculated cell resistance which uses aqueous electrolyte is found to be one order of magnitude less than that of the cell which uses the organic electrolyte ($86 \Omega \text{cm}^2$ in 1 M LiNO_3 and $643 \Omega \text{cm}^2$ in 1 M $\text{LiClO}_4/\text{EC}–\text{DMC}$ electrolyte). The EIS study of electrode–solution interface at LiFePO_4 exhibits a remarkable difference in aqueous and non-aqueous electrolytes [12]. The Nyquist plots of the impedance spectra of LiFePO_4 obtained in 1 M $\text{LiClO}_4/\text{EC}–\text{DMC}$ electrolyte is complex with several submerged semicircles among which one is due to the diffusion of lithium ion through SEI layer. There is an increase in the global interfacial resistance in organic electrolytes which may be due to the following facts; (a) the formation of stable surface–electrolyte interface (SEI) layer, (b) in organic solvents, the solvation of lithium ion cannot be ignored due to the higher dipole moment of the solvent (for $\text{EC}/\text{DMC} \sim 16 \times 10^{30} \text{Cm}$ vs. $6.07 \times 10^{30} \text{Cm}$ for H_2O) and (c) less

* Corresponding author. Tel.: +91 80 22453665; fax: +91 80 26654920.

E-mail address: sureshssmrv@yahoo.co.in (G.S. Suresh).

efficient surface wettability of organic solvents. This confirms the better rate capability of LiFePO_4 in 1 M $\text{LiNO}_3/\text{H}_2\text{O}$ electrolyte. Since the electrolyte does not exist inside the solid matrix of LiFePO_4 , the major influence of the nature of electrolyte must be on the electrode–solution interface. Therefore the electrochemical kinetics of LiFePO_4 electrode is dominated by the charge–transfer process at the electrode–solution interface. Lee and Pyun [14] have also reported similar results for LiMn_2O_4 electrode in aqueous and non-aqueous electrolytes. EIS studies of LiMn_2O_4 cathode material shows that the impedance spectra in aqueous electrolytes are quite different from those obtained in non-aqueous electrolytes. They proposed that the surface–electrolyte interface (SEI) layer is absent in aqueous systems and bare electrode is directly exposed to the electrolyte. The charge transfer resistance is lowered by one order of magnitude compared to that in non-aqueous electrolyte. In conclusion, the lithium de-insertion/insertion kinetics is mainly controlled by the low electrical conductivity and high interfacial resistance in presence of organic electrolyte and in presence of aqueous electrolyte fast reaction kinetics is observed due to high electrical conductivity of the aqueous electrolytes and low interfacial impedance offered by solid solution interface. The study of chemical diffusion coefficient of Li-ion is one of the most important kinetic characteristics of Li-ion insertion compounds. The kinetic studies are generally made under the assumption that the lithium diffusion in the solid state of the electrode is the rate determining step of the overall Li-insertion/de-insertion processes [15]. It has been reported for non-aqueous systems that the potentiostatic current transients measured on various transition metal oxides such as LiCoO_2 , LiNiO_2 , LiMn_2O_4 and V_2O_5 never follow the diffusion-controlled reaction, i.e. the Cottrell behavior [16]. The cyclic voltammetry studies can only offer time or average values of D related to the potential range around the voltammetric peak. When highly resolved data on the kinetic parameters of the Li^+ de-intercalation and intercalation are required, one should apply well resolving (with respect to potential) electro analytical techniques [17].

Weppner and Huggins [18–20] developed a useful electro analytical approach known as potentiostatic intermittent titration technique (PITT) to characterize the kinetics of the electrochemical formation of some metallic alloys. Later the technique was applied for the characterization of the diffusion kinetics of guest ions in ion-insertion electrodes [21–28]. The determination of diffusion constants in PITT relies on Fick's diffusion equation. The goal of this work is to study the kinetics of Li ion intercalation into LiFePO_4 from aqueous 2 M Li_2SO_4 solution, determine kinetic parameter such as chemical diffusion coefficient of Li ion and compare with that obtained in non-aqueous electrolyte using highly resolved relaxation techniques like PITT and EIS. Recently we have reported the kinetics of lithium insertion/de-insertion in LiMn_2O_4 from aqueous 2 M Li_2SO_4 solution using electrochemical impedance spectroscopy (EIS) [29].

2. Theory

Potential-step chronoamperometry and its particular extension, generally called potentiostatic intermittent titration technique used for the characterization of insertion electrodes were based on the standard theory of linear diffusion. This standard theory of linear slab diffusion treats spatially restricted diffusion as the rate determining step of overall lithium insertion reaction and ignores all other contributing stages like the ohmic potential drops in the solution/bulk of the electrode, double layer charging and phase transitions. Under such conditions of diffusion control (very fast insertion reaction kinetics), linear and restricted diffusion, the equivalent expression (Eq. (1)) for the output current response to

a potential step is obtained by solving the linear diffusion equation (Eq. (2)).

$$I(t) = \frac{\Delta Q}{(\pi t t^0)^{1/2}} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(\frac{-n^2 t^0}{t}\right) \right] \quad (1)$$

$$\frac{\partial c_{\text{Li}^+}}{\partial t} = D \frac{\partial^2 c_{\text{Li}^+}}{\partial x^2} \quad (2)$$

where I is the diffusion current, t -elapsed time from the beginning of the step, t^0 is the characteristic diffusion time constant and ΔQ is the total Faradaic charge inserted during a potential step. ΔQ is obtained by integrating the current–time curve which will be equal to $FAL\Delta c$ (where Δc or ∂c are the small change in the concentration of electro active species during a small potential step Δt or ∂t). D is the chemical diffusion coefficient of Li^+ ion. This expression (Eq. (1)) is suitable for measurements in short-time domain ($t \ll t^0$) and it converges rapidly in the long time domain ($t \gg t^0$). Neglecting all the exponential terms in Eq. (1) and substituting the values for t^0 ($t^0 = L^2/D$), the well known Cottrell relationship is obtained for short times.

$$It^{1/2} = \frac{D^{1/2} \Delta Q}{L\pi^{1/2}} \quad (3)$$

where L is the diffusion length. The effects of ohmic potential drops and slow charge-transfer kinetics on the semi-infinite diffusion (Cottrell behavior) response of the classical, solute redox species were discussed qualitatively by Bard and Faulkner [30]. The first theoretical work focusing on the response of insertion electrodes to a potential step by taking into account the kinetic limitations of surface processes was given by Krapivinyi et al. [31,32] for hydrogen extraction from metallic sheets using large amplitude potential steps. A similar work was reported later by Chen et al. [33] for hydrogen absorption process in thin metal films or foils under restricted linear diffusion conditions assuming no hydride formation. This model which assumes the metallic-type potential distribution in host/electrolyte system as discussed by Levi and Aurbach [21] is also applicable to ion-insertion processes in thin films, foils or particles of host materials with planar geometry. A comprehensive paper by Montella [34] has derived theoretical expressions for the linear slab diffusion current transients caused by small potential steps by extending the model used by Chen et al. [33] to consider the effects of ohmic potential drops and slow interfacial kinetic limitations. The author has convincingly proved that the effects of the slow interfacial charge-transfer and ohmic potential drop have strong and unavoidable influence on chronoamperometric and chronocoulometric data. In addition to the effects of slow diffusion due to ohmic resistance and slow charge-transfer process, the kinetics of lithium insertion is also complicated by the ion-transport through the SEI layer. This factor has been elaborated by Churikov et al. [35,36]. They suggested that the passive surface layer is the chief factor which limits the transfer rate of guest species in the interface and electrochemical impedance spectroscopy technique is more useful due to the fact that the slow interfacial kinetics cannot be distinguished from ohmic drop effects in experimental chronoamperograms.

Owing to the above facts, any treatment of such data using plain formula like the limiting Cottrell equation with an aim to determine the chemical diffusion coefficient of guest species in the host material leads to underestimated values. Taking advantage of a similar theory with the consideration of retarded diffusion of charged particles in the electrode bulk and hindered charge-transfer through the electrode/solution interface, the papers [34–36] have analytically treated the process proceeding in the intercalation electrodes on applying a potential step. Montella [34] and Churikov [36] have derived the following expressions (Eqs. (4) and (5), respectively) for the Faradaic current by treating quantitatively and in general form

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