Prediction of Lithium Diffusion Coefficient and Rate Performance by using the Discharge Curves of LiFePO₄ Materials

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The lithium ion diffusion coefficients of bare, carbon-coated and Cr-doped LiFePO₄ were obtained by fitting the discharge curves of each half cell with Li metal anode. Diffusion losses at discharge curves were acquired with experiment data and fitted to equations. Theoretically fitted equations showed good agreement with experimental results. Moreover, theoretical equations are able to predict lithium diffusion coefficient and discharge curves at various discharge rates. The obtained diffusion coefficients were similar to the true diffusion coefficient of phase transformation electrodes. Lithium ion diffusion is one of main factors that determine voltage drop in a half cell with LiFePO₄ cathode and Li metal anode. The high diffusion coefficient of carbon-coated and Cr-doped LiFePO₄ resulted in better performance at the discharge process. The performance at high discharge rate was improved much as diffusion coefficient increased.

Key Words : LiFePO₄, Carbon coating, Cr doping, Diffusion coefficient, Fitting of the discharge curve

Introduction

Lithium iron phosphate (LiFePO₄) is a promising material for rechargeable lithium ion batteries due to its inexpensiveness, safety and long life. In addition, the efforts to improve ion/electron conductivity have been led to its high power density. Many studies have investigated coating[1-3] and doping[4-6] in order to improve cell performance. However, those studies have not fully explained the effect on lithium ion diffusion and phase transformation due to the difficulty and complexity of a transport process.

Lithium ion diffusion is considered as important factors that decide the performance of the electrode. The effects of ionic diffusivity on transport process have been investigated to reduce transport losses. Electro-analytical methods such as galvanostatic intermittent titration technique (GITT), potentiostatic intermittent titration technique (PITT) and electrochemical impedance spectroscopy (EIS) were used to understand the ion transport.[7,8] The diffusion coefficient obtained by these methods was useful to understand the ion transport process.

However, true ionic diffusion coefficient in the two-phase region is different to the value obtained GITT, PITT and EIS methods since they assumed Fick's law.[9] The apparent Li ion diffusion coefficients in the two-phase region were 2-3 orders of magnitude lower.[10-12] Therefore, the true diffusion coefficient has to be used to investigate the transport losses.[9]

In this paper, the lithium ion diffusion coefficient of three electrodes including bare, carbon-coated (LiFePO₄/C), carbon-coated and Cr-doped LiFePO₄ (LiFe₀.₉Cr₀.₁PO₄/C) were calculated in order to examine the improvement of diffusion coefficients through carbon coating and Cr doping. The LiFePO₄/C and Cr-doped LiFePO₄ showed excel-lent rate performance by facilitating the phase transformation and increasing conductivity.[13] Diffusion coefficient of LiFe₀.₉Cr₀.₁PO₄/C was supposed to be improved.

Diffusion coefficients were obtained by fitting discharge curves with experimental data. Diffusion losses were fitted to equations developed by the noninteracting gas model for the chemical potential of ions distributed in a solid matrix.[14] The equations were expressed as a function of the degree of Li.

Experimental

LiFePO₄ was obtained from mixtures of Li₂CO₃, FeC₂O₄·2H₂O, and NH₄H₂·PO₄ by heat treatment in a tube furnace at 600 °C under the atmosphere of Ar + 5% H₂ for 10 hours. Mixture was carried out for 3 h bowl milling at the 250 rpm rotating speed before heat treatment. LiFePO₄/C and LiFe₀.₉Cr₀.₁PO₄/C were obtained by adding 3% of carbon black powder and 10% of (CH₃CO₂)₇Cr₃(OH)₂ before mechanochemical reaction. These mixtures were heat treated at 750 °C.

The active materials were mixed with 5% polyvinylidene fluoride (PVDF) and 10% acetylene black (w/w) in an *n*-methyl pyrrolidone (NMP) solvent and coated onto a Al foil. After drying in a vacuum oven at 80 °C for 12 h, the electrode thickness was measure to be 60 μm and the mass of active material was about 5-7 mg cm⁻². The electrodes were placed in a standard coin cell (2032 type) with 1 M LiPF₆ in an ethylene carbonate/dimethyl carbonate/ethyl-methyl carbonate (EC/DMC/EMC) solution as electrolyte and a lithium foil as a counter and reference electrode. The Maccor 4000 battery cycler with cut-off voltages of 2.5-4.3 V was used to conduct charging and discharging process

of cathodes. EIS measurements of the cell were performed by using a Schlumberger model SI 1260 impedance/gain-phase analyzer connected to a Schlumberger model SI 1286 and the amplitude of the AC signal was 5 mV over the frequency range between 100 kHz and 10 mHz.

Results and Discussion

Theory and Calculations. Generally, discharge curve of LiFePO$_4$ shows two rapid voltage drop and flat regions. Rapid drop regions are the first and end of the Li intercalation process and flat region is two phase stage of FePO$_4$ and LiFePO$_4$. Discharge curves have been fitted to equations as a function of the degree of Li intercalation using resistances that caused voltage losses.[15-17] Charge transfer resistance (R_{ct}), ohmic resistance in the electrolyte (R_{ohm}) and diffusion resistance (R_{diff}) were main voltage losses that determine the discharge curve.[17] Among these, diffusion resistance was dominant one to determine the rapid drop at the end of the intercalation.

Discharge curves can be fitted by using these resistances and expressed as a function of the degree of Li intercalation. The equation describing the voltage curve is defined as:

$$E(x) = E_{ocv} - E_{ct} - E_{ohm} - E_{diff} \quad (1)$$

where E_{ocv} is the open circuit voltage of LiFePO$_4$ (3.4 V) and E_{ct}, E_{ohm} and E_{diff} are the potential drops due to charge transfer, ohmic loss in the electrolyte and progressive diffusion of lithium, respectively.

Based on the Tafel equation, the potential drop due to charge transfer is expressed as:

$$E_{ct} = \frac{RT}{nF\alpha} \ln\left(\frac{i}{i_0}\right), \quad (2)$$

where R is the gas constant, T is the absolute temperature, n is the electron moles, F is the Faraday constant, α is the transfer coefficient (assumed to 0.5), i is the current and i_0 is the exchange current.

At a very small current, the potential drop due to charge transfer can be written as:

$$E_{ct} = \frac{RT}{nF\alpha}\left(\frac{i}{i_0}\right), \quad (3)$$

Here, i_0 can be obtained from the value R_{ct} of measured by EIS by using the following equation[8]:

$$i_0 = \frac{RT}{nFR_{ct}}. \quad (4)$$

R_{ohm} and R_{ct} are the first and second intercepts of the semicircle in EIS measurements of Figure 1. The values of R_{ohm} for three kinds of electrode materials are similar to each other but those of R_{ct} are different from each other. The value of R_{ct} for the LiFePO$_4$/C is less than that of the LiFePO$_4$. LiFePO$_4$/C electrodes showed improvement of electronic conductivity. So, the value of R_{ct} for the LiFePO$_4$/C was highly reduced.

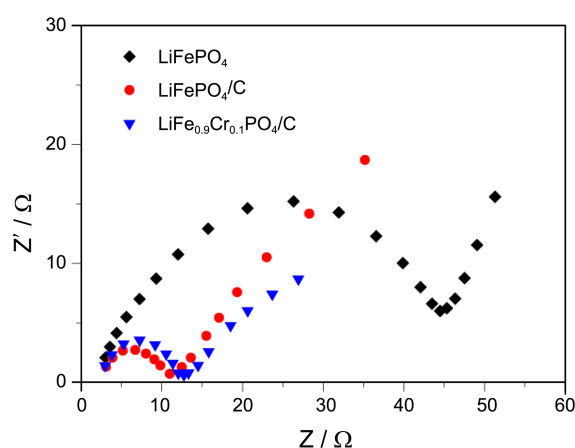R_{ohm} and R_{ct} were assumed as constant along the Li

Figure 1. EIS measurements of three LiFePO$_4$ cells at $x = 0.3$.

intercalation, since the effects of the difference at EIS measurements on the performance were negligible when compared to R_{diff}. R_{diff} was main resistance that determine the rapid potential drop along the Li intercalation.

From Ohm's law, the potential drop due to ohmic loss can simply be written as:

$$E_{ohm} = R_{ohm} \cdot i, \quad (5)$$

while the potential drop due to progressive diffusion of lithium can be expressed as:

$$E_{diff} = R_{diff}(x) \cdot i \quad (6)$$

Here, $R_{diff}(x)$ is defined as[14]:

$$R_{diff}(x) = \frac{L^2}{D \cdot Ve^2 N \frac{dx}{d\mu}} \quad (7)$$

where L is the characteristic diffusion length, D is the diffusion coefficient, V is the active material volume, e is the positive elementary charge, N is the number density proportional to the size of the host, x is the occupancy fraction of intercalation and μ is the chemical potential of the function of the ion intercalation and defined as [14]:

$$\mu(x) = E_0 + k_B T \ln\left(\frac{x}{1-x}\right). \quad (8)$$

where E_0 is the energy of sites and k_B is the Boltzmann constant.

The characteristic diffusion length, L, was assumed as the radius of the particle. XRD profiles and SEM images were used to observe the size distribution of LiFePO$_4$ particles. Radii of the particles were 20 nm, 18 nm, 23 nm for LiFePO$_4$, LiFePO$_4$/C, and LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C, respectively.

In the quasi-equilibrium approximation, the diffusion coefficient, D, is defined as[14,18]:

$$D = \frac{D_J}{k_B T} x \frac{d\mu}{dx} \quad (9)$$

where D_J is a kinetic or jump coefficient:

Table 1. Parameters used for the fitting the discharge curves

Parameters	Values
Gas constant, R	8.32 J K^{-1} mol^{-1}
Absolute temperature, T	298.15 K
Faraday constant, F	96,500 C mol^{-1}
Transfer coefficient, α	0.5
Positive elementary charge, e	1.6022×10^{-19} C
Charge density, $N \cdot e$	2.386×10^9 C m^{-3}
Boltzmann constant, k_B	1.38×10^{-23} J K^{-1}

Table 2. Resistances of three LiFePO$_4$ cells

	R_{ct} (Ω)	R_{ohm} (Ω)	R_{diff} (Ω)
Bare LiFePO$_4$	48	3	$27/(1-x)^9$
LiFePO$_4$/C	11	3	$5/(1-x)^2$
LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C	13	3	$0.05/(1-x)^5$

$$D_J = \frac{M_0}{x}\exp\left(\frac{\mu}{k_B T}\right)P(0,0) \qquad (10)$$

Here, M_0 is the ionic mobility coefficient for $x = 0$ and $P(0,0)$ is the probability for two nearest neighbor lattice sites to be vacant. For noninteracting lattice ga ses, $P(0,0) = (1-x)^2$, but it is a function of x in general.[14,18] However, for the case of intercalation electrodes in consideration, the determination of the functional form for D_J becomes an empirical process rather than a rigorous derivation, because significant effects such as the interactions amongst ions and the lattice distortions induced by the guest species have to be described as a function of x. To fit the experimental data, various functional forms for D_J were looked for and thus the following expression for R_{diff}:

$$R_{diff}(x) = \frac{L^2 k_B T}{D_J(x) \cdot V e^2 N x} = \frac{A}{(1-x)^B} \qquad (11)$$

was found to fit the data very well, where A and B are fitting parameters. Predicted $E(x)$ based on the calculated values of R_{diff} with Eq. (11) showed good agreement with the experimental voltage curves for three different electrode materials. Fitting parameters and constant values used in this study are summarized in Table 1. R_{ct}, R_{ohm} and R_{diff} of three LiFePO$_4$ are presented in Table 2.

Prediction of the Diffusion Coefficients. Figure 2 shows voltage losses of bare LiFePO$_4$ cell with 2C rate caused by R_{ct}, R_{ohm} and R_{diff}. The Values of R_{diff} from Eq. (11) calculated voltage losses of bare LiFePO$_4$ cell with 2C rate. In Figure 2, fitted discharge curve showed good agreement with experimental curve. Note that E_{diff} is main voltage loss compared other voltage drops in Figure 2. E_{diff} is a key factor that determine voltage drop at the end of the Li intercalation process.

Figure 3 shows E_{diff} of bare LiFePO$_4$, LiFePO$_4$/C and LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C in accordance with the amount of Li. E_{diff} of bare LiFePO$_4$ are higher than those of LiFePO$_4$/C and LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C. The range of LiFePO$_4$/C and
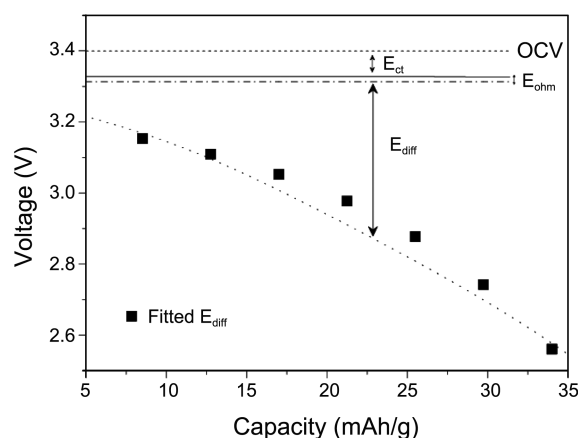
Figure 2. Voltage drops of bare LiFePO$_4$ cell caused by R_{ct}, R_{ohm} and R_{diff} with fitted values at 2C rate.
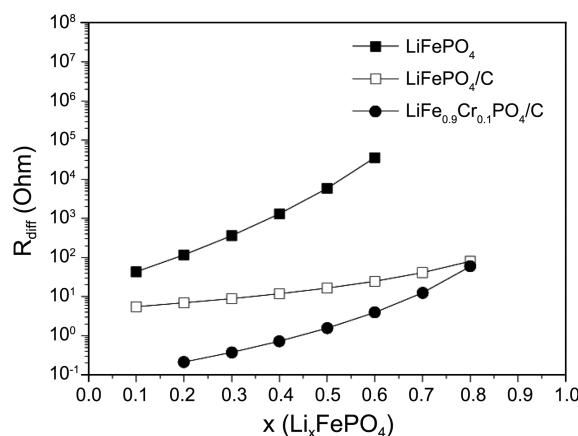
Figure 3. R_{diff} of bare LiFePO$_4$, LiFePO$_4$/C and LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C.
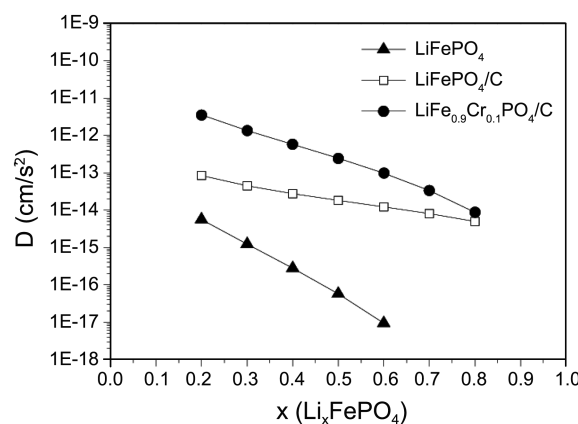
Figure 4. D of bare LiFePO$_4$, LiFePO$_4$/C and LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C.

LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C are between 0.1 and 100 which are 2-4 orders of magnitude lower than those of bare LiFePO$_4$.

D can be obtained by using Eq. (7), (8) and R_{diff}. In Figure 4, D of three electrodes are presented with logarithmic scale. D seems to be inversely proportional to R_{diff}. D of LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C and LiFePO$_4$/C are much higher than those of bare LiFePO$_4$. D of LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C are higher than those of LiFePO$_4$/C about 1 orders of magnitude. The
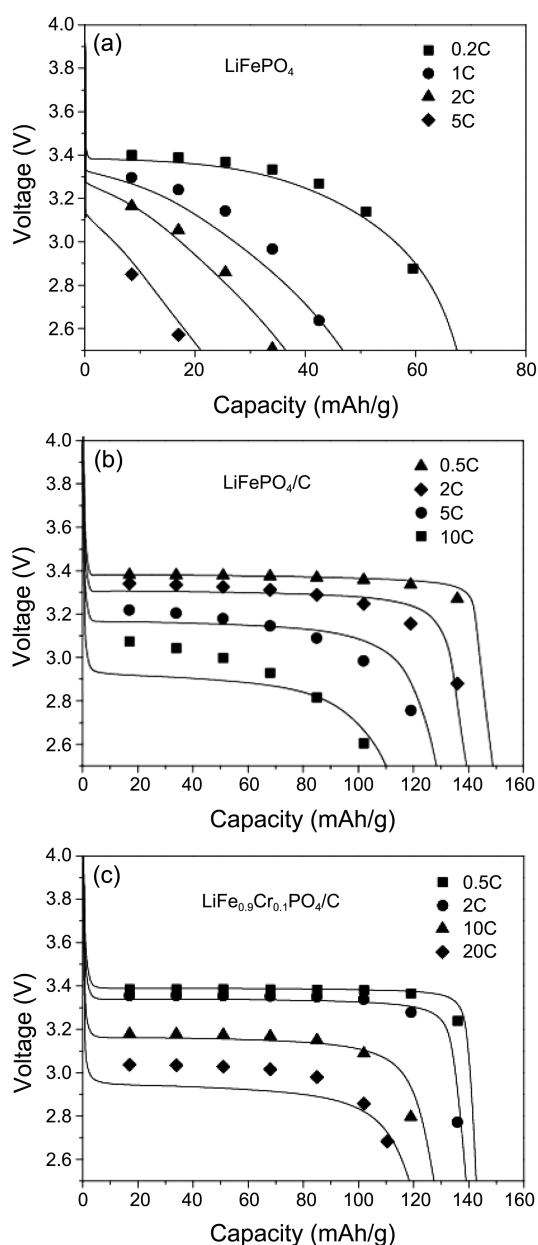
Figure 5. Discharge curves fitting: (a) bare LiFePO$_4$, (b) LiFePO$_4$/C and (c) LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C.

Figure 6. Predicted rate performances of three LiFePO$_4$: (a) bare LiFePO$_4$, (b) LiFePO$_4$/C and (c) LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C.

higher D of LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C is due to the formation of defects created by Cr dopant and fast phase transformation.[13] D of LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C are on the order of 10^{-13} cm/s^2 which are similar to the true diffusion coefficient[9] of phase transformation electrodes.

Mathematical expression of Eq. (11) was obtained after R_{diff} was fitted to four experimental discharge curves at the various charge rates. Figure 5 shows discharge curves of three electrodes and fitted values. From 0.2C discharge rate to 5, 10 or 20C, calculated expression of R_{diff} from Eq. (11) were fitted well to experimental curves. There were small differences between fitted values and experimental curves but cell performances were similar at the end of Li intercalation process.

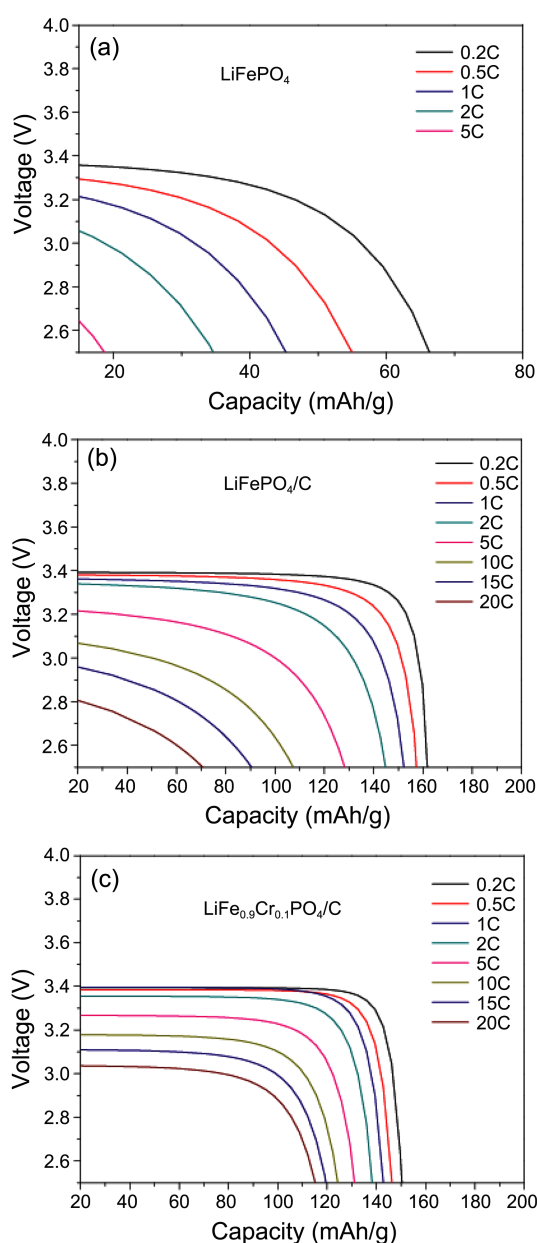**Rate Performances of LiFePO$_4$ Cells.** Mathematical ex-

pressions of R_{diff} could predict rate performances at various discharge rates. Predicted rate performances of three electrodes are presented in Figure 6. Bare LiFePO$_4$ showed the lowest performance as discharge rate increased due to its high diffusion resistance. Bare LiFePO$_4$ showed little performance when discharge rates were over than 10C. LiFePO$_4$/C showed better performance at the low discharge rate (about 0.2-1C) but performance reduced rapidly as discharge rate increased. At the low discharge rate, LiFePO$_4$/C led to a better performance since R_{ct} of LiFePO$_4$/C were lower compared to others. However, LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C showed good performance at the high discharge rate due to the low R_{diff} caused by the improvement of Li ion diffusion and fast phase transformation.

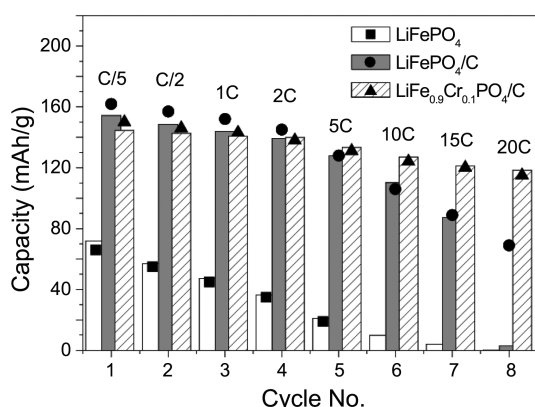Figure 7 shows rate performances of three LiFePO$_4$ with

Figure 7. Rate performances of bare LiFePO$_4$, LiFePO$_4$/C and LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C with predicted values (●, ▲, ■).

predicted values in Figure 6. Predicted results were found to be similar to the experimental rate performances. LiFePO$_4$/C showed better performance at the low discharge rate but LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C showed excellent rate performance at the high discharge rate. The enhancement of D at LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C causes great rate performance since diffusion resistance is main factor that determine the performance.

Prediction of Rate Performances by Simulation. Mathematically fitted equation could predict all discharge voltage. It is efficient and convenient methods to predict discharge curves by fitting only three or four discharge curves. As shown in Figure 6, many voltage curves could be obtained by using mathematically fitted equation.

Mathematically fitted equation showed characteristic of LiFePO$_4$, LiFePO$_4$/C and LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C electrodes because equation was based on R_{ct}, R_{ohm} and R_{diff}. Performance of LiFePO$_4$/C and LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C electrodes was enhanced by reducing R_{ohm} in Figure 6. By Cr-doping, LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C electrode showed excellent rate performance due to the improvement of R_{diff}.

Not only carbon coated and Cr-doped electrodes but other LiFePO$_4$ electrodes can be fitted to equations with R_{ct}, R_{ohm} and R_{diff}. Mathematically fitted equation with R_{ct}, R_{ohm} and R_{diff} can predict rate performance of other LiFePO$_4$ electrodes. Moreover, prediction system can optimize the electrode by using various R_{ct}, R_{ohm} and R_{diff}.

There have been many approaches to predict Li battery performances by conducting modeling. Transport phenomena models (Doyle and Newman) have been widely used in battery design because these models could predict battery system. Although mathematically fitted methods in this study are less accurate and difficult to predict performance without experiment, these methods are simple and time-saving models than transport phenomena models. It is easy and efficient methods to predict rate performance and diffusion coefficient than other models.

Conclusion

The lithium ion diffusion coefficients of bare, LiFePO$_4$/C

and Cr-doped LiFePO$_4$ were obtained by fitting the discharge curves. Charge transfer resistance (R_{ct}), ohmic resistance in the electrolyte (R_{ohm}) and diffusion resistance (R_{diff}) dependent on the electrode and discharge rate were used in order to calculate diffusion coefficients. R_{diff} was fitted to general mathematical expression and showed good agreement with the experimental voltage curves. Diffusion coefficients calculated with R_{diff} were similar to the true diffusion coefficient of phase transformation electrodes. D of LiFePO$_4$/C are on the order of 10^{-14} cm/s^2. D of LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C are higher than those of LiFePO$_4$/C about 1-2 orders of magnitude. Mathematical expressions of R_{diff} also predicted rate performances at various discharge rates. Bare LiFePO$_4$ showed lowest performance as discharge rate increased due to the high diffusion resistance. LiFePO$_4$/C showed better performance at the low discharge rate but LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C showed excellent rate performance the high discharge rate. LiFe$_{0.9}$Cr$_{0.1}$PO$_4$/C showed good performance at the high discharge rate due to the high D caused by the improvement of Li ion diffusion and fast phase transformation.

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