Electronic Supporting Information for

A superconcentrated ether electrolyte for fast-charging Li-ion batteries

Yuki Yamada,[a,b] *Makoto Yaegashi,*[a] *Takeshi Abe*[b,c] *and Atsuo Yamada**[a,b]

[a] Department of Chemical System Engineering, The University of Tokyo, Tokyo 113-8656, Japan

[b] Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, Kyoto 614-8246, Japan

[c] Department of Energy and Hydrocarbon Chemistry, Kyoto University, Kyoto 615-8510, Japan

*E-mail: yamada@chemsys.t.u-tokyo.ac.jp

Experimental Methods.

Materials. 1, 2-dimethoxyethane (DME) solvent and 1.0 mol dm^{-3} $LiPF_6$ / ethylene carbonate (EC) : dimethyl carbonate (DMC) (1:1 by vol.) solution were purchased from Kishida Chemical co. Ltd,. Lithium bis(fluorosulfonyl)amide (LiFSA) was provided by Nippon Shokubai Co., Ltd. The reagents were all Li-battery grade with a low water content (<20 ppm) and used without further purification. Solutions were prepared by adding a given amount of the LiFSA to DME under mild heating and stirring in an Ar-filled glove box. The molar concentration is defined as the molar amount of Li salt divided by the volume of the “whole solution” (not solvent only) in accordance with IUPAC.[1] For instance, 3.6 mol dm^{-3} LiFSA/DME solution corresponds to 1 L of LiFSA/DME solution containing 3.6 mol of LiFSA. Natural graphite powders (mean particle size: 10 μm) were provided by SEC Carbon, Ltd. and used without any pre-treatment. Olivine $LiFePO_4$ powders were synthesized by a solid-state reaction from stoichiometric amounts of Li_2CO_3 (Wako, 99.0%), $FeC_2O_4 \bullet 2H_2O$ (JUNSEI, 99%), and $(NH_4)_2HPO_4$ (Wako, 99.0%) as a starting material. The average particle size was controlled to around 80 nm by altering sintering temperature and milling condition.[2]

Raman spectroscopy. Raman spectra of the solution were recorded with NRS-1000 (JASCO Corporation) using an exciting laser of 514 nm to study the solvation/association state of the solution. To prevent any contamination from air, the solution was put into a quartz cell and tightly sealed in it in an Ar-filled glove box. The laser was radiated through the quartz crystal window. Peak deconvolution of obtained spectra was performed with Voigt function (*i.e.*, combination of Gauss and Lorentz functions).

Physicochemical properties. The viscosity of the solutions were evaluated with Lovis 2000 M (Anton Paar GmbH) using the density of the solution obtained with DMA 35 (Anton Paar GmbH). The ionic conductivity was measured by ac impedance method at 1 kHz using Solartron 147055BEC

(Solartron Analytical) using a two-electrode cell equipped with a pair of platinum plate electrodes. The molar ratio (DME/LiFSA) of the solutions was calculated from molar concentration and density.

Electrochemical measurements. A natural graphite electrode was prepared by mixing 90 wt% natural graphite powder and 10 wt% polyvinylidene difluoride (PVdF, Kureha Corporation) in *N*-methylpyrrolidone (NMP, Wako Pure Chemical Industries, Ltd.). A $LiFePO_4$/C composite electrode was prepared by mixing 78 wt% $LiFePO_4$, 11 wt% carbon black (Ketjen Black, Lion Corp., ECP), and 11 wt % PVdF in NMP. The slurry was uniformly spread onto a current collector (10 μm thickness) with a 50 μm doctor blade and dried at 120 °C under vacuum overnight. The current collector used was copper and aluminum for graphite and $LiFePO_4$, respectively. The obtained sheets were punched out to form a 16 mmϕ disk electrode. The active material loading was 0.7-1.0 mg cm^{-2} and 1.2-1.5 mg cm^{-2} for graphite and $LiFePO_4$ electrodes, respectively. Cyclic voltammetry was performed by VMP-3 (BioLogic) using a three-electrode cell with natural graphite working electrode and lithium metal foil reference and counter electrodes. Scan rate was set at 0.1 mV s^{-1}. Charge-discharge tests were carried out by a charge-discharge unit (TOSCAT, Toyo System Co., Ltd., or HJ1001SD8, Hokuto Denko Corporation) using a 2032-type coin cell with a lithium metal anode and a glass fiber separator (Whatman GF/F, 420 μm thickness). The temperature was controlled at 25 °C. Charge-discharge current was set at the ones corresponding to C/20, C/10, C/5, C/2, 1C, 2C, and 5C without using a constant-voltage mode at both ends of charge and discharge. Here the notation of xC rate corresponds to the current of $372\times x$ mA g^{-1} and 170×x mA g^{-1} on the weight basis of natural graphite and $LiFePO_4$, respectively. Cutoff voltage was set at 0-2.5 V and 2.5-4.2 V for graphite/lithium and $LiFePO_4$/lithium cells, respectively. All the electrochemical measurements were carried out under Ar atmosphere. In secondary batteries, the two electrodes should be referred to as positive/negative electrodes in IUPAC nomenclature, but in this paper, we use cathode/anode in accordance with customary practice.

Table S1 Assignment of Raman bands in LiFSA/DME solution.[3-5]

Raman shift (cm^{-1})	Species	Interaction	Conformation[a]	Vibration mode
720	FSA	free	-	S-N stretching, C-N stretching
732	FSA	CIP	-	
746	FSA	AGG	-	
823	DME	free	TTT, TGG‘, TTG	CH_2 rocking
851	DME	free	TGT	C-O stretching, CH_2 rocking
879	DME	solvating	TGT	Li-O breathing

[a] TTT: *trans-trans-trans*, TGG’: *trans-gauche-gauche*, TTG: *trans-trans-gauche*, TGT: *trans-gauche-trans*.

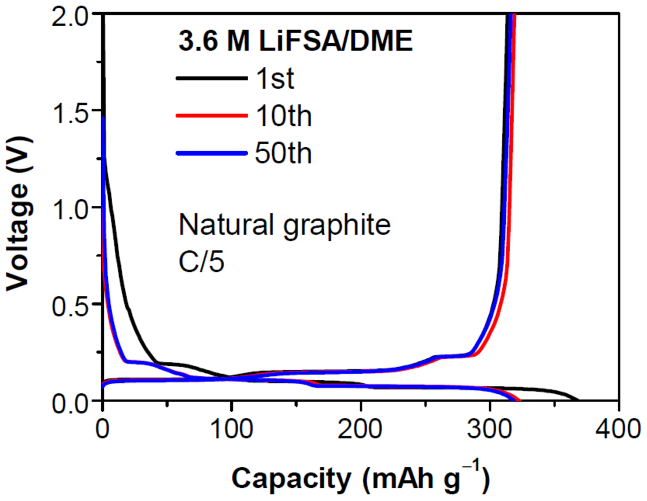

Figure S1 Charge-discharge curves of a natural graphite / Li metal half cell with 3.6 mol dm^{-3} LiFSA/DME electrolyte at a C/5 rate at 25 °C. There are several plateaus in a voltage range of 0-0.25 V, which correspond to sequential formation of several stage structures of lithium-graphite intercalation compounds (Li-GIC).[6,7] The reversible capacity at a C/5 rate was ca. 320 mAh g^{-1}, which is close to the theoretical value of 372 mAh g^{-1} based on fully lithiated LiC_6.

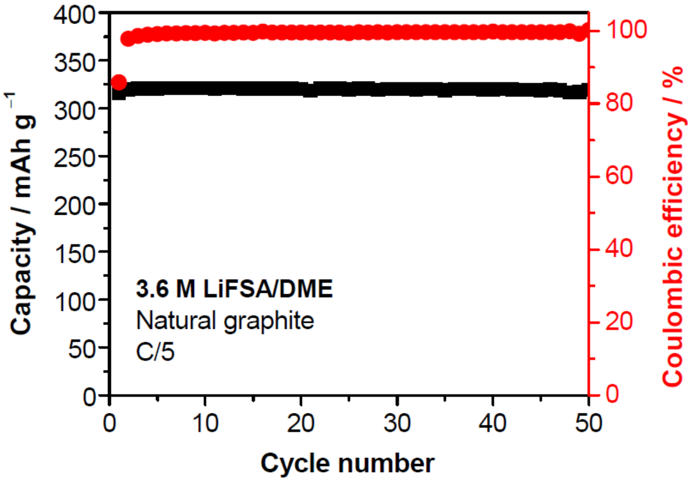

Figure S2 Cycling performance of a natural graphite / Li metal half cell with 3.6 mol dm^{-3} LiFSA/DME electrolyte at a C/5 rate at 25 °C. The reversible capacity of 320 mAh g^{-1} was retained even after 50 cycles with almost 100 % coulombic efficiency.

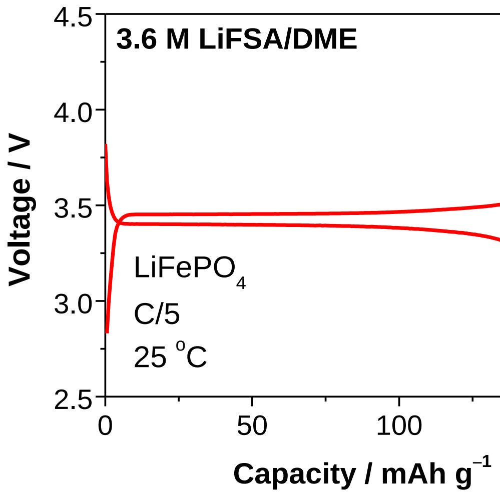

Figure S3 Charge-discharge curves of a LiFePO$_4$ / Li metal half cell with 3.6 mol dm^{-3} LiFSA/DME electrolyte at a C/5 rate at 25 °C. The reversible capacity was ca. 155 mAh g^{-1}, which is close to the theoretical value of 170 mAh g^{-1}.

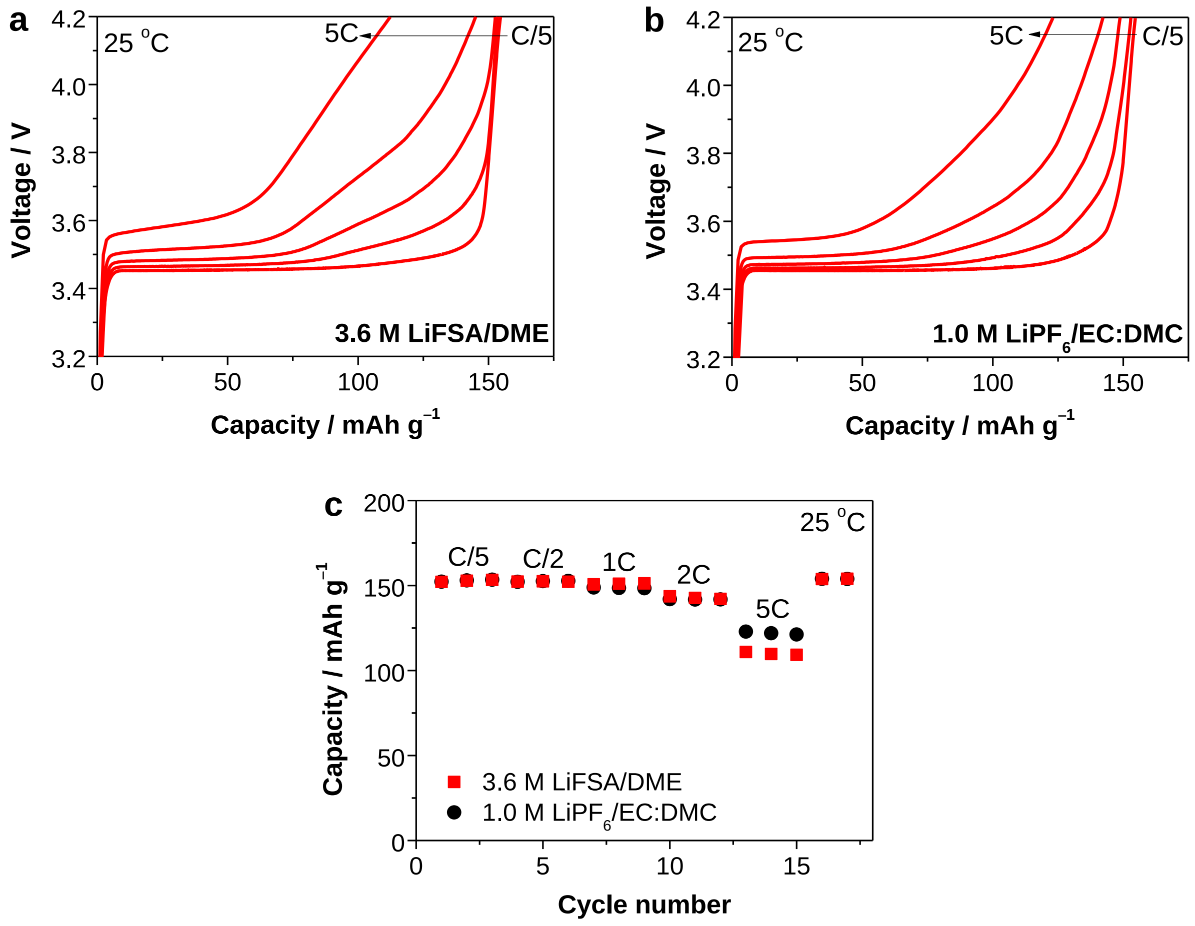

Figure S4 Charge curves of a $LiFePO_4$ / Li metal half cell with a) superconcentrated 3.6 mol dm^{-3} LiFSA/DME and b) commercial 1.0 mol dm^{-3} $LiPF_6$/EC:DMC (1:1 by vol.) electrolytes at various C-rates (C/5, C/2, 1C, 2C, and 5C) at 25 °C. c) Reversible capacity of a $LiFePO_4$ / Li metal half cell with the two electrolytes at various charging C rates at 25 °C. Discharge current was fixed at C/5 rate to ensure full discharge. In contrast to the case in a graphite negative electrode, the charging rate capability of a $LiFePO_4$ cathode is almost the same in the superconcentrated and commercial electrolytes. The slightly high rate capability with small polarization in the commercial electrolyte results from the small difference in ionic conductivity. However, it should be noted that the charging rate capability of the cathode is much higher than that of the graphite anode with comparable active material loading; for example, in the commercial electrolyte, the capacity retention at 2C rate (i.e., the capacity at 2C divided by that at the lowest rate) is 93 % and 28 % for $LiFePO_4$ and natural graphite, respectively. This indicates that the Li^+ intercalation kinetics at the graphite anode dominates the overall charging rate of the full Li-ion battery. Hence, our superconcentrated electrolyte, allowing for ultrafast Li^+ intercalation into graphite, will surely contribute to remarkable improvement of charging rate of full Li-ion cells.

Reference

1. Quantities, Units and Symbols in Physical Chemistry, Third Edition, IUPAC, RSC Publishing.
2. G. Kobayashi, S. Nishimura, M. S. Park, R. Kanno, M. Yashima, T. Ida, A. Yamada, *Adv. Funct. Mater.* 2009, **19**, 395.
3. D. M. Seo, O. Borodin, S.-D. Han, P. D. Boyle and W. A. Henderson, *J. Electrochem. Soc.*, 2012, **159**, A1489.
4. H. Yoshida and H. Matsuura, *J. Phys. Chem. A*, 1998, **102**, 2691.
5. B. L. Papke, M. A. Ratner and D. F. Shriver, *J. Electrochem. Soc.*, 1982, **129**, 1434.
6. J. R. Dahn, *Phys. Rev. B*, 1991, **44**, 9170.
7. T. Ohzuku, Y. Iwakoshi and K. Sawai, *J. Electrochem. Soc.*, 1993, **140**, 2490.