Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information (ESI†)

Ionic liquid incorporated in quasi-solid-state electrolyte for high-temperature supercapacitor applications

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Materials and Methods

1. Materials

$EMIBF_4$ of extremely high purity was purchased from KOEI Chemical Co., LTD. PEGDMA (molecular weight: 550) and azobisisobutyronitrile (AIBN) were purchased from Sigma Aldrich. The electrode materials, commercial activated carbon, Super-P black, and polytetrafluoroethylene (PTFE) were purchased from Kansai Coke, MMM Carbon Co., Belgium, and Daikin Industries, respectively.

2. Electrode

The electrochemical performance was evaluated with a rubber-type electrode, prepared with activated carbon, Super-P black, and PTFE as a binder in a 90:5:5 (w/w/w) ratio, after fully mixing with ethanol in an agate mortar. The rubber type electrode was prepared with the resulting slurry using a roll press and was attached onto the flexible Ta substrate as a current collector using carbon ink, followed by drying at 200 °C for 2 h. The working electrode thus prepared was sandwiched between cellulose membranes. The single electrode mass and density of the rubber-type electrode are 0.012 g and 0.53 g cc^{-1}.

3. Preparation of supercapacitor assembled with ionic liquid incorporated quasi-solid-state electrolyte (ILQSE)

The ILQSE was prepared by mixing 20 g of $EMIBF_4$ (KOEI Chemical Co., LTD), 2 g of PEGDMA (Sigma Aldrich) and 0.2 g of AIBN (Sigma Aldrich) for 20 min in a drying room. Both activated carbon electrodes were dipped in the mixture solution and were heated at 80 °C in an ethylene glycol bath for 15 min to form a quasi-solid, which was dried under vacuum at 80 °C for 1 h to evaporate volatile residue.

Characterization

The thermal properties of ILQSE, $EMIBF_4$, PEGDMA, and c-PEGDMA were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) using NETZSCH STA 409 and were heated from 20 to 600 °C at a rate of 10 °C min^{-1} under N_2 flow. X-ray photoelectron spectroscopy (XPS) was used to investigate the elemental composition and chemical states of electrolyte materials using a PHI 5000 VersaProbe (Ulvac-PHI).

The electrochemical tests of the two-electrode supercapacitors were carried out using a VSP potentiostat (Biologic, France). The ionic conductivity (s, mS cm^{-1}) was measured at various temperatures using an electrochemical impedance spectroscopy method (EIS), and results were calculated using the following equation, where L (cm) is the distance between the two tantalum sheets.[1]

$$\sigma = \frac{L}{R_b S} x\, 1000 \qquad (1)$$

R_b (Ω) is the bulk resistance, and S (cm^2) is the contact area between the ILQSE and the tantalum sheets. The AC impedance analysis was carried out across the frequency range of 100 mHz to 100 kHz at a signal level of 10 mV. The specific capacitance (C, F g^{-1}, equation 2) of the supercapacitors was obtained by galvanostatic charge-discharge (GCD) studies at constant currents and the electrode specific capacitance (C_s, F g^{-1}) was obtained using equation 3. The GCD behavior of the supercapacitor was examined in the voltage range of 0-1.5 V at various current densities (2-50 mA cm^{-2}).[2]

$$C = \frac{I\Delta t}{\Delta V m_{ac}} \qquad (2)$$

$$C_s = 4C \qquad (3)$$

Where I(A) is the set discharge current, Δt (s) is the discharge time, m_{ac} (g) is the total mass of the active materials in the electrode, and ΔV (V) is the voltage window upon discharge. Cyclic voltammetry (CV) curves at various scan rates (5-100 mV s^{-1}) were also obtained. The maximum voltage in the experiment was limited to 1.5 V at 150 °C, even though the decomposition limit voltage was within the safe range for ILQSE operation during heating. The energy density (*E*, Wh kg^{-1}) and power density (*P*, W kg^{-1}) of the supercapacitor were calculated using the equations.[3]

$$E = \frac{C_s(\Delta V)^2}{2} \qquad (4)$$

$$P = \frac{E}{\Delta t} \qquad (5)$$

Where Δt (s) is also the discharge time, C_s is the specific capacitance from GCD test.

Supplementary figures

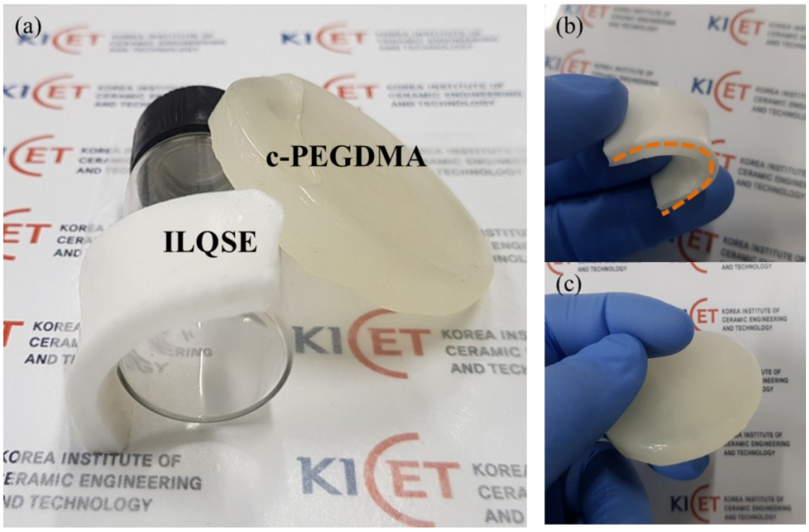

Figure S1. Photographs (a) compared ILQSE and c-PEGDMA, (b) ILQSE, and (c) c-PEGDMA

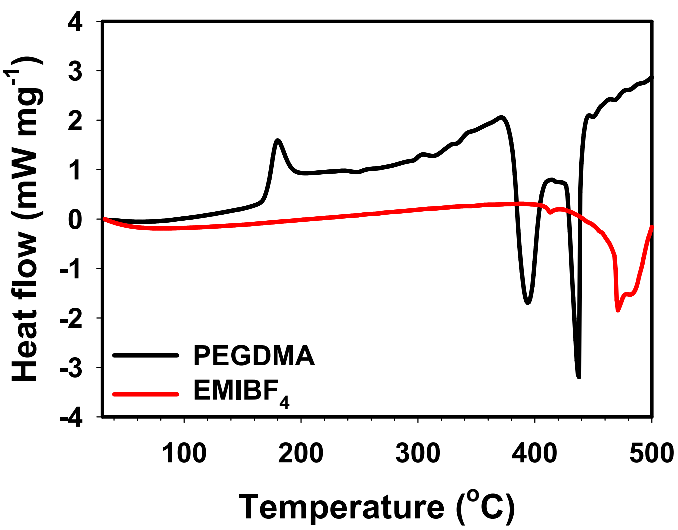

Figure S2. DSC curves of PEGDMA and $EMIBF_4$

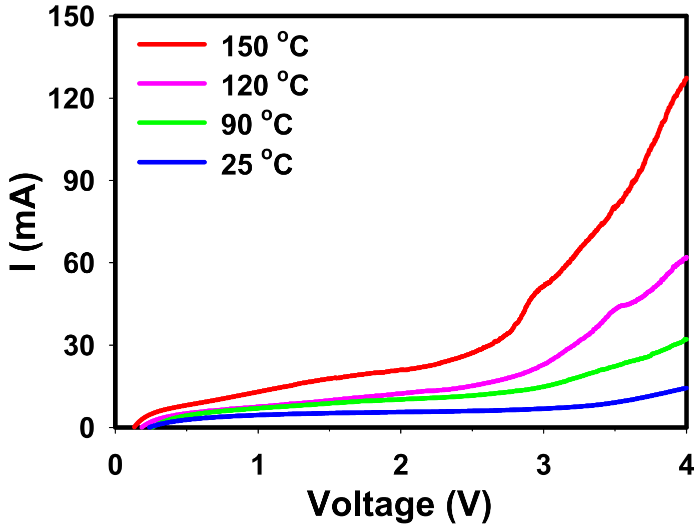

Figure S3. LSV curves of supercapacitor assembled with ILQSE at different temperatures, recorded at a scan rate of 10 mV s^{-1}. The electrochemical stability of ILQSE reduced with an increase in operating temperature, and the available voltage range was also decreased from 3.5 to 2.5 V. Based on the cyclic voltammetry (CV) curves as shown in Fig. 4(a), the voltage window was set to 1.5 V for a stable operation.

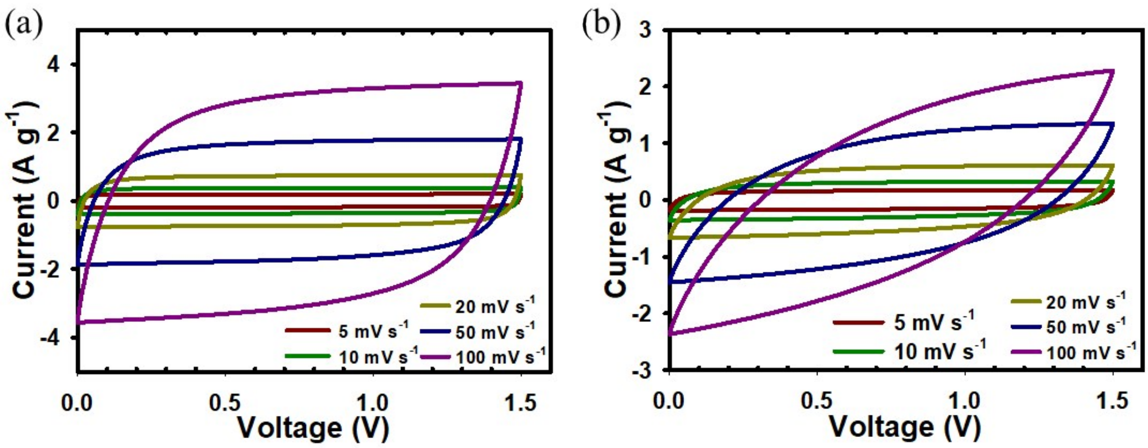

Figure S4. CV curves measured at (a) 150 °C and (b) 25 °C with different scan rates.

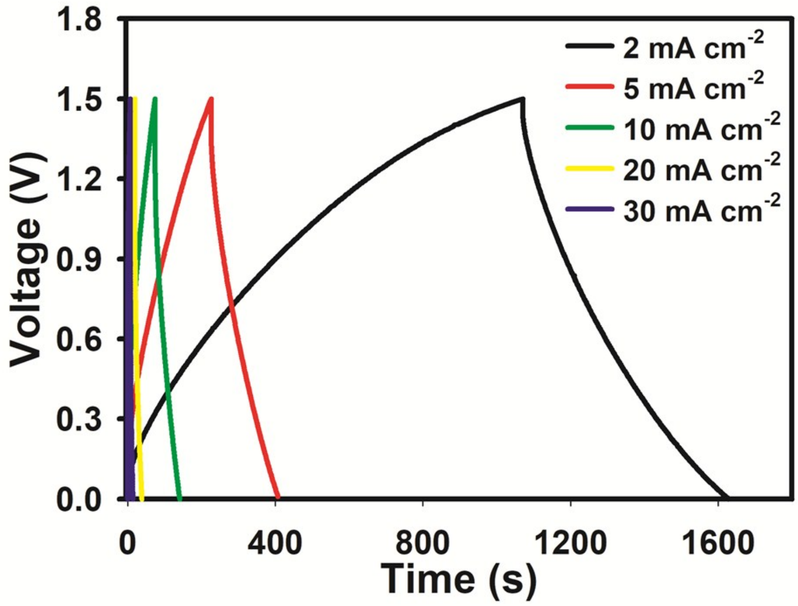

Figure S5. Galvanostatic charge/discharge profile of supercapacitor assembled with ILQSE recorded at 150 °C.

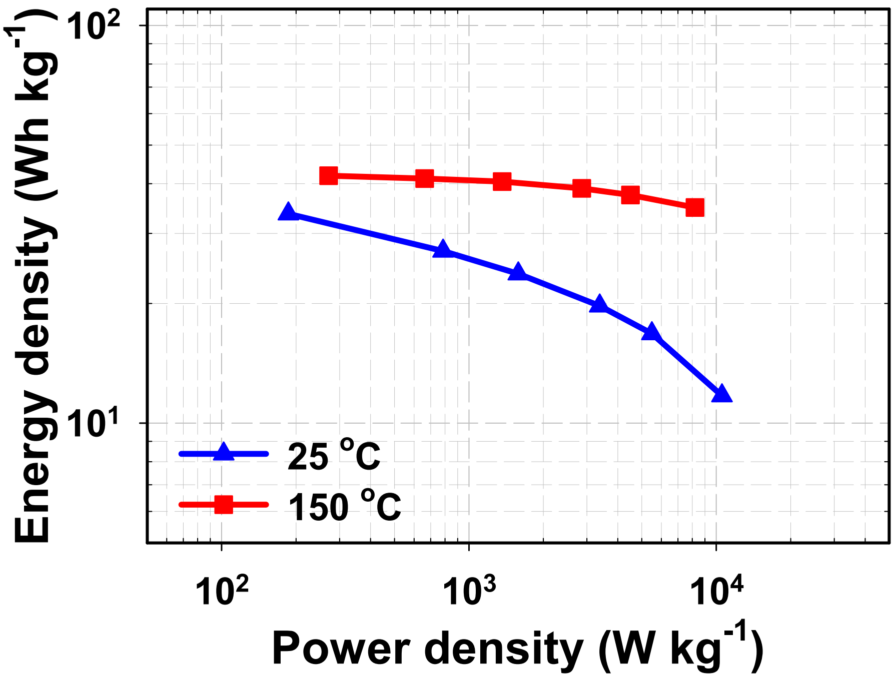

Figure S6. Ragone plot based on galvanostatic charge/discharge profiles at 25 and 150 °C of supercapacitor assembled with ILQSE.

Notes and references

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2 Meng, C., C. Liu, L. Chen, C. Hu, and S. Fan, Nano Letters, 2010, 10, 4025-4031

3 H. Guo, Q. Gao, J. Power Sources, 2009, 186, 551-556