



Evaluation of apparent lithium-ion diffusion coefficients in FePO₄/LiFePO₄ cathode material particles from linear non-equilibrium thermodynamics and principle of electroneutrality



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ABSTRACT

A generalized mathematical model, which describes the process of lithium extraction/insertion in active material particles of insertion cathodes, is developed from linear non-equilibrium thermodynamics and the principle of electroneutrality. The model reveals theoretical relations between the intrinsic and apparent transport parameters of lithium-ions and electrons. Calculation formulas for apparent lithium-ion diffusion coefficient D_1^* are deduced from the model. A simple trial calculation is introduced to evaluate the cross-phenomenological coefficient of the Onsager reciprocal relationship.

By means of referenced intrinsic diffusion coefficients, calculated by ab initio methods, calculations of D_1^* upon charge/discharge for the lithium iron phosphate cathode material (FePO₄/LiFePO₄) are presented. The calculated values of D_1^* are within those previously measured experimentally. In the range of lithium ion contents $0.02 \leq x \leq 1.0$, the values of D_1^* during charge/discharge vary in the range 10^{-12} – 10^{-14} cm² s⁻¹ and decrease with increasing x . The mean value of D_1^* is about 10^{-13} cm² s⁻¹, which is five to six orders of magnitude lower than the intrinsic diffusion coefficients.

The calculation results indicate that lithium ion diffusion in the active material particles is coupled with electron conduction, and the co-diffusion of lithium ions and electrons is limited by the electron conduction due to the low intrinsic conductivity of FePO₄/LiFePO₄.

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1. Introduction

Lithium ion insertion compounds, e.g. Li_xFePO₄, Li_xCoO₂, and Li_xMn₂O₄, have been used as electroactive materials of insertion cathodes in lithium ion secondary batteries [1,2]. Compared with other electroactive materials of insertion electrodes, olivine-type lithium iron phosphate [3–5] shows better electrochemical performance as an active cathode material, having the following advantages:

- 1) stable structure, operational safety;
- 2) good cycling performance of the insertion/extraction processes of lithium ions;
- 3) inexpensive; and
- 4) non-toxic.

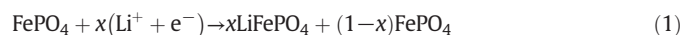
However, it has two major drawbacks:

- 1) a low conductivity, only 10^{-9} – 10^{-10} S cm⁻² [2,4,5], which causes a significant Ohmic loss in the electrode and

- 2) in practice, the utilization of the active material decreases significantly with an increase in the discharge current. For application of a lithium iron phosphate cathode, a thin electrode and fine particles of the active material are required to reduce the solid diffusion distance of lithium ions [6].

The process of Li ion insertion/extraction, i.e. the process of discharge/charge of the cathode, occurs in the active material of the lithium iron phosphate cathode. Stoichiometric expressions for FePO₄/LiFePO₄ cathode reactions can be written as follows:

Discharge reaction (insertion):



Charge reaction (extraction):



where x ($0 \leq x \leq 1$) is the lithium content i.e. the Li-ion insertion degree.

According to Eqs. (1) and (2), the composition of the active material constantly changes during the processes of discharge/charge, and the

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processes are inseparable from the motions of both lithium ions and electrons in the active material.

From an electrode kinetics point of view, the process of lithium ion insertion (i.e., the discharge reaction) is comprised of at least three series steps: (i) lithium ions transport from electrolyte to the surface of active material FePO_4 in the solid cathode by mass transfer and migration; (ii) lithium ions insert into the lattice of FePO_4 on the surface with the gain electrons, which is regarded as “electrochemical insertion reaction” driven by overpotential [6]; and (iii) lithium ions with electrons diffuse from the surface to the bulk of FePO_4 , and form the new phase LiFePO_4 , which is regarded as “solid-phase diffusion” driven by concentration difference [6,7]. On the other hand, the process of Li ion extraction (i.e., the charge reaction) involves the reverse sequence of steps. Notably, the diffusion of lithium ions in LiFePO_4 has been experimentally investigated by Nishimura et al. in Ref. [8] in which a lithium motion as a curved one-dimensional chain was proved by a long-awaited experimental evidence, and lithium distribution along the [010] direction was clearly visualized.

The solid-phase diffusion of lithium ions is the characteristic step of the insertion electrode that distinguishes it from other common electrodes. Moreover, the diffusion of Li ions in $\text{FePO}_4/\text{LiFePO}_4$ is typically the slowest step, making it the rate-limiting step of the insertion or extraction process [2,3,6]. Hence the diffusion coefficient of lithium ions is clearly one of the most important physical parameters for a mathematical description of the insertion/extraction kinetics. Unfortunately, the diffusion coefficient needs to be obtained on-line during discharge or charge, but is difficult to measure accurately by common electrochemical methods under such circumstances [2,9–11].

It is unsatisfactory that the reported values of the apparent lithium ion diffusion coefficients measured for $\text{FePO}_4/\text{LiFePO}_4$ cathodes cover a wide range of 10^{-10} – 10^{-17} $\text{cm}^2 \text{s}^{-1}$ [2,11]. The variation in measured values of the apparent diffusion coefficient arises from various factors, such as the synthesis procedure, particle size, quality of carbon coating, state of discharge/charge, measurement and simulation technique. However, it is generally believed that the apparent lithium ion diffusion coefficients are of the order of 10^{-13} – 10^{-16} $\text{cm}^2 \text{s}^{-1}$ [2,9,10,12].

The rapid development of first-principles methods, i.e. density functional theory (DFT) and ab initio calculations, has now potentially provided the theoretical tools for researchers to calculate Li-ion diffusion coefficients in the diffusion process [7]. Morgan assumed a high concentration of highly mobile electrons [13], and thereby he evaluated so-called “intrinsic” Li-ion diffusion coefficients using ab initio calculations for the active material of $\text{FePO}_4/\text{LiFePO}_4$ electrodes. The theoretical values of the intrinsic Li-ion diffusion coefficients are 10^{-7} $\text{cm}^2 \text{s}^{-1}$ for FePO_4 ($x = 0$) and 10^{-8} $\text{cm}^2 \text{s}^{-1}$ for LiFePO_4 ($x = 1$), which are five to eight orders of magnitude larger than the experimentally measured values. Ignoring electronic conduction is most probably the main reason for the huge discrepancy between the intrinsic diffusion coefficients and the measured apparent diffusion coefficients.

It is suggested that electronic conduction is facilitated by small polarons in the lattice; the strong bonding of localized polarons will contribute to a high barrier for lithium ion transport, and may explain the discrepancies between the theoretical and experimental values [14–18]. In ref. [19], different components of Li-ion diffusion kinetics, including bulk diffusion, surface diffusion, polaron hopping, and lattice strain, were considered, and DFT + U was used to model electrons to localize polarons on Fe centers in FePO_4 . Li-ion diffusion coefficients were calculated as 6×10^{-7} $\text{cm}^2 \text{s}^{-1}$ in the bulk and 10^{-12} – 10^{-17} $\text{cm}^2 \text{s}^{-1}$ on the surface respectively. The authors concluded that surface diffusion could have a rate-limiting effect, albeit covering quite a wide range. However, the effect of electron conduction on the apparent diffusion coefficient remains unclear and is worthy of further exploration [2,3].

Studies have shown that [3,6,20], on discharge/charge of a lithium iron phosphate cathode, two solid-phase compounds exist in the active material; however, these are not in the forms of pure LiFePO_4 and pure FePO_4 as expressed in Eqs. (1) and (2), but two solid solutions of

“Li-rich” phase $\text{Li}_{1-\alpha}\text{FePO}_4$ ($\alpha \approx 0$) and “Li-deficient” phase $\text{Li}_\beta\text{FePO}_4$ ($\beta \approx 0$, with a small fraction of Li inserted into the lattice). Hence, the Li-ion diffusion mechanism of insertion/extraction may be related to the existing forms of the two solid solutions undergoing phase transition.

Currently, there are four physical models for the $\text{FePO}_4/\text{LiFePO}_4$ phase transition, which can be referred to as the “mosaic” model (2001) [21], the “shrinking core” model (2004) [6], the “domino-cascade” model (2008) [22], and the “class extended recovery” model (2009) [23]. Each model offers a different interpretation of the likely existing forms of the two solid solutions. For the solid-state diffusion of lithium ions, an important point is whether the Li-deficient and Li-rich solutions are separated by a phase interface, i.e., whether each solution exists in the form of a single phase within each particle. The equilibrium of Li ion concentration at such an interface, if present, would considerably reduce the concentration gradient, thereby retarding the diffusion rate [3,6]. However, there is considerable controversy concerning this long-term discussed topic of the solid-phase diffusion of Li ions in insertion electrodes [23,24].

While it remains difficult to acquire reliable apparent diffusion coefficients of lithium ions experimentally or by ab initio calculations, especially to meet the requirements of engineering design, herein we aim to open a new perspective based on non-equilibrium thermodynamics. In this way, we explore an effective evaluation method that may not only be embraced by engineers, but also provide a sound thermodynamic basis for further analyses of the microscopic kinetics of insertion electrodes.

2. Generalized model for Li-ion insertion electrodes

2.1. “Flows” of Li ions and electrons

As is well known, Lars Onsager and Ilya Prigogine, established linear non-equilibrium thermodynamics [25]. This approach permits the theoretical description of coupled multiform irreversible transport processes, such as electrical conduction and heat conduction, mass diffusion and heat conduction [25], binary diffusion [26,27], and so on. They pointed out that in these systems an irreversible process will cause a generalized thermodynamic “flow” that is driven by a certain generalized thermodynamic “force”, and that the “flow” and “force” satisfy a linear phenomenological relationship such as the phenomenological Fick’s law, Ohm’s law and Fourier’s Law. Importantly, when a variety of generalized “flows” occur simultaneously in multiform processes, they will interfere with each other to cause interaction (cross) effects.

Gibbs proved that the relation between diffusion flux (“flow”) and chemical potential gradient (“force”) is linear under isothermal conditions, thereby deduced the Fick’s law [25]. In the case of charged components, the electrochemical potential replaces the chemical potential, and can be expressed as a linear combination of chemical potential and Fermi energy. Accordingly, the relation between the flux and the gradient of electrochemical potential is linear. In a similar way, the flux of the charged species can be expressed as a linear combination of Fick and Ohm laws. Additionally, unlike the metals, the intrinsic electron conductivities in the insertion materials are quite low. According to the dilute solution theory the motion of electron (or hole) in the insertion materials can be treated as conduction of charged species [28,29].

In insertion electrodes, the active materials are in the form of micro-particles, in which the multiform transport processes occur. For an isothermal system, there are at least two flows in the particles, that is, lithium ion flow and electron flow. Therefore linear non-equilibrium thermodynamics should be able to describe the motion of a large number of lithium ions and electrons therein by using phenomenological relationships between “force” and “flow” as well as to clarify the interaction between the Li-ion “flow” and electron “flow”.

It’s a physical principle of nature that electric charge is conserved. Distinct from ordinary multiform processes, the Li-ion flow with

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