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Facilitated Li^+ ion transfer across the water/1,2-dichloroethane interface by the solvation effect†

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We demonstrate that the solvation effect can be the driving force for ion transfer across the water/1,2-dichloroethane interface. Voltammetric behaviours of facilitated Li^+ ion transfer by the solvents of lithium-based batteries are investigated, which is valuable for the dual-electrolyte Li–air batteries, but also for the ion detection, separation and extraction.

Lithium-based batteries, including the metallic lithium battery and lithium-ion battery, have been the subject of extensive research due to their excellent energy density.[1–3] Recently, a dual-electrolyte Li–air battery, a novel metallic lithium battery, has been studied extensively as the next generation power source because of its high energy density, high electromotive force and the lithium oxides deposition-free discharging process on the air electrode.[4–7] The aqueous–aprotic dual-electrolyte Li–air battery involves Li^+ ion transfer between the aqueous phase and the organic phase through a Li^+ ion conducting ceramic membrane (LISICON)[4–6] or an interface of "aqueous electrolyte–polymerized aprotic electrolyte"[7] during the charging–discharging processes. Li^+ ion transfer across the aqueous/aprotic interface should overcome the difference in Gibbs solvation free energies in each solution.[8,9] Therefore, it is essential to investigate the interfacial Li^+ ion transfer for fully understanding the chemical mechanisms of lithium-based batteries.

The liquid/liquid (L/L) interface, also called the water/oil (W/O) interface, or the interface between two immiscible electrolytic solutions (ITIES), is a kind of soft interface which can be polarized to study the interfacial charge transfer phenomena. Nitrobenzene (NB),[10] 1,2-dichloroethane (1,2-DCE),[11,12] *o*-nitrophenyl octyl ether (NPOE),[13] ionic liquids,[14,15] and their mixtures have been used as organic solvents to form an L/L interface with aqueous solution. In general, there exist three kinds of elemental charge transfer reactions across the L/L interface: (1) simple ion transfer, in which an ion transfers across the interface directly; (2) facilitated ion transfer, in which ion transfer is assisted by its ionophores; (3) electron transfer, in which an electron transfers between the redox couples in each phase. Charge transfer across the L/L interface can generate Faraday current. Therefore, electrochemistry of the L/L interface has been well developed to investigate both thermodynamic and kinetic properties of interfacial charge transfer, and becomes an important branch of modern electroanalytical chemistry.

Propylene carbonate (PC) is one of the most frequently used solvents in lithium-based batteries.[16] The solvation effect is crucial to the mass transfer and the intercalation–deintercalation of Li^+ ions during charging–discharging processes.[17] Here we present facilitated Li^+ ion transfer phenomena driven by the solvation effect. When PC was added into the 1,2-DCE phase, Li^+ ion transfer across the W/1,2-DCE interface was facilitated due to the better affinity of PC for Li^+ ions than 1,2-DCE. Through the interfacial interaction between Li^+ ions and PC molecules, the thermodynamic and kinetic properties of the solvation effect were evaluated. The results are valuable not only for the dual-electrolyte lithium–air batteries in green energy, but also for the ion detection, separation and extraction in analytical chemistry.

In our experiments, micropipettes were employed to support the W/1,2-DCE interface. The details of an electrochemical cell are provided elsewhere[18–20] and expressed as follows:

$$\text{Cell 1: Ag}|\text{AgTPBCl}|5\ \text{mmol L}^{-1}\ \text{BTPPATPBCl} + x\text{PC (1,2-DCE)}\|y\ \text{mmol L}^{-1}\ \text{LiCl (water)}|\text{AgCl}|\text{Ag}$$

where, ‖ represents the W/1,2-DCE interface, x is the volume ratio of PC in the 1,2-DCE phase, and y is the concentration of Li^+ in the water phase. The interface is formed spontaneously

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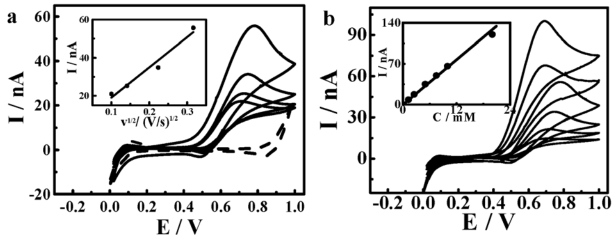

Fig. 1 The cyclic voltammetric behaviours of PC facilitated Li^+ ion transfer across the W/1,2-DCE interface with cell 1 when x = 1/3. (a) The scanning rates are 0.01, 0.02, 0.05 and 0.10 V s^{-1} from bottom to top, the concentration of LiCl is 2.5 mM, the dashed line is the background, *i.e.*, x = 0; the inset shows the linear relationship between the peak current and the square root of the scanning rate. (b) The concentrations of LiCl are 1.25, 2.5, 5, 7.5, 10 and 20 mM in sequence. The diameter of the micropipette orifice is 8.4 μm. The inset shows the linear relationship between the peak current and the concentration of Li^+ ions in aqueous solution.

through the capillary effect due to the hydrophilicity of the glass wall. The experimental details are provided in S1 (ESI†). The cyclic voltammograms obtained for cell 1 are shown in Fig. 1.

If there was no PC in the 1,2-DCE phase, a well-shaped potential window was observed as the dashed line. However, when PC is added into the 1,2-DCE phase with a volume ratio of 1 : 3, the facilitated Li^+ ion transfer across the W/1,2-DCE interface occurred. It can be observed that the anodic segment was peak shaped but the cathodic segment was sigmoidal. Actually, at the micropipette supported interface, the diffusion field is linear for ion transfer egress the micropipette but hemispheric for ion transfer ingress the micropipette. Although PC is an organic solvent and totally miscible with 1,2-DCE, it has low solubility in water with a molar ratio of 3.6%.[21] The Li^+ ion complexes with the PC molecules dissolved in the aqueous phase and then transfers into the 1,2-DCE phase. This process is exactly the ACT mechanism, *i.e.*, aqueous complexation followed by interfacial transfer, suggested by Shao and Girault.[22] Based on the ACT mechanism, the diffusion coefficient, 2.29×10^{-5} cm^2 s^{-1}, obtained from the following equation should be attributed to the complex ion of $Li(PC)_z^+$:[12,22]

$$i_{\rm p} = 0.4463 \times 10^{-3} n^{3/2} F^{3/2} A (RT)^{-1/2} D^{1/2}_{{\rm Li(PC)}_z^+} C \nu^{1/2} \qquad (1)$$

where $i_{\rm p}$ is the peak current, n the number of transferred charges, F the Faraday constant, $D_{{\rm Li(PC)}_z^+}$ the apparent diffusion coefficient of the $Li(PC)_z^+$ ion, A the radius of the micropipette orifice, and C the apparent concentration of the $Li(PC)_z^+$ ion. The Gibbs transfer free energy of Li^+ ions from water into PC is pretty low (24 kJ mol^{-1}),[8] which indicates the good affinity of PC for Li^+ ions. Since $C_{\rm PC} \gg C_{\rm Li^+}$, the interfacial concentration of $Li(PC)_x^+$ can be considered to be the same as $C_{\rm Li^+}$ in bulk aqueous solution. This hypothesis was proved by the experimental graph shown in Fig. 1b, in which the peak current is in proportion to the bulk concentration of Li^+ ions in the water phase.

The next step was to figure out the stoichiometric ratio between the Li^+ ion and the solvent molecules. It is noted that PC molecules act as neutral ionophores which can complex with and facilitate Li^+ ion transfer across the water/1,2-DCE interface. In experiments, the concentrations of PC in the 1,2-DCE phase are much higher than those of Li^+ ions in the water phase ($C_{\rm PC} \gg C_{\rm Li^+}$), the volume of the 1,2-DCE phase is much higher than that of the water phase ($V_{\rm 1,2\text{-}DCE} \gg V_{\rm water}$), and the solubility of PC in the 1,2-DCE phase is much higher than that in the aqueous phase. Considering the ACT mechanism of the facilitated Li^+ ion transfer, the following equation should be met:[22,23]

$$\Delta_{\rm O}^{\rm W}\varphi^{1/2}_{\rm Li^+-PC} = \Delta_{\rm O}^{\rm W}\varphi^{1/2}_{\rm Li^+} + \frac{RT}{F}\ln\left(\frac{\beta_{\rm m}^{\rm w}}{\beta_{\rm m}^{\rm o}(P_{\rm PC})^{z}}\right) \qquad (2)$$

where $P_{\rm PC} = C_{\rm PC}^{\rm O}/C_{\rm PC}^{\rm W}$, $\Delta_{\rm O}^{\rm W}\varphi^{1/2}_{\rm Li^+-PC}$ and $\Delta_{\rm O}^{\rm W}\varphi^{1/2}_{\rm Li^+}$ are the half-wave potentials of $Li(PC)_z^+$ and Li^+ ion transfer across the water/1,2-DCE interface, $\beta_{\rm m}^{\rm w}$ and $\beta_{\rm m}^{\rm o}$ are association constants of the $Li(PC)_z^+$ ion in each bulk phase, and z is the stoichiometric number of the $Li(PC)_z^+$ ion.

Eqn (2) predicts that the half-wave potential dependence on the logarithm of the molar concentration of PC in the 1,2-DCE phase can provide thermodynamic information about the solvation effect. In order to determine the half-wave potential, TMA^+ was used as the inner reference with a formal transfer potential of 160 mV based on the "TATB hypothesis".[8] From the data shown in Fig. 2, the stoichiometric number (z) was determined to be 4, *i.e.*, the solvated ion is $Li(PC)_4^+$.

The rest is to answer how fast the solvated ion $Li(PC)_4^+$ transfers across the W/1,2-DCE interface. Ultramicroelectrode methodology is facile to investigate the kinetics of fast charge transfer reaction due to the enhanced mass transfer rate of reactants.[24] If the potential dependence of the reaction rate constant followed the Butler–Volmer equation, the kinetic parameters of heterogeneous electron transfer reactions at ultramicroelectrodes can be determined as reported by Mirkin and Bard in 1992.[25] Shao and Mirkin introduced this method into the charge transfer reaction across the L/L interface.[26] If the orifice of the micropipette decreases to nanometer size and the scanning rate slows down, a steady-state curve will be obtained to define the values of $E_{1/2}$, $E_{1/4}$ and $E_{3/4}$ (as shown in Fig. 3). Once the values are derived, the transfer coefficient (α: 0.50 ± 0.05) and the standard rate constant (k^0: 0.20 ± 0.03 cm s^{-1}) can be obtained as shown in Table 1, which shows good reversibility of PC facilitated Li^+ ion transfer across the W/1,2-DCE interface.

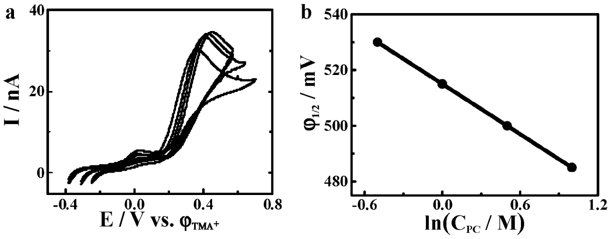

Fig. 2 (a) The voltammograms of PC facilitated Li^+ ion transfer across the water/1,2-DCE interface with $V_{\rm PC}/V_{\rm 1,2\text{-}DCE}$ ratios of 1/3, 1/6, 1/9, and 1/15 at a scanning rate of 0.02 V s^{-1}. (b) Logarithmic relationship between the half-wave potential and the molar concentration of PC in the 1,2-DCE phase.

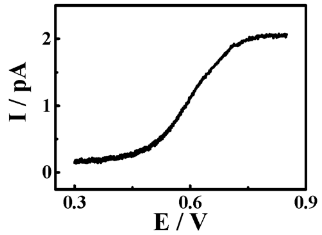

Fig. 3 Steady-state voltammogram of PC facilitated Li^+ ion transfer across a nanopipette supported W/1,2-DCE interface with an orifice diameter of 20 nm; the concentration of LiCl is 20 mM, the scan rate is 0.02 V s^{-1}, and $V_{PC}/V_{1,2\text{-DCE}}$ is 1/3.

Table 1 Kinetic parameters for PC facilitated Li^+ ion transfer across the nanopipette supported W/1,2-DCE interface, where $V_{PC}/V_{1,2\text{-DCE}}$ = 1/3, C_{Li^+} = 10 mM, $\Delta E_{1/4} = E_{1/2} - E_{1/4}$, and $\Delta E_{3/4} = E_{3/4} - E_{1/2}$

a (nm)	$\Delta E_{1/4}$ (mV)	$\Delta E_{3/4}$ (mV)	α	k^0 (cm s^{-1})
20	33.5	36.0	0.58	0.23
53	32.5	37.5	0.47	0.21
71	31.3	34.0	0.51	0.18
98	30.5	32.5	0.45	0.16

The solvation effect also applies to diethyl-carbonate (DEC) and dimethyl-carbonate (DMC), which is shown in S2 (ESI†).

We find that the solvation effect between Li^+ ions and the lithium-based battery solvents such as PC, DEC and DMC can facilitate Li^+ ion transfer across the W/1,2-DCE interface. Since PC has low solubility in water, a mixed solvent layer is formed and the ACT mechanism works. The thermodynamic and kinetic parameters of the solvation between PC and Li^+ ions are obtained through the micropipette methodology of the L/L interface. In physical chemistry, it provides a novel method to study the solvation effect. In analytical chemistry, it can provide a facile method for ion detection, separation and extraction.

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