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Kinetics of lithium insertion into $LiMnPO_4$ from aqueous saturated LiOH: A study using galvanostatic and potentiostatic intermittent titration techniques

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ABSTRACT

Galvanostatic and potentiostatic intermittent titration techniques have been used to study the lithium ion insertion into $LiMnPO_4$ from aqueous sat. LiOH electrolyte and 1 M $LiPF_6$/EC-DMC. The potential–time and current–time responses of $LiMnPO_4$ obtained from chronopotentiometry and chronoamperometry respectively have been discussed for lithium insertion into $LiMnPO_4$ from the aqueous electrolyte and it is compared with that obtained with the non-aqueous 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 characteristic diffusion time constant (t^o) in sat. LiOH is found to be 24.1 s and that in non-aqueous 1 M $LiPF_6$/EC-DMC electrolyte is 51.2 s. The chemical diffusion coefficient (D), an important kinetic parameter, calculated from GITT and PITT during intercalation process is found to be varying between 10^{-11} and 10^{-13} $cm^2\,s^{-1}$ in both aqueous and non-aqueous electrolytes.

1. Introduction

Since lithium iron phosphate ($LiFePO_4$) was introduced as cathode material for rechargeable lithium batteries by Padhi et al. [1], attempts have been made to substitute iron with other transition metals including Mn, Ni, Co etc. [2,3]. These cathode materials with a phospho-olivine structure have potential advantages such as lower toxicity, low cost, superior chemical and thermal stability and high theoretical capacitance (170 mAh g^{-1}) over the other cathode materials such as $LiCoO_2$, $LiNiO_2$ and spinel $LiMn_2O_4$. The presence of strong covalent bonds in $(PO_4)^{3-}$ tetrahedral poly anions do not allow any structural rearrangement during lithium insertion/extraction processes. Most of the work on this class of cathode materials has been devoted toward the synthesis and characterization of $LiFePO_4$ due to its attractive features such as cheap, less toxic and environmental friendlyness. However, $LiFePO_4$ suffers from poor electrical conductivity of the order of 10^{-9} S cm^{-2} [4]. To overcome this problem, $LiMnPO_4$ appears to be the best candidate among $LiMPO_4$ family despite its poor electrochemical performance in non-aqueous electrolytes [5–7]. $LiMnPO_4$ is particularly attractive as cathode material for rechargeable lithium batteries due to its high electrode potential of 4.1 V vs. Li which is superior to $LiFePO_4$ (3.6 V vs. Li). In aqueous electrolytes, the literature available on electrochemical performance of $LiMnPO_4$ is limited. Minakshi et al. [8] have reported the preliminary investigations of $LiMnPO_4$ in sat. LiOH solution. It undergoes electro-oxidation to form $MnPO_4$ and the reaction is reversible. Later they have improved its performance by adding TiO_2 additive which is proven to suppress the proton de-insertion/insertion from aqueous solutions [9]. However, the cycling efficiency of $LiMnPO_4$ is poor. It is well known that the cycling efficiency and/or rate capability depends on the kinetics of lithium insertion/de-insertion reactions. Therefore a better understanding of kinetics of lithium insertion into $LiMnPO_4$ from aqueous solutions is necessary in realizing an aqueous rechargeable lithium battery which is thought to the safe in applications such as hybrid electric vehicles (HEVs). The chemical diffusion coefficient of lithium (D) is the important kinetic parameter. Cyclic voltammetry can only offer time or average values of D related to the potential range around the voltammetry peak. When highly resolved data on the kinetic parameters of the Li^+ de-intercalation and intercalation processes are required, one should apply well resolving (with respect to potential) electro analytical techniques.

Weppner and Huggins [10–12] developed useful electro analytical techniques known as galvanostatic and potentiostatic intermittent titration techniques [GITT and PITT] to characterize the kinetics of the electrochemical formation of some metallic alloys. Later the technique was applied to the characterization of the diffusion kinetics of guest ions in ion-insertion electrodes [12–19]. The determination of diffusion constants in PITT relies on Fick's diffusion equation. Our goal is to study the kinetics of Li ion intercalation into $LiMnPO_4$ from aqueous sat. LiOH

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solution and determine kinetic parameter such as chemical diffusion coefficient and compare that with the values obtained in non-aqueous electrolyte using highly resolved relaxation techniques such as GITT and PITT. Recently we have reported the kinetics of lithium insertion/de-insertion in $LiMn_2O_4$ using electrochemical impedance spectroscopy (EIS) [20].

2. Theory

2.1. General conditions

In the present study, the $LiMnPO_4$ electrode used is porous in nature. Lithium transport in porous electrodes is represented by a combination of sequential transfer processes occurring in a single particle of the $LiMnPO_4$ material and in the electrolyte filling the pores. A detailed description of a porous electrode system model has been given by Churikov et al. [21] for $LiFePO_4$ electrode in organic electrolyte. We assume the same model for describing the lithium intercalation into $LiMnPO_4$ from the aqueous sat. LiOH electrolyte and 1 M $LiPF_6$/EC-DMC organic electrolyte. The model treats the electrode system as a combination of separate spherical $LiMnPO_4$ particles surrounded by electrolyte and all particles have electric contact with the current collector. The $LiMnPO_4$ undergoes lithium de-insertion/insertion processes in accordance with the following reaction.

$$LiMnPO_4 \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} Li^+ + MnPO_4 \tag{1}$$

The transport of lithium ions in a single particle of $LiMnPO_4$ i.e. diffusion process proceeds only in the spherical layer adjoining the particle surface. Compared to the entire radius of the particle this layer is very thin. Therefore a flat configuration of the diffusion space is assumed. In such a case a planar linear diffusion task should be solved. The z-axis is normal to the support surface. The origin $z = 0$ corresponds to the internal boundary between the support ($z < 0$) and the host material ($z > 0$). L is the diffusion path length, c, the concentration of mobile Li^+ ions, t, time, I, the current density, A, total surface area of all particles, E, electrode potential, n, the number of electrons and F, Faraday's constant.

The phase transition $LiMnPO_4 \leftrightarrow MnPO_4$ on the internal phase boundary is a boundary condition of diffusion task. The insertion material is assumed to be at equilibrium when $t \leq 0$. So the initial concentration of the inserted lithium ions c_0 is the same through out the thickness of the diffusion layer ($0 \leq z \leq L$) and governed by the initial equilibrium electrode potential E_0. The boundary $z = 0$ is impermissible for guest species i.e. $c = 0$ when $z < 0$. On the external boundary, the transport processes in lithium containing electrochemical systems are restricted by retarded charge transfer across the external interface. This could also be due to the formation of Solid Electrolyte Interface (SEI) layer. A theoretical approach describing current response and potential responses in the presence of surface inhibition layer is reported [22]. The surface inhibition generates a difference between the concentration levels on both sides of SEI. The parameters, ΔE_{SEI} (polarization in SEI) and R_{SEI} (the electrical resistance of SEI) are the concerning factors of this interface. The rate constant H_S can be employed for the description of the restricted transport processes at the electrolyte/electrode interface corresponding to slow-interfacial Li-ion transfer across the SEI/particle boundary and the resistances due to the electrolyte and the electrode. Under these conditions the task is reduced to solving the one dimensional diffusion equation (Fick's second law),

$$\frac{\partial c_{Li+}}{\partial t} = D\frac{\partial^2 c_{Li+}}{\partial z^2} \qquad 0 \leq z \leq L, \quad t \geq 0 \tag{2}$$

With the initial condition

$$c = c_0, \quad \text{at} \quad t = 0 \tag{3}$$

and boundary conditions

$$\left(\frac{\partial c}{\partial z}\right)_{z=0} + \frac{I}{nFD} = 0, \quad t \geq 0 \tag{4}$$

$$\left(\frac{\partial c}{\partial z}\right)_{z=L} + h(c_{z=L} - c_0) = 0, \quad t \geq 0 \tag{5}$$

Here, one should introduce the concentration–potential relationship and take into account the total polarization of the insertion electrode (ΔE) under current. This total polarization of the electrode is a sum of the ohmic potential drop in the electrolyte, voltage drop across the electrode–electrolyte interface (together called ΔE_S) and a shift in the electrode potential E due to changes in the boundary concentration of the potential determining lithium ions ($c_L = c(L)$). The voltage drop across the electrode/electrolyte interface is caused by the electrode polarization due to gradual charge-transfer (ΔE_{ct}) or the potential drop across the SEI layer (ΔE_{SEI}) and due to resistances of the electrolyte as well as the electrode or the sum of all these contributions (ΔE_S). The type of intercalation isotherm is very important when the potential dependencies of diffusion coefficients are concerned in order to achieve a linear relationship between current, I and potential drop across the electrode–electrolyte interface (ΔE_S). The Frumkin type intercalation isotherm is found to be most reliable one to fit it [23–25]. The PITT, GITT and EIS techniques used in the present study imply the existence of such a linear dependence between the electrode potential variations and the concentration. Thus abstracting from specific kind of absorption isotherm $c(E)$ and assuming the ohmic potential drop to be compensated (by the instrument), the following equation for low concentration deviation can be written [26,27].

$$\Delta E = \Delta E_S + \frac{\partial E}{\partial c_s}\Delta c_s, \quad \Delta c_s > 0 \tag{6}$$

where $\Delta c = (c_L - c_0)$ is the deviation of boundary concentration of guest species from initial concentration, dE/dc is the derivative of the electrode potential with respect to composition at $c = c_0$. The solutions of Eqs. (2)–(6) further depend on the additional conditions defined by the experimenter. For example, in case of small potentiostatic perturbation mode, the current density and surface parameters, ΔE_S and R_Ω satisfy the ohm's law in the linear region assuming ohmic resistances are compensated by the instrument:

$$\Delta E_S = IR_\Omega \qquad \Delta E = \text{const}; \quad t > 0 \tag{7}$$

where R_Ω is the sum of the resistances due to bulk electrolyte and solid electrode. (The experiments are carried out in the absence of IR_Ω drop compensation mode of the instrument.) Therefore, the above theory holds good.

2.2. Chronopotentiometry

In the galvanostatic conditions, the surface polarization, ΔE_{SEI} is constant (Eq. (7)) and it will monitor the concentration distribution. At $z = L$ boundary, retarded lithium transfer occurs. This retarded lithium transfer does influence the rate of the lithium transfer process and hence it is characterized by the rate constant, H. The rate constant is described by Eq. (5) where,

$$h = \frac{H}{D} \tag{8}$$

$c_z = L$ and c_0 is the lithium concentration on both sides of the boundary. Accordingly, a rate constant H_S can be employed for