Decomposition reaction of LiPF$_6$-based electrolytes for lithium ion cells

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Abstract

The decomposition of LiPF$_6$ electrolytes with water was studied by measuring the water content after storage. The solvents used were ethylene carbonate (EC) + diethyl carbonate (DEC), EC + dimethyl carbonate (DMC), propylene carbonate (PC) + DEC, and PC + DMC mixed by the volume ratio 1 to 1, respectively. The experimental results were in good agreement with $-d[H_2O]/dt = k[H_2O]^2[LiPF_6]$. We obtained rate constants (k) from this empirical equation, with k increasing in the order of EC + DMC < EC + DEC < PC + DMC < PC + DEC. This order is in inverse proportion to the order of the dielectric constants of these solvents. Nonionized LiPF$_6$ dissociates to PF$_5$ and LiF in organic solvents, and PF$_5$ reacts with water. A solvent with a high dielectric constant increases the ionization of LiPF$_6$, thereby suppressing the reaction with water.
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1. Introduction

Lithium ion batteries that use LiPF$_6$ electrolytes have two disadvantages in comparison with other kinds of batteries that use aqueous solution. One is their thermal stability and the other is their reactivity with water. In the past decade, the thermal stability or thermal behavior of lithium ion batteries has been investigated energetically by differential scanning calorimetry (DSC) or accelerating rate calorimetry (ARC) [1–5]. Water is undesirable for lithium ion batteries and lithium batteries because it causes a decomposition of their components. It has been reported that water decomposes lithium alkyl carbonates, which are components of the solid electrolyte interphase (SEI) in a carbon anode for lithium ion batteries [6]. In addition, in lithium metal anodes, water reacts with lithium metal to generate hydrogen gas while simultaneously generating hydroxides and oxides, which have no ion

conductivity [7]. As mentioned above, water is detrimental to lithium batteries, but it is impossible to completely eliminate their exposure to water. There is at least 20 ppm water in commercial electrolytes for lithium ion cells [8]. Moreover, many cathode materials are highly absorbent, and they draw a great quantity of water into lithium batteries [8,9]. Methods to protect carbon and lithium metal anodes from water, a contaminant, have been investigated. One way is to cover carbon anodes with copper metal [1], while another is to add substances to electrolytes to protect the lithium metal [2].

The other problem caused by the presence of water in electrolytes is its reactivity with LiPF$_6$, making the handling of LiPF$_6$ electrolytes very difficult. LiPF$_6$ is widely used as salt for electrolytes of lithium ion batteries, however, because of its high ion conductivity. The mechanism of reaction between water and LiPF$_6$ in organic solvents has been studied by Hider et al. [10] and Aurbach et al. [11], and the following equations have been reported:
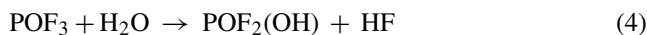
$$LiPF_6 \rightleftharpoons Li^+ + PF_6^- \tag{1}$$

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$$LiPF_6 \rightleftharpoons LiF + PF_5 \qquad (2)$$

$$PF_5 + H_2O \rightarrow POF_3 + 2HF \qquad (3)$$

$LiPF_6$, which is nonelectrolytic dissociative, produces PF_5, a strong Lewis acid, and PF_5 reacts with water.

Furthermore, it is possible that POF_3 may react with water in the following equation:

$$POF_3 + H_2O \rightarrow POF_2(OH) + HF \qquad (4)$$

Several papers regarding kinetic study of the reaction between $LiPF_6$ and water have been published. Regarding the transition of HF and water concentrations in an electrolyte that has 1 M $LiPF_6$ (1 M $LiPF_6$) in ethylene carbonate (EC) and dimethyl carbonate (DMC)(50:50 wt.%), Heider et al. [10] have reported that water concentrations decrease significantly. Exnar et al. [12] have reported the change in HF and water concentrations when water is added in 1 M $LiPF_6$/EC + ethyl methyl carbonate (EMC) (50:50 wt.%). They used a first-order reaction to evaluate a rate constant of the initial reaction in the order of $10^{-5} \, \mathrm{s}^{-1}$. Barlow [13] have studied the kinetics of the reaction between water and solid $LiPF_6$ and between water and $LiPF_6$ in organic solvents.

We investigated the solvation effects of various kinds of mixed solvents for lithium ion batteries and the effects of temperature when water was added to different electrolytes: 1 M $LiPF_6$/EC + diethyl carbonate (50:50 vol.%), 1 M $LiPF_6$/EC + diethyl carbonate (DEC) (50:50 vol.%), 1 M $LiPF_6$/propylene carbonate (PC) + DEC (50:50 vol.%) and 1 M $LiPF_6$/PC + DMC (50:50 vol.%). Based on our experiment, we determined the apparent rate constant of the reaction between water and $LiPF_6$ in alkyl carbonate mixed solvents at various temperatures using a pseudo-second-order reaction.

2. Experimental

The water content of 1 M $LiPF_6$/EC + DEC (50:50 vol.%), 1 M $LiPF_6$/EC + DMC (50:50 vol.%), 1 M $LiPF_6$/PC + DEC (50:50 vol.%), and 1 M $LiPF_6$/PC + DMC (50:50 vol.%), received from Tomiyama Co., was less than 20 ppm. In an argon-filled dry box (dew point under −60 °C), 20 ml of electrolytes and 100 μl of water were poured into Teflon containers (water content is about 5000 ppm), and the containers were shut with a rubber plug. The Teflon containers were taken from the dry box and placed in an incubator kept at
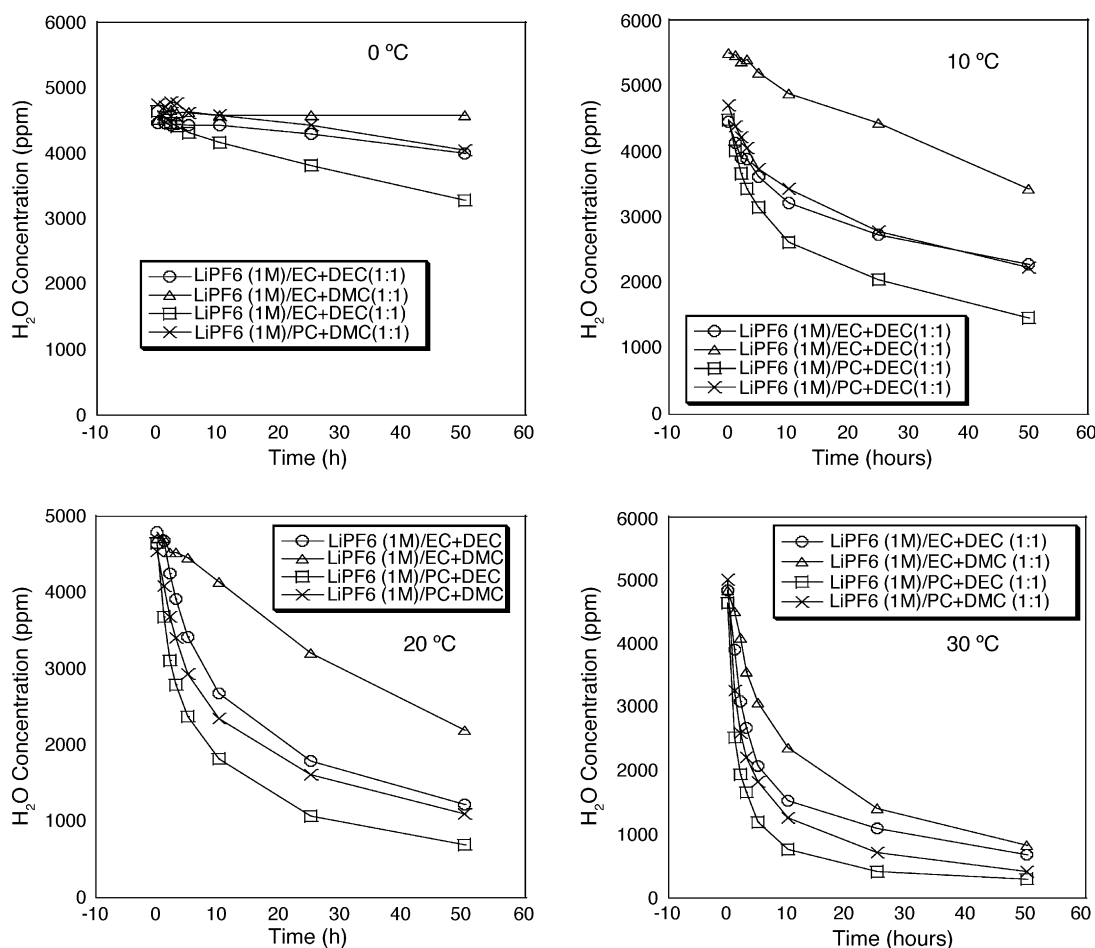

Fig. 1. Change in the water content in 1 M $LiPF_6$/EC + DEC, 1 M $LiPF_6$/EC + DMC, 1 M $LiPF_6$/PC + DEC, and 1 M $LiPF_6$/PC + DMC after adding approximately 5000 ppm water at 0, 10, 20, and 30 °C.

0, 10, 20, and 30 °C. The water content of the mixture was measured after 0, 1, 2, 3, 5, 10, 25, and 50 h by a Karl Fischer aquacounter (Hiranuma Co.). We also measured the density of $LiPF_6$ electrolytes with/without water using a pycnometer at 25 °C to evaluate the molar volume of water in $LiPF_6$ electrolytes.

3. Results and discussion

Fig. 1 shows the change in the water content over time. The water content in the electrolytes after 50 h decreased in the following order: 1 M $LiPF_6$/EC + DMC > 1 M $LiPF_6$/EC + DEC > 1 M $LiPF_6$/PC + DMC > 1 M $LiPF_6$/PC + DEC. The reason why different solvents influence the reaction kinetics between $LiPF_6$ and water is the solvent effect, an effect in which chemical equilibrium and the reaction rate in solvents are influenced by the difference of solvents. The reaction rate, and in extreme cases the reaction mechanism, are changed by the viscosity, polarity, or solvation of the solvents. In this case, we focus on the viscosity and polarity. Table 1 [14] shows the relative permittivity and viscosity of EC, PC, DEC, and DMC. The viscosity of a solvent at 25 °C might increase in the following order: DMC < DEC < PC, where EC is a solid at this temperature. Therefore, generally, PC + DEC has a larger viscosity than PC + DMC at room temperature. The larger a solvent's viscosity, the greater the difficulty of $LiPF_6$ to react with water. However, from the results of Fig. 1, the water content of 1 M $LiPF_6$/PC + DEC (50:50 vol.%) decreased rapidly than that of 1 M $LiPF_6$/PC + DMC (50:50 vol.%) at 20 °C and 30 °C. Therefore, it can be concluded that the viscosity dose not greatly affect the reaction between $LiPF_6$ and water. Table 1 shows that EC has a larger relative permittivity than PC, and DMC has a larger relative permittivity than DEC. Therefore, the relative permittivity of mixed solvent decreases in the following order: EC + DMC > EC + DEC > PC + DMC > PC + DEC. In organic solvents, nonionized $LiPF_6$ (not Li + and PF_6^-) reacts with water [10,11] (see Eq. (1)–(3)). In this case, the larger relative permittivity a solvent has, the more the levels of nonionized $LiPF_6$ decrease in solvents. Therefore, the larger a solvent's relative permittivity, the more difficult it is for $LiPF_6$ to react with water in that solvent. This hypothesis is in agreement with our results (Fig. 1). The difference in
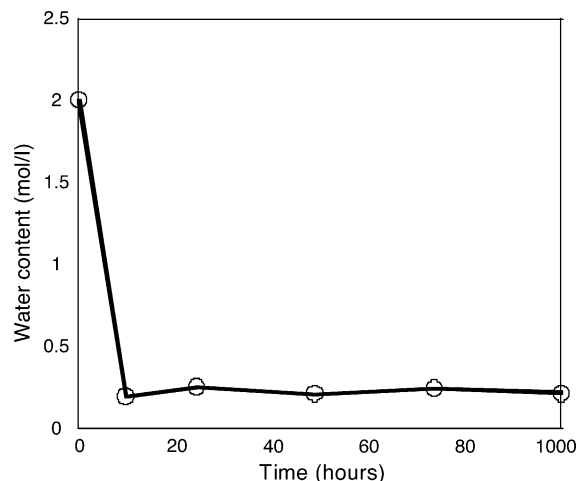

Fig. 2. Change in the water content in 1 M $LiPF_6$/PC + DEC(1:1) after adding 2 mol l^{-1} of water.

the relative permittivity of mixed solvents influences the rate constant of reaction between $LiPF_6$ and water.

The reaction speed of $LiPF_6$ with water in organic solvents also depends on the temperature (Fig. 1). Especially at 0 °C, it has been observed that the reaction hardly took place in EC + DMC even after 50 h.
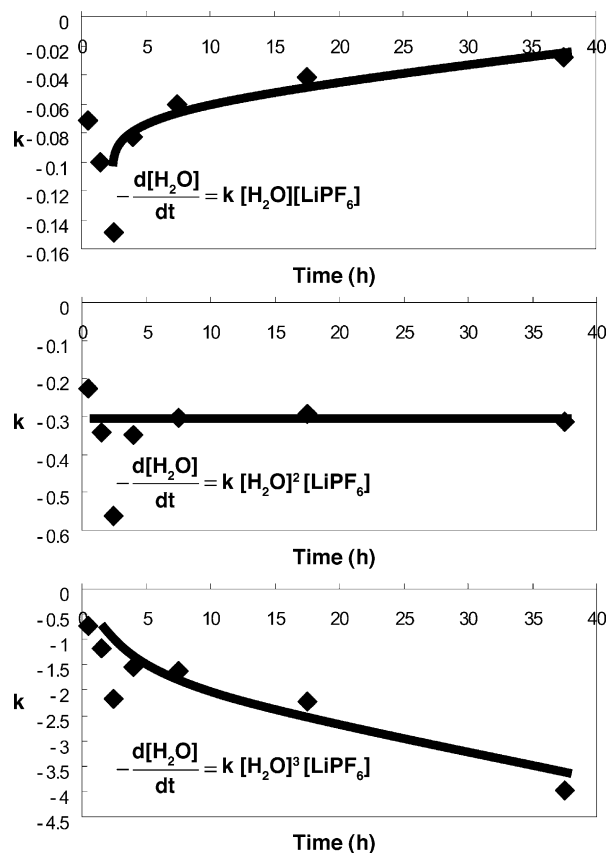

Fig. 3. The rate constant (k) obtained by solving various rate equations, $-d[H_2O]/dt = k[H_2O][LiPF_6]$, $-d[H_2O]/dt = k[H_2O]^2[LiPF_6]$, and $-d[H_2O]/dt = k[H_2O]^3[LiPF_6]$, of reaction between water and $LiPF_6$ in 1 M $LiPF_6$/EC + DMC at 30 °C.

Table 1
Relative permittivity (ε_r) and viscosity (η_0) of EC at 40 °C and PC, DEC, and DMC at 25 °C.

	ε_r	η_0
EC	90[a]	1.9[a]
PC	65	2.5
DEC	2.8	0.75
DMC	3.1	0.59

The data of EC was obtained at 40 °C.

[a] EC is a solid at ordinary temperature.
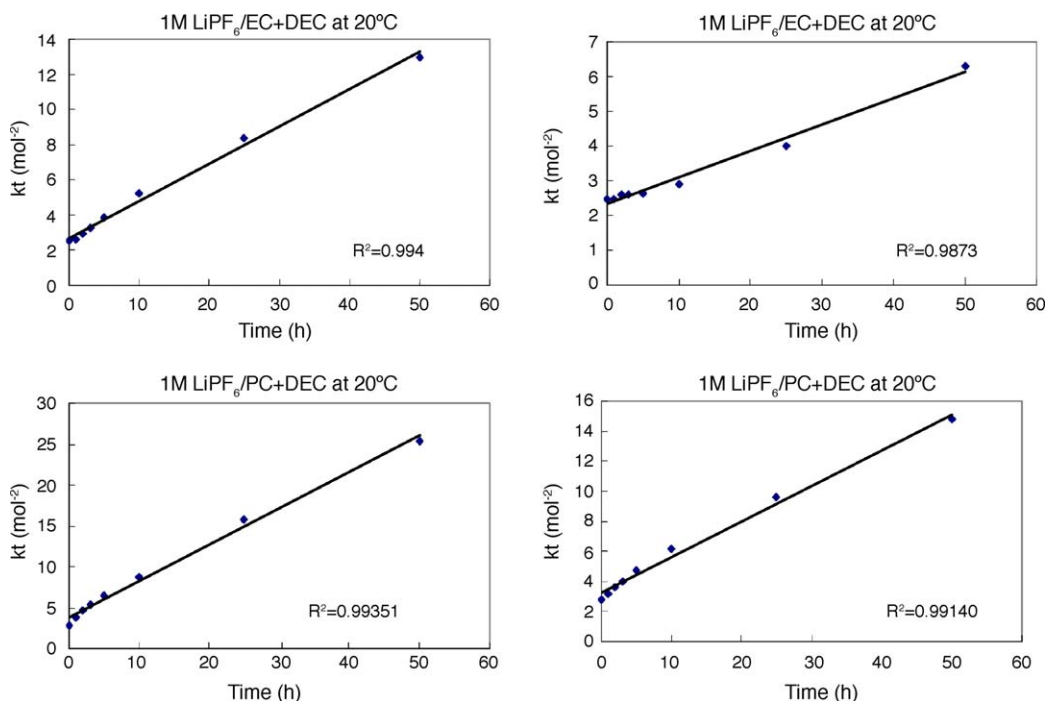
Fig. 4. $kt - C_2$ (mol^{-2}) to t (h) in the reaction between LiPF$_6$ and water in 1 M LiPF$_6$/EC + DEC, 1 M LiPF$_6$/EC + DMC, 1 M LiPF$_6$/PC + DEC, and 1 M LiPF$_6$/PC + DMC at 20 °C.
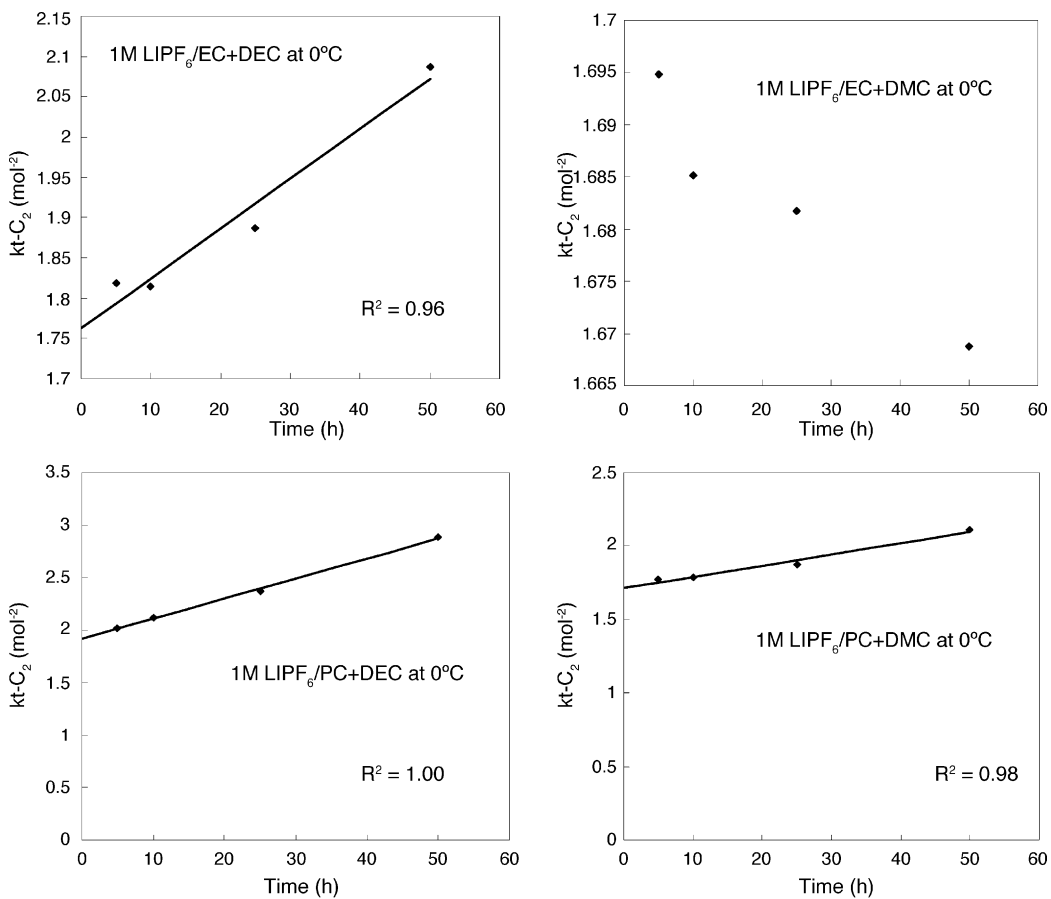
Fig. 5. $kt - C_2$ (mol^{-2}) to t (h) in the reaction between LiPF$_6$ and water in 1 M LiPF$_6$/EC + DEC, 1 M LiPF$_6$/EC + DMC, 1 M LiPF$_6$/PC + DEC, and 1 M LiPF$_6$/PC + DMC at 0 °C after 5 h.

Exnar et al. [12] evaluated the rate constant of initial water decomposition in 1 M LiPF$_6$/EC + EMC (ethylmethyl carbonate) by first-order reaction, and it was estimated to be on the order of 10^{-5} s^{-1}. However, the reaction kinetics can not be explained by a first-order reaction over a long time period. Barlow [13] has reported the reaction kinetics between solid LiPF$_6$ and water and between LiPF$_6$ and water in EC + DMC. Again, their reaction kinetics dose not fit a first-order reaction over a long time period for solid LiPF$_6$ and dose not fit a first-order reaction for any time period in the case of LiPF$_6$ as a solute.

At first, we also attempted to apply a first-order reaction:

$$-\frac{d[H_2O]}{dt} = k[H_2O][LiPF_6] \tag{5}$$

We attempted to evaluate the rate constant using the data from Fig. 1 and Eq. (5). However, the reaction kinetics did not fit the first-order reaction.

Fig. 2 shows the water content of 1 M LiPF$_6$/EC + DEC(1:1 vol.%), which contained 1 mol/l of LiPF$_6$, and to which 2 mol l^{-1} water was added over a fixed time at 40 °C. Within 10 h after, 1.8 mol l^{-1} of water had disappeared. After that the water concentrations slowly decreased. From this

result, we concluded that one LiPF$_6$ molecule reacted with two or more water molecules in organic solvent.

Based on the above, we attempted to use the competitive successive reaction model to explain the reaction between LiPF$_6$ and water in organic solvent. The competitive successive reaction means that the reactions of Eqs. (3) and (4) proceed simultaneously; that is to say, water is consumed by both PF$_5$ and the reaction product. However, the reaction kinetics did not fit the competitive successive reaction model. The mechanism for the reaction between LiPF$_6$ and water in organic solvent seems to be very complex because we must consider both the degree of dissociation and the degree of electrolytic dissociation.

PF$_5$ is a compound produced by the dissociation of non-ionized LiPF$_6$, and the amount of PF$_5$ in electrolytes is very small. Furthermore, PF$_5$ is very reactive and is quickly consumed by hydrolysis. It is therefore very difficult to evaluate PF$_5$ concentrations in electrolytes when water has been added. We therefore tried to find an empirical formula. PF$_5$ concentrations can be expressed approximately with the following equation from Eqs. (1) and (2):

$$[PF_5] = K(1 - \alpha)[LiPF_6]_T \tag{6}$$

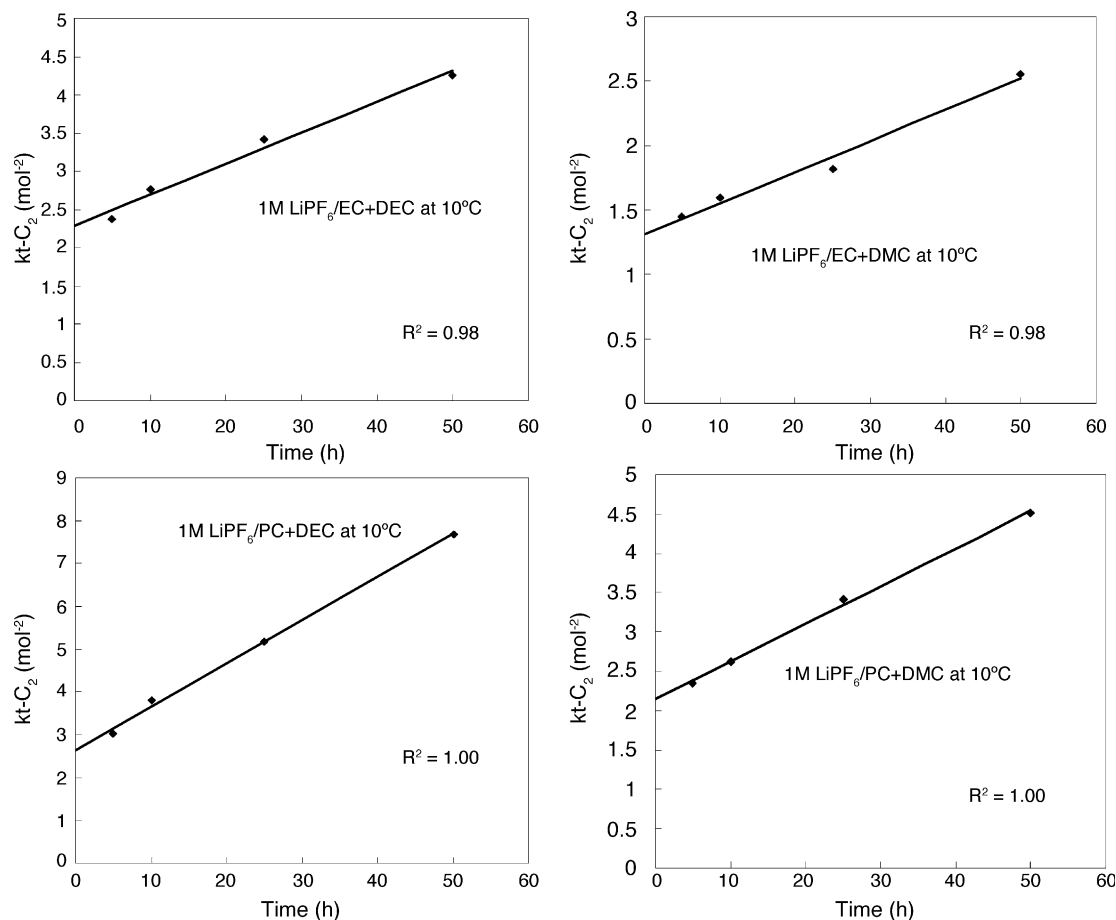Fig. 6. $kt - C_2$ (mol^{-2}) to t (h) in the reaction between LiPF$_6$ and water in 1 M LiPF$_6$/EC + DEC, 1 M LiPF$_6$/EC + DMC, 1 M LiPF$_6$/PC + DEC, and 1 M LiPF$_6$/PC + DMC at 10 °C after 5 h.

where α is the dissociation constant in Eq. (1), K the equilibrium constant in Eq. (2), [PF$_5$] the concentration of PF$_5$ in organic solvent, and [LiPF$_6$]$_T$ is the total concentration of LiPF$_6$ in organic solvent, including ionized LiPF$_6$.

From Eq. (3), the rate equation can be determined as follows:

$$-\frac{d[H_2O]}{dt} = k_1[H_2O]^m[PF_5]^n, \tag{7}$$

where t is time, k_1 the rate constant in Eq. (3), m and n are the reaction orders, and [H$_2$O] is the water concentration in organic solvents.

From Eqs. (6) and (7), the rate equation becomes

$$-\frac{d[H_2O]}{dt} = k[H_2O]^m[LiPF_6]_T^n, \tag{8}$$

where k is $k_1 K^n(1-\alpha)^n$. We substituted suitable values for m and n in Eq. (8) and we developed three rate equations:

$$-\frac{d[H_2O]}{dt} = k[H_2O][LiPF_6]_T \tag{9}$$

$$-\frac{d[H_2O]}{dt} = k[H_2O]^2[LiPF_6]_T \tag{10}$$

$$-\frac{d[H_2O]}{dt} = k[H_2O]^3[LiPF_6]_T \tag{11}$$

to obtain an empirical formula for the reaction between LiPF$_6$ and water in organic solvent.

We next substituted values in Eqs. (9) and (10), which were obtained from data for 1 M LiPF$_6$/EC + DMC (1:1 vol.%) of Fig. 1. [LiPF$_6$]$_T$ was calculated assuming that 1 mol of water will react with 1 mol of LiPF$_6$ when Eq. (9) is used and assuming 2 and 3 mol of water will react with 1 mol of LiPF$_6$ when Eqs. (10) and (11) are used. And the value of d[H$_2$O]/dt at a fixed time was obtained by calculation. Finally, we obtained Fig. 3. The plotted data points in Fig. 3 are the rate constant (k) obtained from Eqs. (9)–(11). When the value of the rate constant (k) was found by solving Eqs. (9) and (11), the value of k diverged. On the other hand, when a value of k was found by solving Eq. (10), the value of k converged to one value (see Fig. 3).

We therefore decided to use the second-order-reaction model (Eq. (10)) to evaluate the rate constant of the reaction.

Eq. (10) can be transformed into

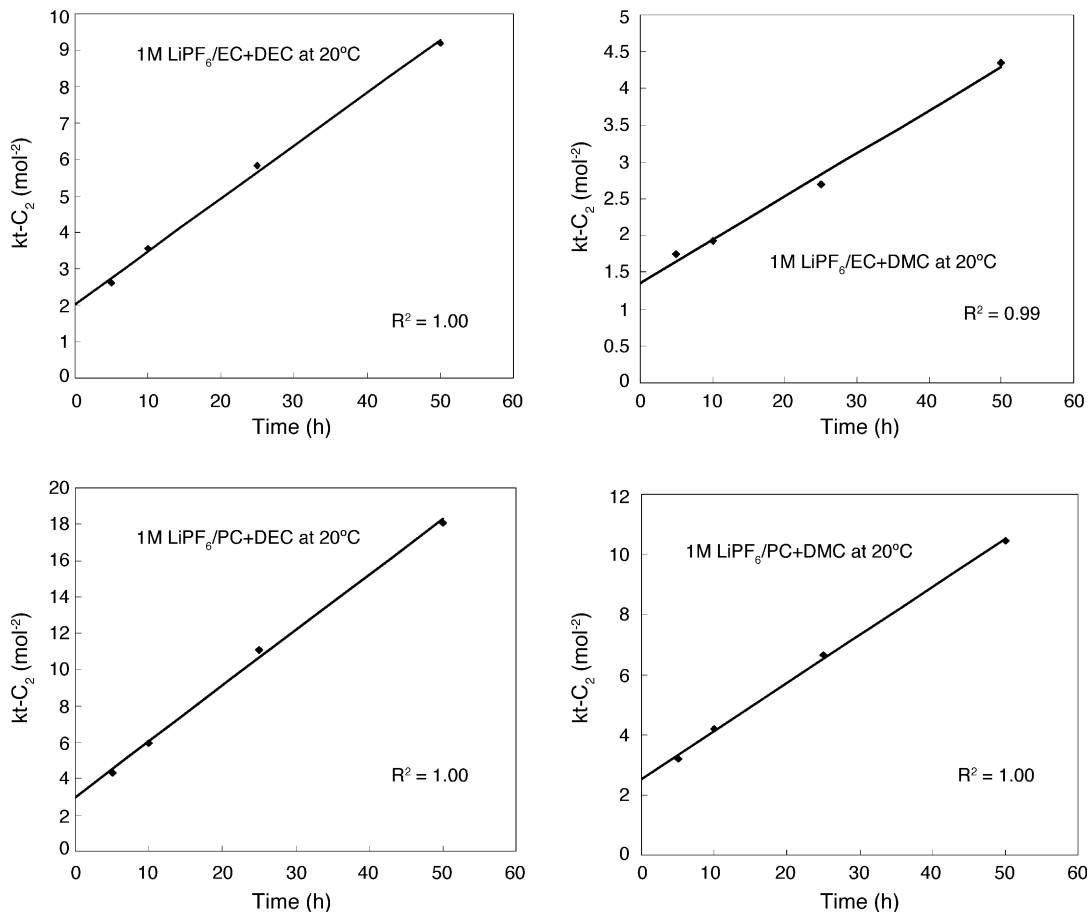$$-\frac{dy}{dt} = ky^2\left(c_1 + \frac{y}{2}\right), \tag{12}$$

Fig. 7. $kt - C_2$ (mol^{-2}) to t (h) in the reaction between LiPF$_6$ and water in 1 M LiPF$_6$/EC + DEC, 1 M LiPF$_6$/EC + DMC, 1 M LiPF$_6$/PC + DEC, and 1 M LiPF$_6$/PC + DMC at 20 °C after 5 h.

Fig. 8. $kt - C_2$ (mol^{-2}) to t (h) in the reaction between LiPF$_6$ and water in 1 M LiPF$_6$/EC + DEC, 1 M LiPF$_6$/EC + DMC, 1 M LiPF$_6$/PC + DEC, and 1 M LiPF$_6$/PC + DMC at 30 °C after 5 h.
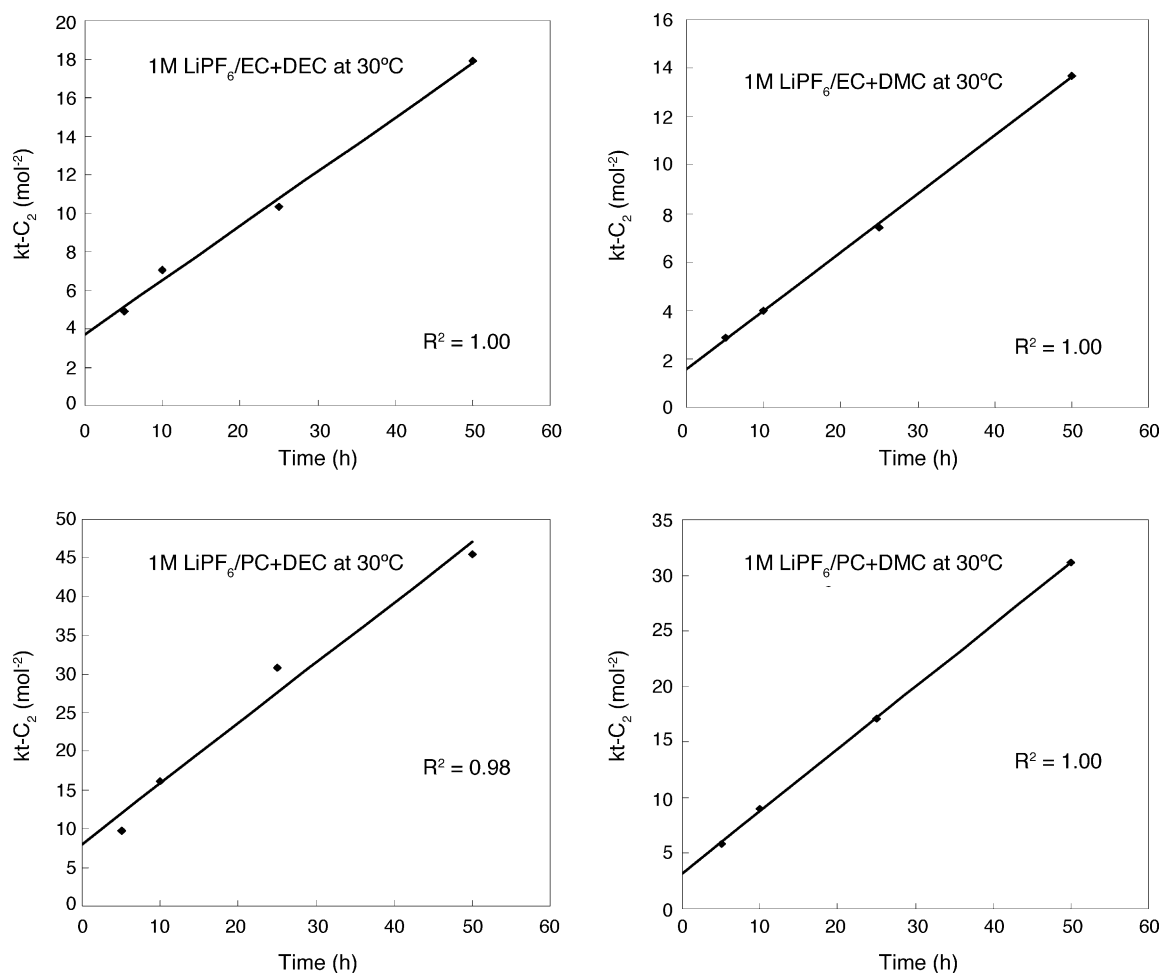
where y is [H$_2$O] and c_1 is the value that is obtained by subtracting half of the initial concentration of water from the initial concentration of LiPF$_6$ ($c_1 = $[LiPF$_6$]$_{T\,t=0} - \frac{[H_2O]_{t=0}}{2}$).

Furthermore, Eq. (12) can be transformed into

$$-k \int_0^t dt = 2 \int_{[H_2O]_{t=0}}^{[H_2O]_{t=t}} \frac{dy}{y^2(2c_1 + y)} \tag{13}$$

Solving this integral, we obtained

$$kt = \frac{1}{c_1} \left(\frac{1}{y} - \frac{1}{2c_1} \ln \frac{2c_1 + y}{y} \right) + C_2 \tag{14}$$

where C_2 is a constant number.

Inserting numerical values into c_1, y, and t, we plotted a straight line by graphing the first clause of the right-hand side of Eq. (14) to t, and calculated the rate constant (k) from its

Table 2
Density of 20 ml of LiPF$_6$ electrolytes with/without 100 μl water and 50 h after adding 100 μl of water at 25 °C, and the difference between the initial density of electrolytes immediately after adding 100 μl water and 50 h after this addition

	Density of electrolyte (g/l)	Density after addition of 20 μl of water		Change of density in 50 h after water added (%)
		Initial (g/l)	50 h after (g/l)	
1 M LiPF$_6$/EC + DEC	1672	1665	1661	0.285
1 M LiPF$_6$/EC + DMC	1734	1726	1724	0.096
1 M LiPF$_6$/PC + DEC	1579	1576	1570	0.406
1 M LiPF$_6$/PC + DMC	1642	1637	1631	0.367

Solvents of all electrolytes were mixed at a volume ratio of 1 to 1.

Table 3
Rate constant of the reaction between $LiPF_6$ and water in $LiPF_6$ electrolytes at 0, 10, 20, and 30 °C over a long time span

	PC + DEC	PC + DMC	EC + DEC	EC + DMC
0 °C [$(mol/l)^{-2}s^{-1}$]	5.3×10^{-6}	2.1×10^{-6}	1.7×10^{-6}	–
10 °C [$(mol/l)^{-2}s^{-1}$]	2.8×10^{-5}	1.3×10^{-5}	1.1×10^{-5}	6.7×10^{-6}
20 °C [$(mol/l)^{-2}s^{-1}$]	8.5×10^{-5}	4.4×10^{-5}	4.0×10^{-5}	1.6×10^{-5}
30 °C [$(mol/l)^{-2}s^{-1}$]	2.2×10^{-4}	1.6×10^{-4}	7.8×10^{-5}	6.7×10^{-5}

slope. Because the difference between the initial density of electrolytes and the density after 50 h was within 0.5% (see Table 2), the molar ratio of water in electrolytes for various timeframes was obtained by using the initial density.

Fig. 4 graphs kt (mol^{-2}) against t (h) at 20 °C. The correlation coefficient (R^2) of the nearly straight line was found to be 0.98–0.99. Plotted points of less than 5 h were not in agreement with a straight line in any of the graphs. From these results, it seems similar first-order reactions occur in the early stages of a reaction, as reported by Exnar et al. [13].

We therefore graphed values obtained after 5 h to obtain a rate constant applicable to an extended period. Figs. 5–8 plot kt to t at 0, 10, 20, and 30 °C. As stated previously, a straight line could not be drawn for 1 M $LiPF_6$/EC + DMC at 0 °C because $LiPF_6$ and water hardly reacted, and the measurement error was large. For other data, the correlation coefficient (R^2) was 0.96–1.00. The rate constants of the reaction between $LiPF_6$ and water in each electrolyte at 0, 10, 20, and 30 °C obtained from the second-order-reaction model are shown in Table 3.

4. Conclusion

We investigated the influence of organic mixed solvents on the reaction between $LiPF_6$ and water in $LiPF_6$ electrolytes for lithium ion batteries. The order of the reaction rates is as follows: 1 M $LiPF_6$/PC + DEC > 1 M $LiPF_6$/PC + DMC > 1 M $LiPF_6$/EC + DEC > 1 M $LiPF_6$/EC + DMC. This order is in inverse proportion to the order of the dielectric constants of these solvents. Nonionized $LiPF_6$ dis-

sociates to PF_5 and LiF in organic solvents, and PF_5 reacts with water. A high dielectric constant solvent increases the ionization of $LiPF_6$. Therefore, the reaction with water is suppressed in solvents with high dielectric constants.

The experimental results were found to be in good agreement with $-d[H_2O]/dt = k[H_2O]^2[LiPF_6]$. We obtained the rate constant (k) from the empirical equation.

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