Correlation between Redox Potential and Solvation Structure in Biphasic Electrolytes for Li Metal Batteries

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The activity of lithium ions in electrolytes depends on their solvation structures. However, the understanding of changes in \( \text{Li}^+ \) activity is still elusive in terms of interactions between lithium ions and solvent molecules. Herein, the chelating effect of lithium ion by forming \([\text{Li}(15\text{C}5)]^+\) gives rise to a decrease in \( \text{Li}^+ \) activity, leading to the negative potential shift of Li metal anode. Moreover, weakly solvating lithium ions in ionic liquids, such as \([\text{Li}(\text{TFSI})_2]^-\) (TFSI = bis(trifluoromethanesulfonyl)imide), increase in \( \text{Li}^+ \) activity, resulting in the positive potential shift of LiFePO₄ cathode. This allows the development of innovative high energy density Li metal batteries, such as 3.8 V class Li | LiFePO₄ cells, along with introducing stable biphasic electrolytes. In addition, correlation between \( \text{Li}^+ \) activity, cell potential shift, and \( \text{Li}^+ \) solvation structure is investigated by comparing solvated \( \text{Li}^+ \) ions with carbonate solvents, chelated \( \text{Li}^+ \) ions with cyclic and linear ethers, and weakly solvating \( \text{Li}^+ \) ions in ionic liquids. These findings elucidate a broader understanding of the complex origin of \( \text{Li}^+ \) activity and provide an opportunity to achieve high energy density lithium metal batteries.

1. Introduction

The future of electromobility rests significantly on the advancement of the battery technology toward improving the energy and power densities of rechargeable batteries.\(^1\) For this reason, great efforts have been devoted to i) developing high specific capacity electrode materials for Li-ion batteries, including Ni-rich layered oxide cathode materials\(^6\) and Li metal/ Si alloy anode materials,\(^10\) and ii) exploring new electrochemical systems, such as nonaqueous lithium-sulfur (Li-S)\(^14\) and lithium-oxygen batteries\(^16\) and aqueous rechargeable batteries.\(^18\) However, unfortunately, few electrolytes are suitable for these advanced electrode materials and battery systems because of the narrow electrochemical stability window and poor chemical stability of conventional electrolytes. In this regard, new electrolytes have been intensively investigated to improve the chemical and electrochemical properties of electrolytes.\(^23\) State-of-the-art electrolytes not only serve as a medium that transports \( \text{Li}^+ \) ions between electrodes, but also provide functionality that regulates solid electrolyte interphase (SEI) and solvation structures.\(^1,23\) For example, the electrochemical stability window of water-in-salt,\(^18\) hydrate-melt,\(^20\) and molecular crowding electrolytes\(^21\) were improved by regulating the solvation structure of aqueous electrolytes. Localized high concentration electrolytes (LHCE) were introduced to enhance the chemical stability of nonaqueous electrolytes against Li metal under the condition of low \( \text{Li}^+ \) ion concentration.\(^27\) The cell potential was also controlled by modulating the solvation structures of \( \text{Li}^+ \) ions.\(^28\) In addition, biphasic electrolytes were developed to enhance the electrochemical stability window of electrolytes for Li-ion batteries and to suppress polysulfide crossover in Li-S batteries.\(^37\) However, when two electrolytes are separated by a \( \text{Li}^+ \) ion-selective membrane, such as biphasic electrolytes, the Nernst equation can be expressed as\(^37\)

\[
E_{\text{Overall}} = E_{\text{Cathode}} - E_{\text{Anode}} = (E'_{\text{C}} - E'_{\text{A}}) + \frac{RT}{nF} \ln \frac{a_{\text{Li}^+(C)}}{a_{\text{Li}^+(A)}}
\]  

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Figure 1. a) Voltage profiles of i) conventional cell, ii) [Li(15C5)]+ cell, and iii) [Li(15C5)]+/Li cell at a 0.5C rate and 30 °C. b) OCV profiles of Li metal electrodes each with i) 0.5 m LiPF6 in EC/DMC and 0.5 m LiPF6 in EC/DMC/15C5 at 30 °C (solid line) and each with ii) 1 m LiPF6 in EC/DMC and 1 m LiPF6 in EC/DMC/15C5 at 25 °C (dashed line). Cells with LiPF6 in EC/DMC and LiPF6 in EC/DMC/15C5 are denoted as Li/Li+ and Li/[Li(15C5)]+, respectively. OCV was measured using the Ag/Ag+ reference electrode. c) Schematic illustration for the increased cell potential of the [Li(15C5)]+/Li+ cell compared to the conventional cell. d) Voltage profiles of LiFePO4 and Li metal electrodes obtained using the four-electrode cell at a 0.5C rate and 30 °C for the measurement of a liquid junction potential (inset: illustration of a four-electrode cell configuration).

where $E$, $E_0$, $n$, $F$, $T$, $R$, and $a$ represent cell potential, standard electrode potential, the number of electrons transferred in the reaction, Faraday constant, temperature, gas constant, and activity, respectively (Discussion S1, Supporting Information). In contrast to the single-phase electrolyte, we can achieve a difference in the activity values of each Li+ ion dissolved in phase C and phase A for the biphasic electrolytes. For this reason, overall cell potential can be modulated by the logarithm term of the relative Li+ activity ratio between two electrolyte phases. Herein, we show a significant change in the activity of Li+ ions in electrolytes containing the Li+ ion complex with cyclic crown ether, 15-crown-5, leading to a remarkable decrease in the redox potential of Li metal, compared to conventional carbonate-based electrolytes. The new redox couple of Li/[Li(15C5)]+ (15C5 = 15-crown-5, [Li(15C5)]+ = Li+·15C5 complex) showed the lower formal potential of −3.32 V (vs NHE) compared to the standard electrode potential of Li/Li+, −3.041 V (vs NHE) in aqueous electrolytes. This is due to the complexation effect of Li+ chelated with 15-crown-5. Moreover, we constructed 3.7 V class Li | LiFePO4 cells using the stable biphasic electrolyte using an ion-selective membrane, in which the electrolytes of anode and cathode sides contained LiPF6 in carbonate/dimethyl carbonate (EC/DMC) with and without 15-crown-5, respectively. Consequently, the biphasic electrolyte with chelating agents improved the energy density of Li | LiFePO4 batteries compared to conventional 3.4 V class Li | LiFePO4 containing a single-phase electrolyte. We also demonstrated a significant increase in the Li+ activity in ionic liquid electrolytes containing abundant bis(trifluoromethanesulfonyl)imide (TFSI−) anions, leading to a positive potential shift of the LiFePO4 cathode due to the formation of a weakly solvating lithium ion structure, such as [Li(TFSI)_2]+. The combination of the complexation effect and the
Figure 2. a) Cycle performance and b) the corresponding voltage profiles of \([\text{Li}(15\text{C}5)]^+ / \text{Li}^+\) cell consisting of LiFePO\(_4\) cathode and Li metal anode at a 4C rate. c) Voltage profiles and d) the corresponding \(dQ/dV\) plots of the \([\text{Li}(15\text{C}5)]^+ / \text{Li}^+\) cell consisting of LiFePO\(_4\) cathode and Li metal anode at various C-rates.

weakly solvation effect further allowed the construction of 3.8 V class Li | LiFePO\(_4\) cells. Moreover, the relationship between Li\(^+\) activity, potential shift, and Li\(^+\) solvation structure was investigated by examining chelated Li\(^+\) ions with cyclic/linear ethers and weakly solvated Li\(^+\) ions with ionic liquids. More stabilization of Li\(^+\) complex gave rise to a decrease in the activity of Li\(^+\) in electrolytes, whereas weakly solvating Li\(^+\) ions increased the activity of Li\(^+\) in electrolytes, eventually resulting in a significant increase in cell potential. These findings provide an opportunity to design advanced electrolytes for high energy density Li metal batteries.

2. Negative Potential Shift of the Li Metal Anode

We constructed three electrochemical cells, each consisting of a LiFePO\(_4\) cathode and a Li metal anode, as below:

(I) Li | Li\(^+\), PF\(_6^−\) | LiFePO\(_4\)
(II) Li | [Li(15C5)]\(^+\), PF\(_6^−\) | LiFePO\(_4\)
(III) Li | [Li(15C5)]\(^+\), PF\(_6^−\) || Li\(^+\), PF\(_6^−\) | LiFePO\(_4\)

The first cell (I) has a single-phase electrolyte, such as 1 M LiPF\(_6\) in EC/DMC (1/1, v/v), which is denoted as the conventional cell. The second cell (II), denoted as the [Li(15C5)]\(^+\) cell, also has a single-phase electrolyte, such as 0.5 M LiPF\(_6\) in EC/DMC/15C5 (2/2/1, v/v/v), in which the molar ratio of 15C5 to Li\(^+\) is 2:1. The third cell (III), denoted as the [Li(15C5)]\(^+\)/Li\(^+\) cell, contains the biphasic electrolytes separated by a Li\(^+\) ion-selective Nafion membrane. The electrolyte of the LiFePO\(_4\) cathode side was 0.5 M LiPF\(_6\) in EC/DMC, whereas that of the Li metal anode side was 0.5 M LiPF\(_6\) in EC/DMC/15C5. Crown ethers are known to form complexes with lithium cations, such as [Li(15C5)]\(^+\), and to homogenize Li\(^+\) flux, leading to uniform electroplating of Li metal.[38–39] Home-made cells (Figure S1, Supporting Information) and 2032-type coin cells were used for biphasic electrolytes and single-phase electrolytes, respectively. We also prepared the Li\(^+\) ion-selective Nafion membrane through ion-exchange between H\(^+\) and Li\(^+\) (Figure S2, Supporting Information).

To verify the impermeability of the Li\(^+\) ion-selective Nafion membrane to 15C5 in the biphasic electrolyte, we built 2-chamber side diffusion cells with the Li\(^+\) ion-selective Nafion
membrane where the donor chamber was filled with 0.5 M LiPF₆ in EC/DMC and the receptor one was filled with 0.5 M LiPF₆ in EC/DMC/15C5. Solutions were retrieved from the donor chamber after various periods of time, and then the membrane permeability to 15C5 was estimated using ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy (Figure S3, Supporting Information). The characteristic peaks of 15C5 were not observed in the solutions of the donor chamber even after one week. We also examined changes in the Li⁺ ion concentration of the solutions in the donor and receptor chambers using inductively coupled plasma atomic emission spectrometer (ICP-AES) (Table S1, Supporting Information). The concentrations of Li⁺ ions in both chambers remained almost unchanged for one week. These results imply that the crossover of 15C5 through the membrane was insignificant.

Figure 1a compares the voltage profiles of the conventional, [Li(15C5)]⁺, and [Li(15C5)]⁺/Li⁺ cells at a 0.5C rate and 30 °C. The conventional and [Li(15C5)]⁺ cells, both having a single-phase electrolyte, showed the same voltage profiles with a cell potential of ≈3.4 V, regardless of the composition of electrolytes. This is due to the fact that the solvation energies and desolvation energies of Li⁺ ions are cancelled when a single-phase electrolyte is used. The cell potential of the [Li(15C5)]⁺/Li⁺ cell was, however, ≈3.7 V, which was significantly higher than those of the conventional and [Li(15C5)]⁺ cells. The open-circuit voltage (OCV) of the [Li(15C5)]⁺/Li⁺ cell was 3.67 V at the state of charge (SOC) of 50% (Figure S4, Supporting Information) To clarify the origin of the potential shift in the [Li(15C5)]⁺/Li⁺ cell, we compared the redox potentials of Li+/Li⁺ and Li/[Li(15C5)]⁺ couples using the Ag/Ag⁺ reference electrode (Figure 1b). The Ag/Ag⁺ reference electrode was calibrated with reference to the ferrocene/ferrocenium ion couple (Figure S5, Supporting Information). Whereas the equilibrium potential of the Li/Li⁺ was ≈−3.23 and −3.20 (vs Ag/Ag⁺) for 0.5 M LiPF₆ at 30 °C and 1 M LiPF₆ at 25 °C (standard state, respectively), the Li/[Li(15C5)]⁺ redox couple showed the equilibrium potential of −3.49 and −3.48 V (vs Ag/Ag⁺) each under the same conditions as Li/Li⁺, respectively. The equilibrium potential difference between Li/Li⁺ and Li/[Li(15C5)]⁺ couples was almost the same as the potential shift in the [Li(15C5)]⁺/Li⁺ cell compared to the conventional cell (Figure S4 and S6, Supporting Information). This is also supported by the voltage profile of a symmetric cell for Li | [Li(15C5)]⁺, PF₆⁻ | Li⁺, PF₆⁻ | Li under the condition of an areal capacity of 0.5 mA h cm⁻² at a current density of 0.5 mA cm⁻² (Figure S7, Supporting Information). The equilibrium potential for the plating and stripping of Li metal was ≈−0.25 V, which was coincident with the potential difference between the Li/Li⁺ and Li/[Li(15C5)]⁺ redox couples. Therefore, these results supported that the increased cell potential of the [Li(15C5)]⁺/Li⁺ couple was due to a negative potential shift of Li metal anode, as shown in Figure 1c. Moreover, this reveals that the formal potential of the Li/[Li(15C5)]⁺ couple is −3.32 V (vs NHE). The correlation between the redox potentials of Li/Li⁺, Ag/Ag⁺, and NHE references was detailed in Discussion S2 in the Supporting Information. In the same manner, when we switched electrolytes for each other in the biphasic electrolyte of the [Li(15C5)]⁺/Li⁺ cell as below, the cell potential was rather decreased to ≈3.2 V (Figure S8, Supporting Information). This was due to a negative potential shift of the LiFePO₄ cathode:

\[
\text{(IV) } \text{Li}^+ + \text{PF}_6^- + \text{[Li(15C5)]}^+ + \text{PF}_6^- \rightarrow \text{LiFePO}_4
\]

In addition, we measured a liquid junction potential of the biphasic electrolyte in the [Li(15C5)]⁺/Li⁺ cell using the four-electrode cell configuration consisting of a Li metal anode, a LiFePO₄ cathode, and two Ag/Ag⁺ reference electrodes (Figure 1d). The redox potential values of the LiFePO₄/FePO₄ and Li/Li⁺ redox couples in the four-electrode cell were ≈±0.20 and −3.49 V (vs Ag/Ag⁺) at 30 °C, respectively. A difference in their redox potentials (3.69 V) was almost the same as the cell potential of the [Li(15C5)]⁺/Li⁺ cell (3.67 V), implying that the liquid junction potential of the biphasic electrolyte was ≈0.02 V, which is negligibly small (Discussion S3, Supporting Information).

Figure 2a,b shows the cycle performance and corresponding voltage profiles of the [Li(15C5)]⁺/Li⁺ cell for LiFePO₄ at a 4C rate and 30 °C, respectively. The [Li(15C5)]⁺/Li⁺ cell showed excellent cycle performance, such as stable capacity retention over 200 cycles, without a change in the equilibrium cell potential.
during cycling. This reveals that the biphasic electrolyte was stable, suppressing the crossover of 15C5 during cycling. This is also supported by changes in the Li⁺ ion concentration on each phase of the biphasic electrolyte during charge and discharge (Figure S9, Supporting Information). The Li⁺ ion concentrations on both phases of the biphasic electrolyte remained almost unchanged during charge and discharge.

We also examined the cycle performances of \([\text{Li}(15\text{C5})]\)\(^{1+}\)/Li⁺ cells for LiFePO₄ using various amounts of electrolytes per capacity at a 4C rate and 30 °C (Figure S10, Supporting Information). The [Li(15C5)]\(^{1+}\)/Li⁺ cell showed more stable capacity retention as the amount of electrolytes increased. This is attributable to the fact that the electrolytes of LiPF₆ in carbonate solvents are vulnerable to Li metal.

The same behavior of the [Li(15C5)]\(^{1+}\)/Li⁺ cell was observed when we replaced LiFePO₄ with LiCoO₂ in the [Li(15C5)]\(^{1+}\)/Li⁺ cell as follows:

\[
\begin{align*}
\text{(V)} & \quad \text{Li} | \text{Li}^{1+}, \text{PF}_6^{−} | \text{LiCoO}_2 \\
\text{(VI)} & \quad \text{Li} | [\text{Li}(15\text{C5})]^{1+}, \text{PF}_6^{−} | \text{Li}^{1+}, \text{PF}_6^{−} | \text{LiCoO}_2
\end{align*}
\]

Figure 3a compares the voltage profiles of the conventional cell (V) and [Li(15C5)]\(^{1+}\)/Li⁺ (VI) cells for LiCoO₂ at a 0.5C rate and 30 °C. The voltage profile of the [Li(15C5)]\(^{1+}\)/Li⁺ cell for LiCoO₂ shifted upward by ≈0.3 V compared to that of the conventional cell for LiCoO₂, which was consistent with the results for LiFePO₄. Assuming that the cell potentials of LiFePO₄ and LiCoO₂ increase by 0.3 V without changes in their specific capacity, the energy densities of LiFePO₄ and LiCoO₂ cathodes theoretically increase from 561 and 741 to 610 and 798 Wh kg⁻¹, respectively (Figure 3b). This suggests that we can achieve an energy density increase of ≈8–9% albeit without changes in electrode materials. Detailed cell parameters for the calculation of energy density were presented in Table S2 (Supporting Information).

We compared changes in the cell potential of [Li(15C5)]\(^{1+}\)/Li⁺ cells containing Li metal and LiFePO₄ at various molar ratios of chelating agent to Li⁺ to demonstrate the role of chelating agents in the potential shift of Li metal. Figure 4a-b shows the cyclic voltammogram and dQ/dV profiles of [Li(15C5)]\(^{1+}\)/Li⁺ cells for Li | LiFePO₄ at various molar ratios of 15C5 to Li⁺. The cell potential of [Li(15C5)]\(^{1+}\)/Li⁺ cells increased with the molar ratio of 15C5 to Li⁺, implying that the activity of Li⁺ (a_{Li⁺}) in the electrolyte of Li metal side decreased with increasing the number of 15C5 chelating with Li⁺ (Figure 5a). The chelation effect is known to show the greater stability of chelated complexes compared to their nonchelated (solvated) analogues largely because of increases in free solvent molecules.[40] This implies that the thermodynamic stability of the solvation structure increased as the entropy of the electrolyte increased.[26,41] Therefore, a decrease in the activity of Li⁺ in the electrolytes containing 15C5 was due to the improved stabilization of [Li(15C5)]\(^{1+}\) complexes.

Figure 4. a) Cyclic voltammograms (scan rate = 0.1 mV s⁻¹) and b) dQ/dV plots (0.5C rate) of Li | 0.5 m LiPF₆ in EC/DMC/15C5 || 0.5 m LiPF₆ in EC/DMC | LiFePO₄ cells for various molar ratios of 15C5 to Li⁺. c) dQ/dV plots (0.5C rate) of Li | 0.5 m LiPF₆ in EC/DMC/triglyme || 0.5 m LiPF₆ in EC/DMC | LiFePO₄ cells for various molar ratios of triglyme to Li⁺.
at the anode side is expressed as
\[ a_{ Li^{+}(15C5) } ] = \frac{ a_{ Li^{+} } }{ a_{ Li^{+}(15C5) } } \] (2)

where \( K_f \) is a formation constant of chelated \( Li^{+} \) ions from solvated \( Li^{+} \) ions. Since \( K_f \) is a constant, each concentration of \( [ Li(15C5) ]^{+} \) and \( Li^{+} \) increases and decreases, respectively, with increasing that of 15C5. This implies that the activity of solvated \( Li^{+} \) is higher than that of chelated \( Li^{+} \) with 15C5, because the activity of \( Li^{+} \) \( ( a_{ Li^{+} } ) \) in the electrolyte of Li metal side decreased with increasing the concentration of \( [ Li(15C5) ]^{+} \). Since the redox potential of the \( Li/[Li(15C5)]^{+} \) was 0.28 V higher than that of the \( Li/Li^{+} \), Equation (1) shows
\[ \frac{ \Delta E }{ AP } \ln \frac{ a_{ Li^{+}(15C5) } }{ a_{ Li^{+} } } = 0.28 \text{ V} \] under a standard condition. This reveals that the \( Li^{+} \) activity in the conventional carbonate-based electrolyte without 15C5 \( ( a_{ Li^{+}(15C5) } ) \) was \( \approx 5.5 \times 10^4 \) times higher than that in the electrolyte containing 15C5 \( ( a_{ Li^{+}(15C5) } ) \) (Discussion S4, Supporting Information). The \( Li^{+} \) activity values indicate the average activity of all species of \( Li^{+} \) cations (solvated and chelated \( Li^{+} \) cations) in electrolytes.

Moreover, we examined linear triethylene glycol dimethyl ether (triglyme) as a complexing agent, leading to the formation of [Li(triglyme)]\(^{+}\) complex (Figure 4c and Figure 5a). [Li(triglyme)]\(^{+}\) showed the same behavior as [Li(15C5)]\(^{+}\). The cell potential of [Li(triglyme)]\(^{+}\)/Li\(^{+}\) cells for Li/LiFePO\(_4\) increased, as the molar ratio of triglyme to \( Li^{+} \) increased. However, the cell potentials of [Li(triglyme)]\(^{+}\)/Li\(^{+}\) cells were lower than those of [Li(15C5)]\(^{+}\)/Li\(^{+}\) cells at the same molar ratio of chelating agent to \( Li^{+} \). This reveals that the \( Li^{+} \) activity in the electrolyte containing 15C5 was lower than that in the electrolyte containing triglyme at the same concentration of chelating agents. This behavior is demonstrated in terms of the macrocyclic effect that cyclic ligands stabilize the complexes more than linear ligands\(^{42-43}\). (Discussion S5, Supporting Information). This implies that the potential shift due to a change in \( Li^{+} \) activity depend on the stabilization degree of the complexes.

In addition, Figure 5b shows the ionic conductivity of 0.5 m LiPF\(_6\) in EC/DMC/15C5 (1/1/2, v/v/v) for various molar ratios of 15C5 to \( Li^{+} \) as a function of temperature. The ionic conductivity of the electrolytes containing 15C5 decreased with increasing the ratio of 15C5 to \( Li^{+} \). This is probably because the viscosity of the electrolytes increased with the ratio of 15C5 to \( Li^{+} \) (Table S3, Supporting Information). We also compared the electrochemical stability window of 0.5 m LiPF\(_6\) in EC/DMC (1/1, v/v) and 0.5 m LiPF\(_6\) in EC/DMC/15C5 (2/2/1, v/v/v), as shown in their linear sweep voltammograms (LSV) (Figure S12, Supporting Information). This reveals that no drastic cathodic decomposition was observed in both electrolytes prior to each Li metal plating.

To elucidate the role of solvation structures in \( Li^{+} \) activity changes, the solvation structures of \( Li^{+} \) in 0.5 m LiPF\(_6\) in EC/DMC/15C5 for various molar ratios of 15C5 to \( Li^{+} \) were examined using Raman, FT-IR, and \(^{13}\)C NMR spectroscopies. The characteristic vibration frequencies and chemical shifts of electrolytes were summarized in Tables S4–S6 in the Supporting Information. Figure 6a shows changes in the Raman spectra of the electrolytes with increasing the molar ratio of 15C5 to \( Li^{+} \).

In the pristine electrolyte containing no 15C5, EC is known to solvate \( Li^{+} \), giving rise to a distinguishable peak at 905 cm\(^{-1}\) for \( Li^{+}\cdots\cdots О–С (EC)\).\(^{46}\) The peak at 905 cm\(^{-1}\) disappeared and a new peak appeared at 875 cm\(^{-1}\) after adding 15C5 to the pristine electrolyte. Moreover, the peak intensity at 875 cm\(^{-1}\) gradually increased with increasing the molar ratio of 15C5 to \( Li^{+} \). This implies that \( Li^{+} \) prefers to complex with 15C5 rather than to be solvated by EC because the peak at 875 cm\(^{-1}\) corresponds to \( Li^{+}\cdots\cdots О–С (ether)\). The complexation of \( Li^{+} \) with 15C5 was also supported by the FT-IR spectra of the electrolytes (Figure 6b). The peak of \( Li^{+}\cdots\cdots О–С (EC) \) at 1772 cm\(^{-1}\) shifted to 1774 cm\(^{-1}\), which is the wavenumber of pure EC, after adding 15C5 to the pristine electrolyte. This reveals that the ion-solvent interaction between \( Li^{+} \) and EC was weakened because of the formation of [Li(15C5)]\(^{+}\) complexes. This behavior was also coincident with the fact that the P–F stretch peak of PF\(_6\)\(^{-}\) shifted from 843 to 841 cm\(^{-1}\) after the addition of 15C5. The formation of [Li(15C5)]\(^{+}\) complexes
Figure 6. a) Raman, b) FT-IR, and c) $^{13}$C NMR spectra of pure solvents and the electrolytes of 0.5 M LiPF$_6$ in EC/DMC/15C5 for various molar ratios of 15C5 to Li$^+$. 
gave rise to weakening the cation–anion interaction, leading to a peak shift to a lower wavenumber.\textsuperscript{[45–46]} \textsuperscript{13}C NMR spectra also show the solvation structures of [Li(15C5)]\textsuperscript{+} with EC and DMC (Figure 6c). When we compared the NMR spectra of the mixed solvent of EC/DMC with and without LiPF\textsubscript{6}, the \textsuperscript{13}C chemical shift of EC was more deshielded than that of DMC. This implies that Li\textsuperscript{+} was preferentially coordinated with EC, such as Li\textsuperscript{+}(EC)\textsubscript{4}, rather than with DMC. For this reason, the \textsuperscript{13}C chemical shift of EC was rather shielded by the addition of 15C5 to the electrolytes containing LiPF\textsubscript{6}, as Li\textsuperscript{+} ions were desolvated from Li\textsuperscript{+}(EC)\textsubscript{4} and chelated with 15C5, forming [Li(15C5)]\textsuperscript{+}.

3. Positive Potential Shift of the LiFePO\textsubscript{4} Cathode

In the same manner, we introduced weakly solvating electrolytes at the cathode side to increase the activity of Li\textsuperscript{+} ions in electrolytes (\textdelta Li\textsuperscript{+}EC), thus increasing the redox potential of the cathode. We constructed two electrochemical cells each consisting of a LiFePO\textsubscript{4} cathode and a Li metal anode, as below:

\noindent (VII) Li | 0.5 m LiTFSI in EC/DMC || 0.5 m LiTFSI in EMIM-TFSI | LiFePO\textsubscript{4}  
(VIII) Li | 0.5 m LiTFSI in EC/DMC || 0.5 m LiTFSI in HMIM-TFSI | LiFePO\textsubscript{4}  
(IX) Li | 0.5 m LiTFSI in EC/DMC/15C5 (2/2/1) || 0.5 m LiTFSI in EMIM-TFSI | LiFePO\textsubscript{4}  
(X) Li | 0.5 m LiTFSI in EC/DMC/15C5 (2/2/1) || 0.5 m LiTFSI in HMIM-TFSI | LiFePO\textsubscript{4}
Figure 7c,d shows the OCV profiles for the cells of (IX) and (X) at the SOC level of 50%. The cells of (IX) and (X) showed the equilibrium potentials of 3.73 and 3.78 V, respectively. The potential shift of the cell (X) compared to the conventional cell was almost the same as the OCV of the Li/Li symmetric cell for Li | 0.5 M LiTFSI in EC/DMC/15C5 || 0.5 M LiTFSI in HMIM-TFSI | Li in Figure S15 in the Supporting Information.

The solvation structures of Li⁺ ions in ionic liquid-based electrolytes were examined using Raman spectroscopy and electrospray-ionization mass spectrometry (ESI-MS) to demonstrate the role of solvation structures in increases in Li⁺ activity for electrolytes at the cathode side. Figure 8a,d shows changes in the Raman spectra of the electrolytes with increasing the concentration of LiTFSI. The peak of free TFSI⁻ at 741.5 cm⁻¹ shifted gradually to higher wavenumbers for both EMIM-TFSI and HMIM-TFSI with increasing the concentration of LiTFSI from 0 to 1 M. This reveals that the peak shift is attributed to the coordination of TFSI⁻ anions with Li⁺ ions. This coordination gave rise to the formation of weakly solvating Li⁺ ions, leading to increases in the activity of Li⁺ in ionic liquid-based electrolytes.

The coordination of Li⁺ with TFSI⁻ in the electrolytes was also supported by the Raman spectra of the cis and trans conformers of TFSI⁻ (Figure 8b,e). In equilibrium, TFSI⁻ anions coexist in cis and trans forms, in which the trans conformer is ≈2.2 kJ mol⁻¹ more stable than the cis conformer.[48] The peak intensities of trans TFSI⁻ and cis TFSI⁻ decreased and increased, respectively, gradually with increasing the concentration of LiTFSI. This implies that cis conformers were preferred over trans conformers as TFSI⁻ coordinated with Li⁺. In addition, ESI-MS spectra showed the solvation sheath structures of TFSI⁻ anions coordinated with Li⁺ (Figure 8c,f). The peaks at the m/z of 567.1 and 280.1 correspond to [Li(TFSI)₂]⁻ and free TFSI⁻ anions, implying that Li⁺ ions were coordinated with TFSI⁻ anions.

4. Conclusion

We demonstrated that the simple replacement of a single-phase electrolyte with a biphasic electrolyte gave rise to a significant increase in cell potential by lowering and raising the redox potentials of the Li metal anode and the LiFePO₄ cathode, respectively.
This strategy is not only limited to Li | LiFePO4 cells, but also applicable to other cathode materials, such as LiCoO2 and Ni-rich layered oxides. This implies that we can improve the energy density of Li metal-ion batteries for all cathode materials, regardless of the redox potential of cathode materials.

We also clarified the correlation between activity, cell potential, and solvation structure. The role of the complexation effect in changes in Li+ activity was examined using carbonate solvent-based nonaqueous electrolytes containing cyclic and linear chelating agents, such as 15C5 and triglyme. The activity of Li+ chelated with 15C5 in the electrolyte of LiPF6 in EC/DMC was approximately five orders of magnitude lower than that of Li+ solvated with carbonate solvents in the conventional electrolyte of LiPF6 in EC/DMC without additives. This was due to the chelation and macrocyclic effect of Li+ complexes. A decrease in Li+ activity led to the negative potential shift of Li/[Li(15C5)]+ and Li/[Li(triglyme)]+ redox couples for Li metal electrodes. Li/[Li(15C5)]+ showed a significantly low formal potential of −3.32 V (vs NHE). In addition, the activity of Li+ coordinated with TFSI− in the ionic liquid-based electrolytes increased with increasing the concentration of LiTFSI. This was attributed to the formation of weakly solvating Li+ ions, such as [Li(TFSI)]1− in ionic liquids. Increases in Li+ activity led to the positive potential shift of the LiFePO4 cathode. Eventually, the combination effect of the negative potential shift of Li metal anode and the positive potential shift of LiFePO4 cathode allows the development of 3.8 V class Li | LiFePO4 along with introducing the biphasic electrolytes with a stable ion-selective membrane. This suggests that an improved understanding of correlation between activity and solvation structure will provide insights on designing new functional electrolytes to improve the energy density of Li metal batteries. However, since the ion-selective Nafion membrane is not considered to be permanently stable, long-term cycle performance is one of the challenging issues for the biphasic electrolyte systems. For this reason, the development of more stable ion-selective membranes, such as charge-reinforced ion-selective membrane,[32] should be considered for the practical use of the biphasic electrolytes.

5. Experimental Section

Materials: LiPF6 salt, EC/DMC (1/1, v/v) solvent, and 15-crown-5 were purchased from Enchem, Soulbrain, and Sigma-Aldrich, respectively, to prepare 0.5 and 1 M LiPF6 in EC/DMC/15C5. Triethylene glycol dimethyl ether (triglyme) was purchased from Thermo Fisher Scientific to prepare 0.5 M LiPF6 in EC/DMC/triglyme. LiTFSI salt (Enchem), EMIM-TFSI and HMIM-TFSI (TCI chemicals) were purchased to prepare the electrolytes with various electrolytes was carried out between 3.0–4.2 V (vs Li/Li+) and vs Li/[Li(15C5)]+ using a battery measurement system (WonAtech WBCS3000). LiCoO2 electrodes were examined in voltage ranges of 3.0–4.2 V (vs Li/Li+) and 3.2–4.4 V (vs Li/[Li(15C5)]+), depending on the type of electrolytes. Cyclic voltammetry (CV) of Li | LiFePO4 cells with various electrolytes was carried out between 3.0–4.2 V (vs Li/Li+) and vs Li/[Li(15C5)]+ at a scan rate of 0.1 mVs−1. Home-made cells and 2032-type coin cells were used for biphasic and single-phase electrolytes, respectively. In addition, H-type cells were used for four-electrode cells and membrane permeability tests. The redox couple of Ag/Ag+ (0.01 M AgNO3, 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile) was used as a reference electrode in a four-electrode cell. The OCV values of lithium metal electrodes as a function of time were measured at 25 and 30 °C using the Ag/Ag+ reference electrode. The OCV profiles and the plating/striping voltage profiles of Li/Li symmetric cells were obtained using the H-type cells, in which the concentration of LiPF6 and LiTFSI were fixed at 0.5 M for each side of the biphasic electrolytes. All cells were assembled in an Ar-filled glove box under the condition of O2 and H2O levels below 0.1 ppm.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.
