Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Information for

A Green and Cost-effective Rechargeable Battery with High Energy Density Based on Deep Eutectic Catholyte

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Experimental Section

Preparation of the deep eutectic catholyte (DEC). The component chemicals, iron (Ⅲ) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 99.0%, Wako Pure Chemical Industries, ltd) and urea (NH_2CONH_2, 99.0%, Kanto Chemical Co., Inc.), were purchased and used as received. The DEC was prepared by mixing the two components in a molar ratio of 2/1 for $FeCl_3 \cdot 6H_2O$/urea in a capped bottle with mild heating (60 ℃) and stirring on a hot plate under ambient atmosphere, till a homogeneous dark-brown liquid was formed. Care must be taken in handling $FeCl_3 \cdot 6H_2O$ as it is rather hygroscopic. Direct grinding of the mixture is better to be carried out in a dry box. The obtained eutectic liquid was kept in a capped PTFE bottle in ambient environment. No observable change in volume of the eutectic liquid was observed even when the liquid was open to direct contact with the ambient air for one month (at room temperature around 25 ℃ during February in Tsukuba, Japan).

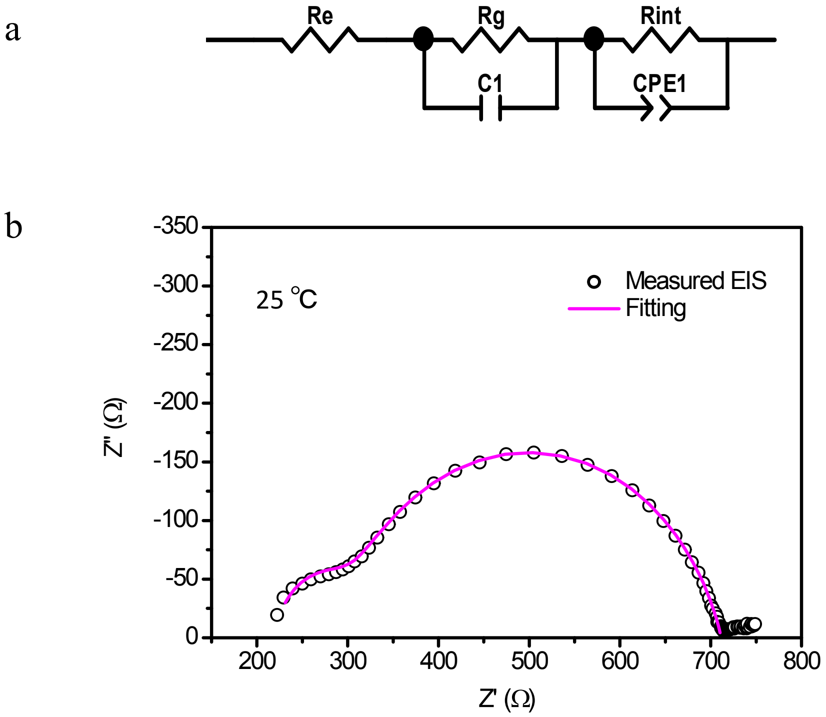
Determination of the freezing point of the DEC. The freezing point of the DEC was determined by direct observation via two methods: (1) measured the temperature change versus time while cooling the eutectic solution (1.60g) from room temperature to -20 ℃ in a cooling bath with a mixture of water and ethanol (in 50 vol%) as the coolant; (2) Cooled the eutectic solution in a constant temperature chamber (Espec LU-113 constant climate cabinet) from 25 ℃ to a target temperature (-3 to -9 ℃) and kept the temperature there up to 10 hours for the direct observation. Both methods gave a freezing point around -7 ℃.

Construction of the battery. The electrochemical properties of the DEC was investigated using a single cell with a cell structure of Li | organic electrolyte | LATP | DEC. Basically, the experimental cell consists of two compartments: an anode and a cathode compartments. The anode compartment contains an organic electrolyte (1 M $LiClO_4$ in ethylene carbonate/dimethyl carbonate) and an anode of lithium metal pressed on a Cu mesh (Nilaco, 100 mesh). The cathode compartment contains liquid DEC and a current collector made by pressing porous carbon-paste on a Ti mesh (Nilaco, 100 mesh). The two compartments are separated by a 0.15-mm-thick LATP plate ($Li_{1+x+y}(Al,Y)_x(Ti,Ge)_{2-x}Si_yP_{3-y}O_{12}$, Ohara. Inc., Japan), which selectively allows the transfer of Li^+. In addition, a layer of glass fiber was put in between the LATP and Li metal electrode to prevent them from direct contact. The porous carbon paste was made by roller-pressing a mixture of Ketjen black (EC600JD) and polytetrafluoroethylene (PTFE) (a 15% emulsion) in weight percentage of 80% and 20%, respectively, into a sheet. The current collector has a geometric area of about 1 cm^2 and with a mass load of the Ketjen black around 12 mg cm^{-2}. The DEC used for each cell was 0.6 ml.

Electrochemical measurements. The battery was rested for 24 hours before and after connecting to external circuit for a better wetting between the DEC and the carbon-paste current collector. The rate and discharge-charge cycle performances of the battery were measured using a SM8 charge/discharge system (Hokutou Denkou Co.) with a voltage range of 2.7-4.3 V. The Electrochemical impedance spectroscopy was measured using the Li-DEC assembly at its initial stage before discharge. The measurement was carried out with a Solartron 1287 Electrochemical Interface and a Solartron 1255B Frequency Respondy Analyser. During the measurements, the battery was kept at the required temperatures, i.e. 25, 30, 35 or 40 ± 1 ℃, in a constant temperature oven.

Charecterizations. The XRD was performed using a Bruker D8 Advanced diffractometer with Cu Kα ($\lambda = 1.5406$ Å) radiation. The $FeCl_3 \cdot 6H_2O$ sample was prepared in glove-box and was covered with ployimde film. The measurements of $FeCl_3 \cdot 6H_2O$ and urea samples were carried out with a scan speed of 0.5 s/step and a 2θ increment of 0.02°. The XRD pattern of the crystalline eutectic mixture was obtained by a quick scan (0.1 s/step with a 2θ increment of 0.02°) of the frozen DEC which was prepared by freezing the liquid DEC on a plastic sample holder covered with a polyimide film. The SEM images were obtained using a field-emission scanning electron microscopy (FESEM, LEO Gemini Supra 35).

Supplementary Figures



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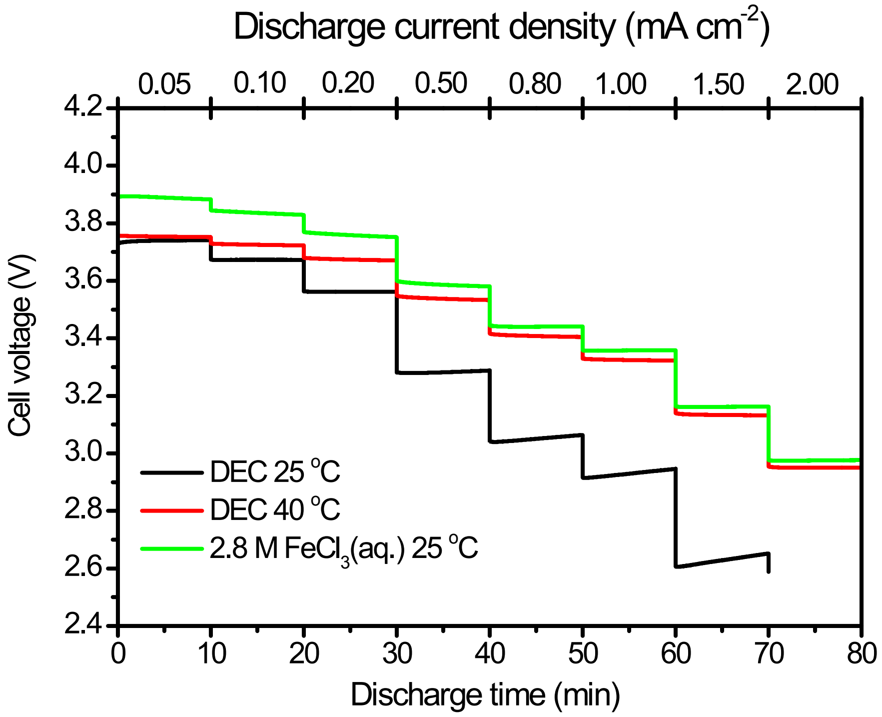
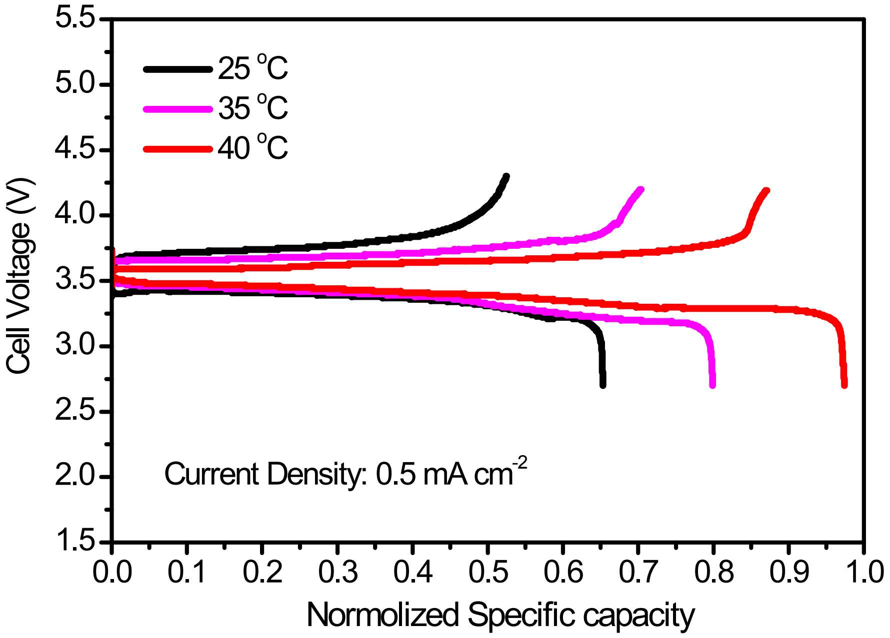
Element	25 ℃	30 ℃	35 ℃	40 ℃
Re/Ω	221.1	213.7	195.8	178.9
Rg/Ω	71.6	58.13	44.08	31.34
Rint/Ω	419.3	298	219.8	152.6

Supplementary Figure 1. Fitting results of the electrochemical impedance spectroscopy measured at different temperatures. (a). Fitting electric circuit. (b) Fitting result of the electrochemical impedance spectroscopy measured at 25 ℃ as an example. (c) Table of the fitting results.



Supplementary Figure 2. A comparison of the discharge rate performances of the DEC and a concentrated $FeCl_3$ (2.8 M) aqueous solution with same battery constructions.



Supplementary Figure 3. The effect of temperature on the 1st full discharge-charge cycle of the Li-DEC battery.