

Supplementary Information of Ionophore-Free Facilitated Li⁺ Ion Transfer across Water/1,2-Dichloroethane Interface by Solvation Effect

S1 Experimental details

Chemicals and Materials:

Lithium chloride (LiCl), Propylene carbonate (PC), dimethylcarbonate (DMC), diethylcarbonate (DEC), 1,2-dichloroethane (1,2-DCE) are analytical grade or better from Sinopharm Co., China. Bis-(triphenylphosphoranylidene) ammonium chloride (BTPPACl, 98%), and potassium tetrakis(4-chlorophenyl)borate (KTPBCl, 98%) are purchased from Sigma-Aldrich.

The organic supporting electrolyte, bis-(triphenyl phosphoranylidene) ammonium tetrakis-(4-chlorophenyl) borate (BTPPATPBCl), are prepared through the precipitation reaction between BTPPACl and KTPBCl, and recrystallized in acetone. The series binary organic solvents were prepared by desired volume ratio of 1,2-DCE and either PC, DMC or DEC. All aqueous solutions were prepared with deionized water (18.2 MΩ, Milli-Q, Millipore Corp.).

Micropipettes with an orifice of micrometer size are prepared through a programmed laser puller P2000 (Sutter Co., USA). An Olympus optical microscopy (Olympus Co., Japan) is used to detect the quality of the pulled micropipettes and read their inner radii.

Electrochemical Measurements

All electrochemical experiments are carried out on CHI620c electrochemical workstation (CH Instruments, Inc., USA) at room temperature ($25 \pm 2^\circ\text{C}$). An Ag/AgCl wire is inserted into the aqueous phase inside the micropipette as the aqueous reference electrode. An Ag/AgTPBCl wire is immersed in the outside organic phase as the organic reference electrode. A special holder was used to hold the micropipette. The interface was formed spontaneously through the capillary effect due to the hydrophilicity of glass wall. To decrease the IR drop, the tip of the Ag/AgCl wire inside the micropipette was etched and extended as close as possible to the orifice. The electrochemical cells used in the experiments are listed as followed:

Cell 1:

Ag | AgTPBCl | 5mmol/L BTPPATPBCl + 1,2-DCE+DMC (DEC or PC) || ymmol/L LiCl | AgCl | Ag
 $V_{1,2-\text{DCE}}:V_{\text{DMC}}$ (DEC or PC) = 3, y = 5, 10, 20, 50 mmol/L

Cell 2:

Ag | AgTPBCl | 5mmol/L BTPPATPBCl+1,2-DCE+PC ($V_{1,2-\text{DCE}}:V_{\text{PC}}=x$) || 2mmol/L TMACl + 10mmol/L LiCl |

AgCl | Ag x = ∞, 15, 12, 9, 6, 3

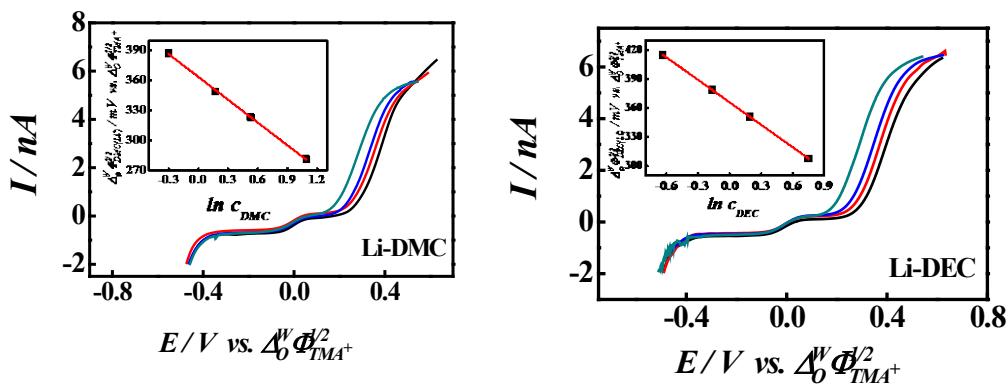
Cell 3:

Ag | AgTPBCl | 5mmol/L TPPATPBCl + 1,2-DCE+DMC ($V_{1,2\text{-DCE}}:V_{\text{DMC}}=x$) || 10mmol/L LiCl + 2mmol/L TMACl | AgCl Ag x=3,6,9,15

Cell 4:

Ag | AgTPBCl | 5mmol/L TPPATPBCl + 1,2-DCE+DEC ($V_{1,2\text{-DCE}}:V_{\text{DEC}}=x$) || 10mmol/L LiCl + 2mmol/L TMACl | AgCl | Ag x=3,6,9,15

S2 Li⁺ ion transfer facilitated by DMC and DEC



Binary electrolytes	DCE/DMC	DCE/DEC
Slope (RTp/nF)	76	77
Intercept (mV)	524	526
stoichiometric number(p)	3	3