



Short communication

## High/low temperature operation of electric double layer capacitor utilizing acidic cellulose–chitin hybrid gel electrolyte

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## ABSTRACT

An acidic cellulose–chitin hybrid gel electrolyte consisting of cellulose, chitin, 1-butyl-3-methylimidazolium, 1-allyl-3-methylimidazolium bromide, and an aqueous H<sub>2</sub>SO<sub>4</sub> solution is investigated for electric double layer capacitors (EDLCs) with activated carbon fiber cloth electrodes. The acidic cellulose–chitin hybrid gel electrolyte shows a high ionic conductivity comparable to that for an aqueous 2 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> solution at 0–80 °C. This system's temperature dependence in EDLC performance is investigated by galvanostatic charge–discharge measurement. An EDLC cell with the acidic hybrid gel electrolyte has higher capacitance than that with the aqueous H<sub>2</sub>SO<sub>4</sub> solution in the range of operation temperatures (–10 to 60 °C). Moreover, the capacitance retention of the EDLC cell with the acidic hybrid gel electrolyte is better than that of a cell with the H<sub>2</sub>SO<sub>4</sub> solution at 60 °C over 10,000 cycles. This suggests that the proposed acidic gel electrolyte has excellent stability in the presence of a strong acid, even at a high temperature of 60 °C.

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### 1. Introduction

Electric double layer capacitors (EDLCs) are promising energy storage devices that have high power density and long cycle life. To secure their high power, it is essential to use highly ion-conductive electrolytes, which are usually liquid and categorized into aqueous, organic, and ionic liquid electrolytes. Aqueous electrolyte systems are intrinsically incombustible and provide an especially low internal resistance in EDLC, which is derived from their high ionic conductivity, thus giving them high-rate charge–discharge ability and high specific capacitance [1]. Strong acid and base solutions, such as aqueous H<sub>2</sub>SO<sub>4</sub> and KOH, are generally employed as an electrolyte for an aqueous EDLC because of their high ionic conductivity. Since they are hazardous liquids, however, they involve handling difficulties and the risk of leakage.

Polymer gel electrolytes have attracted much interest in applications for devices such as capacitors [2–4], Li-ion batteries [5,6], nickel/metal hydride batteries [7,8], and dye-sensitized solar cells [9,10] because they can provide high reliability without electrolyte leakage as well as a thin-form and separator-free cell. However, the application of polymer gel electrolytes to aqueous EDLCs has

so far been limited. The difficulty of this application is attributed to various problems: the relatively low ionic conductivity of most polymer gel electrolytes, especially at low temperature [11–13], the poor electrical contact at an electrode/electrolyte interface, and the low solubility of salts in a polymer matrix.

In our previous paper, we reported on an acidic polymer gel electrolyte derived from cellulose, chitin, binary ionic liquids (ILs), and an aqueous H<sub>2</sub>SO<sub>4</sub> solution for use in EDLCs [14]. It was found that an EDLC cell with the acidic cellulose–chitin hybrid gel electrolyte exhibits higher capacitance and better cycle life than those for a reference aqueous H<sub>2</sub>SO<sub>4</sub> electrolyte cell at room temperature. Moreover, our self-discharge measurement elucidated that the application of the acidic cellulose–chitin hybrid gel electrolyte suppresses the leakage current and potential decay of EDLC. In addition to good stability against a strong acid, cellulose and chitin are representative natural polysaccharides with non-toxicity and biocompatibility, and they are actually the most abundant organic substances in the biosphere [15–18].

In this study, we elucidate the temperature dependence of EDLC performance with the acidic cellulose–chitin hybrid gel electrolyte in a range between –10 and 60 °C. In particular, the aim of this paper is to demonstrate the satisfactory performance of the proposed system even at high and low temperature extremes. Such a temperature–performance relationship is important because it is a practical issue for EDLC cells in a variety of electrical equipment. We found that an EDLC cell with the hybrid gel electrolyte

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exhibits rather better EDLC performance than a cell with a reference aqueous  $\text{H}_2\text{SO}_4$  electrolyte.

## 2. Experimental

### 2.1. Preparation of acidic cellulose–chitin hybrid gel electrolyte

The cellulose–chitin hybrid gel electrolyte was prepared by the following method [19]: mixtures of cellulose and 1-butyl-3-methylimidazolium chloride (BMIImCl, BASF Japan Ltd., purity >95%) and of chitin and 1-allyl-3-methylimidazolium bromide (AMImBr, prepared by a reaction of 1-methylimidazole with 3-bromo-1-propene [20]) were independently heated at  $100^\circ\text{C}$  for 24 h with stirring to yield clear solutions of cellulose (10 wt.%) and chitin (5 wt.%), respectively. These two solutions were then mixed to get a cellulose-to-chitin ratio ca. 3:1 (w/w) at  $100^\circ\text{C}$  for 1 h, followed by casting the resulting solution onto a glass plate at room temperature and leaving for 4 days. During the process, the excess IIs were spontaneously excluded from the deposited gel. The gel was washed with ethanol to remove excess binary IIs and dried under reduced pressure. The obtained cellulose–chitin hybrid gel film was approximately 1.1-mm thick. The resulting weight ratios of cellulose, chitin, BMIImCl, AMImBr, and  $\text{H}_2\text{O}$  in the cellulose–chitin hybrid gel were approximately 2.6, 0.8, 16, 10, and 70.6 wt.%, respectively. Finally, a cellulose–chitin hybrid gel with binary IIs and  $\text{H}_2\text{SO}_4$  was obtained after immersion in an aqueous  $2\text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  solution for 3 h. This finalized acidic cellulose–chitin hybrid gel of 1.00 g can store 0.170 g of  $\text{H}_2\text{SO}_4$ . It had a flexible nature, stability against acid, and transparency.

### 2.2. Fabrication of electrochemical cells

Activated carbon fiber cloths (ACC-507-15, Nippon Kynol Inc., specific surface area: ca.  $1300\text{ m}^2\text{ g}^{-1}$ ) were used as electrode active material. A pair of electrodes (diameter: 10 mm) was immersed in a  $2\text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  solution for 3 h under reduced pressure prior to the test cell assembly. A two-electrode test cell fabricated with a pair of the electrodes and the acidic hybrid gel was employed for the electrochemical measurements; all components were mounted in a Teflon container as a cell exterior with Pt current collectors. For comparison, we also assembled the other type of test cell as a reference. The cell included an aqueous  $2\text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  solution without the hybrid gel; it contained a separator made of glass fiber (GB-100R, Toyo Roshi Kaisha, Ltd.).

### 2.3. Electrochemical measurements

The discharge rate capability of the EDLC cells was evaluated in a constant-current (CC) mode at various discharge current densities between 100 and  $10,000\text{ mA g}^{-1}$  immediately after their charge to 1.0 V in a CC mode at  $100\text{ mA g}^{-1}$ . Extended charge–discharge cycling tests were also carried out in the cell voltage range between 0 and 1.0 V at a current density of  $5000\text{ mA g}^{-1}$ . All of the electrochemical measurements were performed with a Solartron model 1480 multi-stat electrochemical measurement unit.

## 3. Results and discussion

### 3.1. Ionic conductivity of the acidic cellulose–chitin hybrid electrolyte

Fig. 1 shows the temperature dependence of logarithmic ionic conductivity for the acidic cellulose–chitin hybrid gel electrolyte and the aqueous  $2\text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  electrolyte. Within the operation temperature, ionic conductivity of the acidic hybrid gel

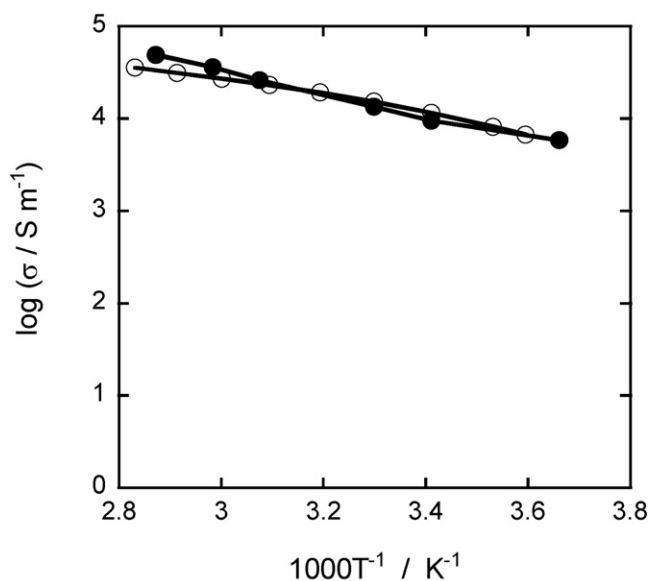


Fig. 1. Temperature dependence of ionic conductivity  $\sigma$  for acidic hybrid gel (●) and for aqueous  $2\text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  (○).

electrolyte is almost the same as that of the aqueous  $\text{H}_2\text{SO}_4$  liquid electrolyte. For example, the ionic conductivity at  $25^\circ\text{C}$  is  $57.8$  and  $61.9\text{ S m}^{-1}$  for the gel and the aqueous  $\text{H}_2\text{SO}_4$  liquid electrolyte, respectively. Generally, ionic conductivity of most polymer gel electrolytes sharply deteriorates at low temperature [2,21]. For the present acidic gel and the aqueous  $\text{H}_2\text{SO}_4$  electrolyte, the relationship between  $\log \sigma$  and  $1000/T$  appears almost linear; it looks like a straight line in an Arrhenius-type manner (ca.  $0$ – $80^\circ\text{C}$ ). Even at a low temperature of  $5^\circ\text{C}$ , the respective ionic conductivities for the gel and the aqueous  $\text{H}_2\text{SO}_4$  solution are  $43.3$  and  $46.0\text{ S m}^{-1}$ .

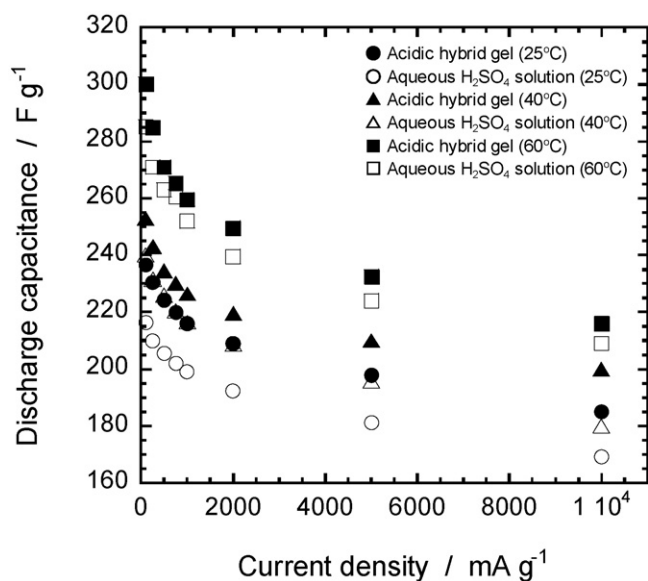
The Arrhenius activation energies of the present gel and the aqueous  $\text{H}_2\text{SO}_4$  solution, estimated from their ionic conductivity in the range from  $5$  to  $80^\circ\text{C}$ , are  $10.0$  and  $8.8\text{ kJ mol}^{-1}$ , respectively. Iwakura et al. [8] reported that the reliable activation energy of cross-linked poly (acrylic acid) containing a  $6\text{ M KOH}$  solution as a high-performance alkaline polymer gel:  $13.7\text{ kJ mol}^{-1}$ . The activation energy of the present gel electrolyte is quite low and almost comparable to that of a strong acid solution. These findings suggest that the acidic gel electrolyte provides fast ion transfer, similar to a liquid electrolyte. Such high ionic conductivity for the acidic gel leads us to expect a high-performance gel EDLC in a wide temperature range.

### 3.2. Charge–discharge characteristics of acidic cellulose–chitin hybrid gel electrolyte at low and high temperature

The temperature dependence (high temperature:  $40$  and  $60^\circ\text{C}$ ) of discharge capacitances with current density is shown in Fig. 2. The discharge capacitance is calculated from the following formula:

$$\text{Discharge capacitance} = \frac{2It}{VX}$$

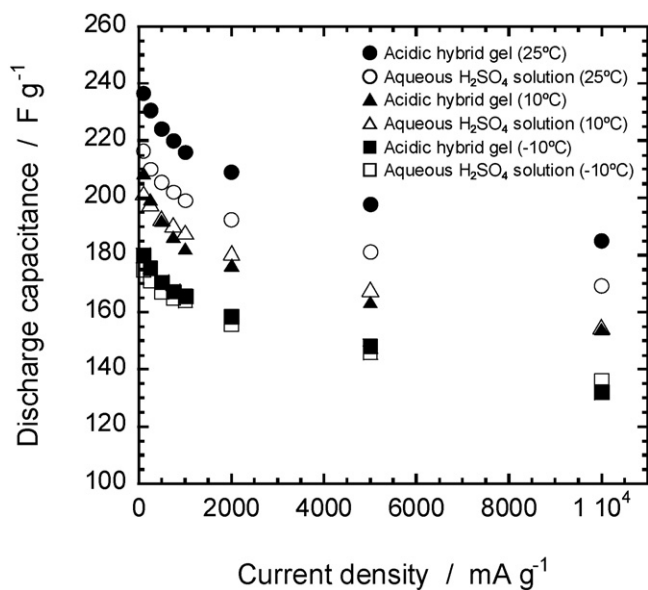
where  $I$  is the discharge current,  $t$  the discharge time,  $V$  the cell voltage change including an  $IR$  voltage drop element, and  $X$  the mass of active material. Both the acidic hybrid gel electrolyte and the aqueous  $\text{H}_2\text{SO}_4$  solution show an increase in discharge capacitance with increasing temperature. At a high temperature of  $60^\circ\text{C}$ , the discharge capacitance for an EDLC cell with the acidic gel at  $100\text{ mA g}^{-1}$  is estimated to be  $300.0\text{ F g}^{-1}$ , which is 27.1% higher than the corresponding value at room temperature ( $25^\circ\text{C}$ ). These



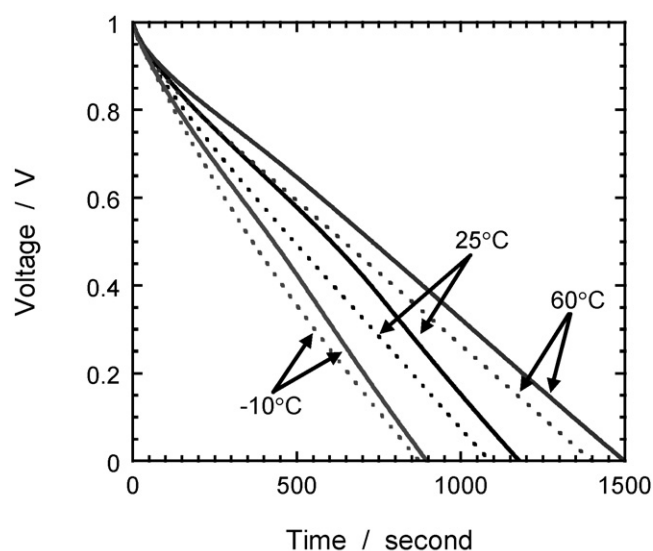
**Fig. 2.** Discharge capacitance as a function of current density for the EDLC cells containing acidic hybrid gel electrolyte and aqueous H<sub>2</sub>SO<sub>4</sub> solution at temperatures of 25, 40, and 60 °C. Operation voltage: 0–1 V.

results agree with the increasing ion conductivity with temperature found from the Arrhenius plots in Fig. 1. At each operation temperature, the discharge capacitance of the acidic gel obviously exceeds that of the aqueous H<sub>2</sub>SO<sub>4</sub> electrolyte. Moreover, even at 60 °C, the coulombic efficiency of the hybrid gel electrolyte at 100 mA g<sup>-1</sup> is almost the same as that of the aqueous H<sub>2</sub>SO<sub>4</sub> solution, suggesting that the hybrid gel has good electrochemical stability at relatively high temperature.

Another important characteristic that should be considered evidence for the acidic gel electrolyte is the EDLC performance at low temperature, since the EDLC performance of conventional gel electrolytes degrades significantly with decreasing temperature due to falling ionic conductivity. Fig. 3 shows the low-temperature effect of discharge capacitance as a function of current density. The discharge capacitance of the acidic gel and the aqueous H<sub>2</sub>SO<sub>4</sub> solution



**Fig. 3.** Discharge capacitance as a function of current density for the EDLC cells containing acidic hybrid gel electrolyte and aqueous H<sub>2</sub>SO<sub>4</sub> solution at temperatures of 25, 10, and -10 °C. Operation voltage: 0–1 V.



**Fig. 4.** Cell voltage profiles in galvanostatic discharge duration for the EDLC cells containing acidic hybrid gel electrolyte (solid line) and aqueous H<sub>2</sub>SO<sub>4</sub> solution (dotted line). Discharge current density: 100 mA g<sup>-1</sup>, operation voltage: 0–1 V.

decreases with decreasing temperature. However, it is noteworthy that the discharge capacitance of the acidic gel and the aqueous H<sub>2</sub>SO<sub>4</sub> solution is almost the same at 0 and even -10 °C. These results indicate that the EDLC cell, including the acidic gel, provides excellent performance even at low temperature.

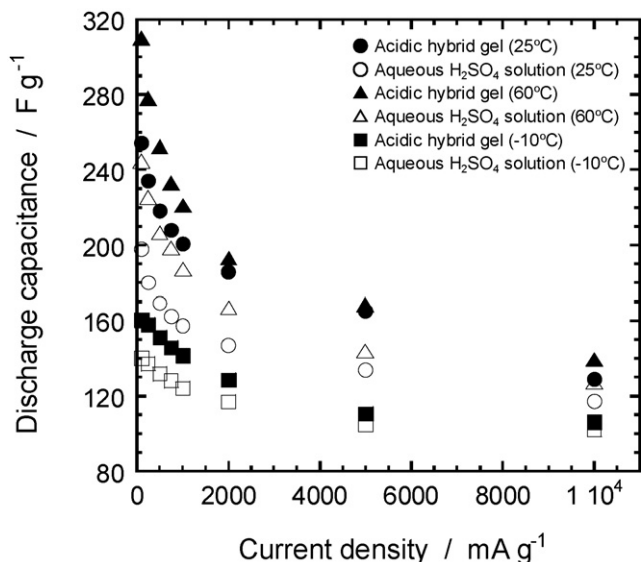
In our previous paper, we reported that the acidic gel has an advantage in increasing energy density over a conventional aqueous H<sub>2</sub>SO<sub>4</sub> solution because the discharge capacitance of the former is higher than that of the latter, which is especially apparent above 0.5 V at room temperature [14,22]. In this context, here we confirm that the EDLC cell containing the acidic gel has higher energy density than a cell with the aqueous H<sub>2</sub>SO<sub>4</sub> electrolyte in the present operating temperature, based on discharge curve profiles. Fig. 4 indicates various discharge profiles for the acidic gel and the aqueous H<sub>2</sub>SO<sub>4</sub> solution in a galvanostatic condition (100 mA g<sup>-1</sup>) at -10, 25, and 60 °C. The EDLC cell with the gel electrolyte obviously shows longer discharge duration than that with the aqueous H<sub>2</sub>SO<sub>4</sub> at each temperature. In particular, the slope of the discharge curves for the gel electrolyte has an inflection at ca. 0.5 V: the gel system apparently has higher capacitance than the aqueous H<sub>2</sub>SO<sub>4</sub> solution above this inflection. The additional capacitance in the high-voltage region could be ascribed to the minor contribution of Br<sup>-</sup> anion derived from AMImBr in the gel; reversible redox processes involving Br species such as Br<sup>-</sup>, Br<sub>2</sub>, and Br<sub>3</sub><sup>-</sup> would occur in the electrode micropores [22]. This high-voltage region contributes to the higher energy density of the EDLC cell containing the acidic hybrid gel than that of the aqueous H<sub>2</sub>SO<sub>4</sub> electrolyte. Therefore, we focus on EDLC performance above 0.5 V, at the more representative level of 0.8–0.9 V.

Fig. 5 shows the dependence of discharge capacitance on current density estimated from galvanostatic discharge curves in a high-voltage region. The discharge capacitance is also calculated from the above formula used in Figs. 2 and 3, and here  $\Delta V$  is the cell voltage change: 0.8–0.9 V. Obtained discharge capacitances of the EDLC cells with the hybrid gel electrolyte and the aqueous H<sub>2</sub>SO<sub>4</sub> electrolyte from Figs. 2, 3 and 5 are listed in Table 1. At relatively low current densities, the discharge capacitance of the EDLC cells with the acidic hybrid gel electrolyte is significantly higher than that with the aqueous H<sub>2</sub>SO<sub>4</sub> solution at each operation temperature. The highest capacitance value is obtained for the hybrid gel electrolyte cell operated with 100 mA g<sup>-1</sup> at 0.8–0.9 V and a

**Table 1**  
Summary of discharge capacitance ( $\text{Fg}^{-1}$ ) of the EDLC cell containing the acidic hybrid gel and the cell with the aqueous  $2 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  solution in the operation voltage of 0–1 V<sup>a</sup>.

| Current density ( $\text{mA g}^{-1}$ ) | Acidic hybrid gel electrolyte |               |               | Aqueous $\text{H}_2\text{SO}_4$ solution |               |               |
|--|-------------------------------|---------------|---------------|--|---------------|---------------|
|  | -10°C                         | 25°C          | 60°C          | -10°C                                    | 25°C          | 60°C          |
| 100                                    | 180.0 (160.4)                 | 236.0 (254.3) | 300.0 (309.9) | 174.8 (140.1)                            | 216.0 (197.7) | 285.2 (244.7) |
| 500                                    | 170.5 (151.2)                 | 224.2 (218.0) | 271.1 (252.3) | 167.1 (131.7)                            | 205.4 (169.1) | 263.0 (206.6) |
| 1000                                   | 165.7 (141.3)                 | 216.0 (200.3) | 259.5 (220.9) | 164.0 (124.1)                            | 199.3 (157.3) | 252.2 (187.1) |
| 5000                                   | 148.2 (110.6)                 | 197.8 (165.1) | 232.5 (168.3) | 146.2 (104.8)                            | 181.2 (133.6) | 224.0 (143.7) |
| 10,000                                 | 132.7 (106.3)                 | 185.2 (128.7) | 216.0 (139.2) | 136.1 (102.1)                            | 169.2 (117.3) | 209.0 (127.0) |

<sup>a</sup> The value in parentheses is the discharge capacitance calculated from the high-voltage (0.8–0.9 V) region.



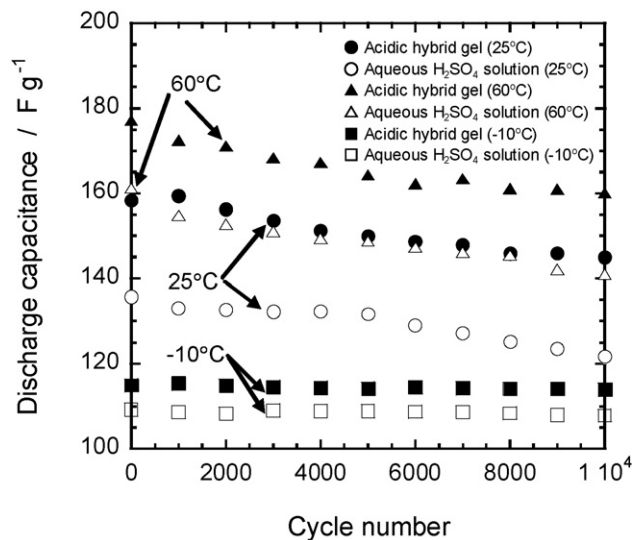
**Fig. 5.** Discharge capacitance estimated at 0.8–0.9 V with various current densities for the EDLC cells containing acidic hybrid gel electrolyte and aqueous  $\text{H}_2\text{SO}_4$  solution at -10, 25, and 60°C.

high temperature of 60°C, and it is estimated to be  $309.9 \text{ Fg}^{-1}$ . Note that this discharge capacitance is 27% higher than the corresponding value for the aqueous  $\text{H}_2\text{SO}_4$  solution. This suggests that the acidic hybrid gel provides higher energy density than a conventional aqueous  $\text{H}_2\text{SO}_4$  solution, especially at high operation temperature.

### 3.3. Extended cycling performance for acidic cellulose–chitin hybrid gel electrolyte

Fig. 6 shows the discharge capacitance for the EDLC cells with the acidic cellulose–chitin hybrid gel electrolyte and the aqueous  $\text{H}_2\text{SO}_4$  electrolyte as a function of cycle number at a current density of  $5000 \text{ mA g}^{-1}$ . The capacitance retention of the acidic hybrid gel and the aqueous  $\text{H}_2\text{SO}_4$  electrolyte is improved with a decrease in temperature. Although the capacitance for both systems decreases with cycling at a high temperature of 60°C, the discharge capacitances for the hybrid gel electrolyte and the aqueous  $\text{H}_2\text{SO}_4$  solution retain 90.4% and 87.5% of their initial value, respectively, even at the 10,000th cycle, suggesting that the cellulose–chitin hybrid gel matrix has excellent stability against a strong acid even at 60°C.

It is worth noting that both the discharge capacitance and the capacity retention of the EDLC cell with the acidic hybrid gel are better than those with the aqueous  $\text{H}_2\text{SO}_4$  solution in the operation temperature range over 10,000 cycles. In our previous paper [23], we showed that the acidic gel can properly maintain not only an acidic component but also moisture without evaporation loss due to the strong hydrophilicity of binary ILs, and thus it achieves stable capacitance retention. In the present study, the favorable



**Fig. 6.** Discharge capacitance as a function of cycle number for the EDLC cells containing acidic hybrid gel electrolyte and aqueous  $\text{H}_2\text{SO}_4$  solution at -10, 25, and 60°C. Charge–discharge current density:  $5000 \text{ mA g}^{-1}$ , operation voltage: 0–1.0 V.

hydrophilicity contributes to retaining the stabilizing capacitance at all of the applied temperatures. We also found that the acidic hybrid gel is stable without degradation or phase transition even at the high and low temperatures attempted here.

The present study demonstrates that the acidic hybrid gel has a clear advantage in enhancing energy density over a conventional aqueous  $\text{H}_2\text{SO}_4$  solution in the tested temperature range. The excellent EDLC performance of the acidic hybrid gel electrolyte is promising for the development of advanced gel-based EDLCs.

## 4. Conclusion

An acidic cellulose–chitin hybrid gel electrolyte, prepared from cellulose, chitin, specific ILs and an aqueous  $\text{H}_2\text{SO}_4$  solution, was applied to EDLC. The temperature dependence of ionic conductivity for the acidic cellulose–chitin hybrid gel electrolyte is Arrhenius-type and similar to an aqueous  $\text{H}_2\text{SO}_4$  electrolyte. An EDLC cell with this electrolyte has a higher capacitance than that with only the aqueous  $\text{H}_2\text{SO}_4$  solution within the range of operation temperatures. In particular, the cell with the acidic hybrid gel provides improved capacitance in the high-voltage region. The discharge capacitance and the capacity retention of the EDLC cell with the acidic hybrid gel electrolyte are better than those with only the  $\text{H}_2\text{SO}_4$  solution within the operation temperature range over 10,000 cycles. This suggests that the proposed gel electrolyte has excellent stability under the acid condition. The EDLC with the acidic hybrid gel electrolyte exhibits excellent performance not only at room temperature but also in the high and low temperature conditions.

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