

## Hybrid capacitor with activated carbon electrode, Ni(OH)<sub>2</sub> electrode and polymer hydrogel electrolyte

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### Abstract

A new hybrid capacitor (HC) cell was assembled using an activated carbon (AC) negative electrode, an Ni(OH)<sub>2</sub> positive electrode and a polymer hydrogel electrolyte prepared from crosslinked potassium poly(acrylate) (PAAK) and KOH aqueous solution. The HC cell was characterized compared with an electric double layer capacitor (EDLC) using two AC electrodes and the polymer hydrogel electrolyte. It was found that the HC cell successfully worked in the larger voltage range and exhibited ca. 2.4 times higher capacitance than the EDLC cell. High-rate dischargeability of the HC cell was also superior to that of the EDLC cell. These improved characteristics strongly suggest that the HC cell can be a promising system of capacitors with high energy and power densities.

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**Keywords:** Hybrid capacitor; Activated carbon; Ni(OH)<sub>2</sub> electrode; Polymer hydrogel electrolyte; Electric double layer capacitor

### 1. Introduction

Electric double layer capacitors (EDLCs) have been commercially used as power sources of various devices because of their high power density and long cycle performance. In order to increase the energy and power densities, extensive works on activated carbon (AC) electrodes and electrolytes in EDLCs have been carried out. However, the increase in the energy density is limited because the charge–discharge mechanism is based on the adsorption and desorption of ions on the AC electrode surface without charge transfer. Pseudocapacitance electrodes using metal oxides [1,2] or conducting polymers [3,4] have been reported to show much higher capacitance than AC electrodes, although the kinetics and/or cycle stability are generally poor due to the redox reaction. For the purpose of gaining both high energy and power densities, several types of hybrid capacitors (HCs) composed of the AC and pseudocapacitance electrodes have recently

been proposed and investigated [5–7]. If the pseudocapacitance electrode with very small polarization is used instead of one of the AC electrodes in EDLCs, the voltage change of the electrode scarcely occurs during charging and discharging, leading to a remarkable increase in the capacitance and energy density of the cell.

Ni(OH)<sub>2</sub> has been also used as electrode material of HCs [8,9]. Park et al. assembled an HC cell using an AC negative electrode, an Ni(OH)<sub>2</sub>/AC composite or Ni(OH)<sub>2</sub> positive electrode and 6 M KOH aqueous solution [8]. The HC showed much higher capacitance than the EDLC due to the high capacitance of Ni(OH)<sub>2</sub>. Previously, we reported that an alkaline polymer hydrogel electrolyte prepared from crosslinked potassium poly(acrylate) (PAAK) and KOH aqueous solution [10,11] exhibited excellent performance in EDLCs and increased the capacitance of the AC electrode probably due to the pseudocapacitance [12–14]. The electrolyte also has the significant advantage of showing very slow electrolyte creepage [15]. Furthermore, it was found that charge–discharge reactions occurred smoothly and reversibly at the interface between the electrolyte and Ni(OH)<sub>2</sub> elec-

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trode in nickel/metal hydride cells [16]. In this work, a new HC cell was assembled replacing one of two AC electrodes in the EDLC cell with the polymer hydrogel electrolyte by an  $\text{Ni}(\text{OH})_2$  electrode, and the charge–discharge characteristics were investigated compared with those of the EDLC cell.

## 2. Experimental

The polymer hydrogel electrolyte was prepared from PAAK and 10 M KOH aqueous solution and impregnated into a nonwoven fabric separator as described in our previous paper [14]. An AC fiber cloth (Kuraray Co., Ltd.) with a specific surface area of  $2000 \text{ m}^2 \text{ g}^{-1}$  was used as a negative electrode material of the HC cell. The AC cloth ( $10 \text{ mm} \times 10 \text{ mm}$ ) was dried at  $120^\circ\text{C}$  for 24 h in order to remove impurities such as adsorbed organic compounds. The AC cloth was impregnated with the polymer hydrogel electrolyte in the same manner as the separator. The resulting AC cloth with the electrolyte was stuck on a nickel sheet with the carbon paste. On the other hand, a commercial sintered  $\text{Ni}(\text{OH})_2$  electrode ( $10 \text{ mm} \times 10 \text{ mm}$ ) was used as a positive electrode of the HC cell. Before assembling the cell, the  $\text{Ni}(\text{OH})_2$  electrode was activated by five charge–discharge cycles at a rate of  $0.5\text{C}$  in 10 M KOH aqueous solution, and then fully charged and discharged to the depth of discharge of 50%.

An experimental HC cell was assembled as shown in Fig. 1. The separator with the polymer hydrogel electrolyte was stacked between the AC and  $\text{Ni}(\text{OH})_2$  electrodes. A similar type EDLC cell was also assembled using two AC electrodes for comparison [14]. Thickness of each cell composed of the two electrode and separator was ca. 1.0 mm. In all charge–discharge cycling tests, the HC and EDLC cells were charged and discharged in the voltage ranges of 0.4–1.2 and 0.2–0.8 V, respectively, at a constant current. Cyclic voltammetry for the AC electrode was carried out in the potential range of  $-1.0$  to  $0.2 \text{ V}$  versus  $\text{Hg}/\text{HgO}$  at a scan rate of  $10 \text{ mV s}^{-1}$ . The temperature in all measurements was kept at  $25^\circ\text{C}$ .

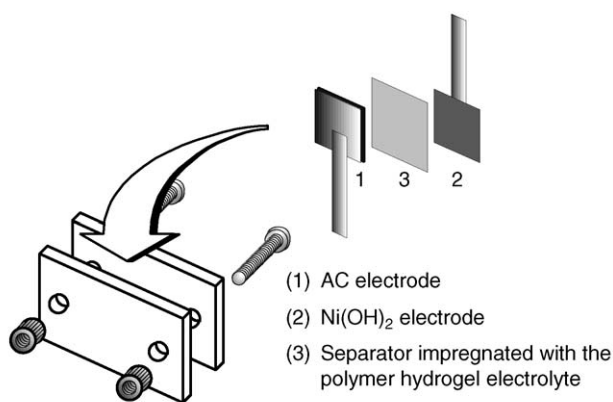


Fig. 1. Schematic representation of the experimental cell assembly.

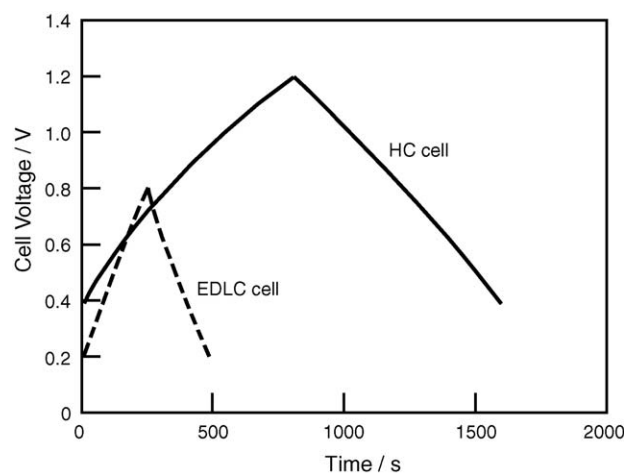


Fig. 2. Charge–discharge curves at  $1 \text{ mA cm}^{-2}$  of the HC and EDLC cells.

## 3. Results and discussion

Fig. 2 shows typical galvanostatic charge and discharge curves of the HC and EDLC cells with the polymer hydrogel electrolyte ( $1 \text{ mA cm}^{-2}$ , 10th cycle). Almost linear charge and discharge curves were observed in each case. In our previous papers, good electrode/electrolyte interface could be constructed using the polymer hydrogel electrolyte and either the AC electrode [12–14] or the  $\text{Ni}(\text{OH})_2$  electrode [16]. It can be considered that the good electrode/electrolyte interface was also formed in the present experimental HC cell and, therefore, the cell successfully worked as a capacitor. IR drop was scarcely observed in each curve under this experimental condition, which is ascribed to high ionic conductivity of the polymer hydrogel electrolyte (ca.  $6.0 \times 10^{-1} \text{ S cm}^{-1}$  at  $25^\circ\text{C}$ ) and its good contact with both the electrodes. From the discharge curve, the discharge capacitance of the HC cell was evaluated to be  $0.97 \text{ F}$ , which was ca. 2.4 times higher than that of the EDLC cell,  $0.40 \text{ F}$ . It is clear that the capacitance of the cell was markedly increased by replacing one of the AC electrode in the EDLC with the  $\text{Ni}(\text{OH})_2$  electrode. In addition, it was found that the HC cell could work until a larger cell voltage such as  $1.2 \text{ V}$ , compared with that for the EDLC cell,  $0.8 \text{ V}$ . The coulomb efficiencies were ca. 98 and 95% for the HC and EDLC cells, respectively, in the voltage ranges as shown in Fig. 2. This leads to a large increase in both the power and energy densities of the cell.

In order to elucidate the reason for the improved charge–discharge characteristics of the HC cell, potential changes of the negative and positive electrodes were examined using an  $\text{Hg}/\text{HgO}$  reference electrode during the charge–discharge cycle test of the cell. As can be seen from Fig. 3, both the negative and positive electrodes showed almost linear charge–discharge curves in the HC and EDLC cells. In case of the HC cell, the potential change of the  $\text{Ni}(\text{OH})_2$  positive electrode was very small (ca.  $0.36$ – $0.38 \text{ V}$  versus  $\text{Hg}/\text{HgO}$ ), compared with that of the AC positive electrode in the EDLC cell. On the other hand, the potential of the

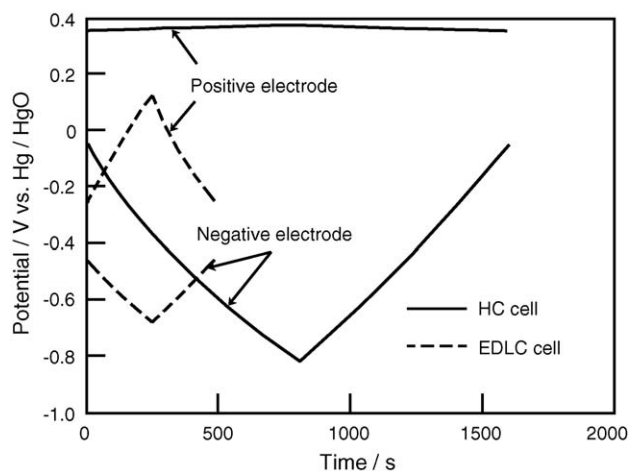


Fig. 3. Charge–discharge curves at  $1 \text{ mA cm}^{-2}$  of the positive and negative electrodes in the HC and EDLC cells.

AC negative electrode in the HC cell changed in the range of ca.  $-0.82$  to  $-0.04 \text{ V}$  versus  $\text{Hg}/\text{HgO}$ . Fig. 4 shows the cyclic voltammogram of the AC electrode in the HC cell with the polymer hydrogel electrolyte. The AC electrode shows nearly typical capacitive behavior, and hydrogen and oxygen evolution reactions are hardly observed in the potential range of ca.  $-0.82$  to  $-0.04 \text{ V}$  versus  $\text{Hg}/\text{HgO}$ . This is the reason that the HC cell showed the high coulomb efficiency close to 100% even in the voltage range of  $0.4$ – $1.2 \text{ V}$  as described above. From the discharge curves in Fig. 3, it can be calculated that discharge capacitances of the positive electrodes in the HC and EDLC cells are ca.  $38$  and  $0.64 \text{ F}$ , respectively, while those of the negative electrodes are almost the same, ca.  $1.0 \text{ F}$ , in both the cells. It is clear that the charge–discharge characteristics of the HC cell are largely regulated by the AC negative electrode due to the much higher capacitance of the  $\text{Ni}(\text{OH})_2$  positive electrode. This is responsible for the remarkable increase in the discharge capacitance of the cell.

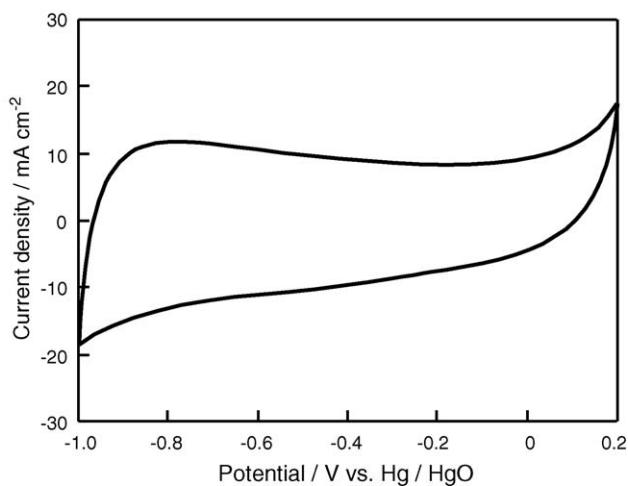


Fig. 4. Cyclic voltammogram at  $10 \text{ mV s}^{-1}$  of the AC electrode in the HC cell.

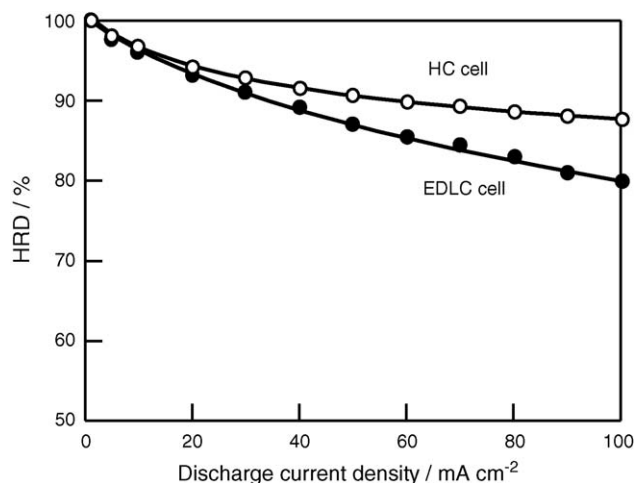


Fig. 5. High-rate dischargeabilities (HRD) for the HC and EDLC cells.

High-rate dischargeability (HRD) of the HC cell was investigated compared to that of the EDLC cell. The cells were charged at  $1 \text{ mA cm}^{-2}$  and then discharged at various current densities. The ratio of discharge capacitance at a current density to that at  $1 \text{ mA cm}^{-2}$  was evaluated as the value of HRD. As can be seen from Fig. 5, the HC cell exhibited more excellent HRD than the EDLC cell. The values of HRDs of the HC and EDLC cells at  $100 \text{ mA cm}^{-2}$  were estimated to be ca.  $88$  and  $80\%$ , respectively. This disagreement with the result reported by Park et al. that HRD of the HC cell using an  $\text{Ni}(\text{OH})_2$  or  $\text{Ni}(\text{OH})_2/\text{AC}$  composite electrode was inferior to that of the EDLC using only AC electrodes [8]. This might be due to the difference in the electrolytes or  $\text{Ni}(\text{OH})_2$  electrode used.

The cause for the improved HRD was investigated by comparing discharge curves of the negative and positive electrodes at different current densities. The discharge curves at  $50$  and  $100 \text{ mA cm}^{-2}$  are shown in Fig. 6. In each cell, the slope of the discharge curve of the negative electrode hardly changed with increasing the current density, while the IR drop slightly increased. Thus, the capacitance loss of the AC negative electrode can be estimated to be close to zero. On the other hand, the slopes of the curves of the positive electrodes in both the cells changed to a certain extent. The changes are equivalent to capacitance losses of ca.  $15$  and  $8\%$  for the positive electrodes in the HC and EDLC cells, respectively. This implies that the  $\text{Ni}(\text{OH})_2$  positive electrode has poorer HRD than the AC positive electrode due to the redox reaction. However, as can be seen from Fig. 6, the discharge capacitances of the HC and EDLC cells are largely controlled by those of the negative and positive electrodes, respectively, even at high current density such as  $100 \text{ mA cm}^{-2}$ . Therefore, the capacitance decay with increasing the current density of the HC cell is smaller than that of the EDLC cell.

Fig. 7 shows discharge capacitance as a function of cycle number for the HC and EDLC cells during the charge–discharge cycling at  $10 \text{ mA cm}^{-2}$ . Although the cycle

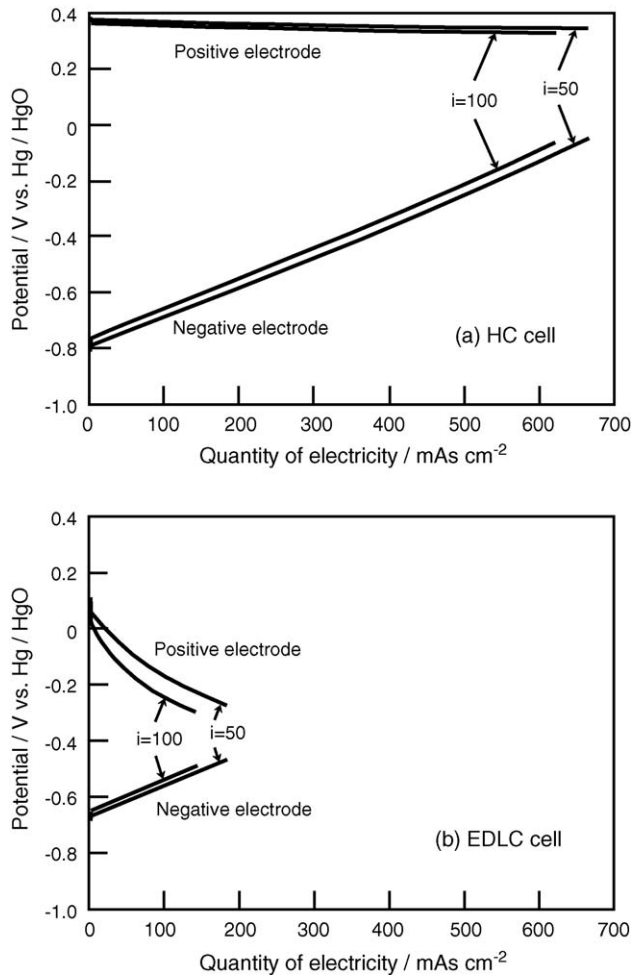


Fig. 6. Discharge curves at 50 and 100 mA cm<sup>-2</sup> of the negative and positive electrodes in the (a) HC and (b) EDLC cells.

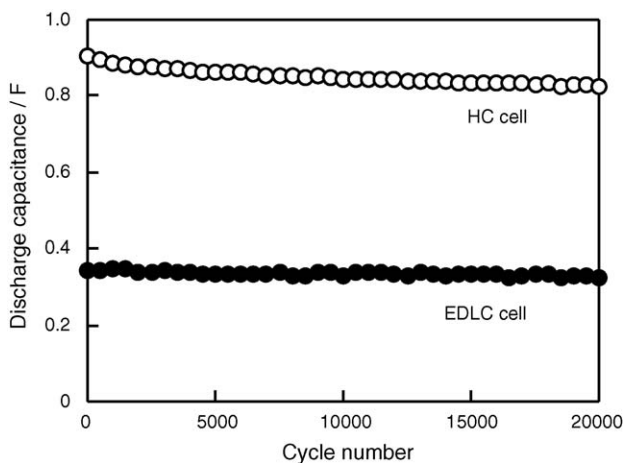


Fig. 7. Discharge capacitance as a function of cycle number for the HC and EDLC cells.

stability of the HC cell was slightly inferior to the EDLC cell, over 90% of initial discharge capacitance was maintained at 20,000th cycle for the HC cell, which is still ca. 2.3 times higher than that for the EDLC cell. The cycle stability of the HC cell is promising compared with those of other capacitors using pseudocapacitance electrodes with the redox reaction. The results as mentioned above strongly suggest that the HC cell assembled in this work can be a new system of electrochemical capacitors with the high energy and power densities.

#### 4. Conclusions

A new HC cell was assembled using AC negative and Ni(OH)<sub>2</sub> positive electrodes and the polymer hydrogel electrolyte. From charge–discharge cycle tests, it was found that the HC cell worked as a capacitor in the large voltage range up to 1.2 V with a high coulomb efficiency compared with the EDLC cell. The capacitance of the HC cell was ca. 2.4 times higher than that of the EDLC cell. This can be ascribed to the very small polarization of the Ni(OH)<sub>2</sub> positive electrode during charge–discharge cycling. Moreover, the HC cell exhibited more excellent HRD than the EDLC cell. This is because the capacitance of the HC cell is mainly regulated by that of the AC negative electrode with the excellent HRD. The discharge capacitance at 20,000th cycle of the HC cell was over 90% of initial value, which is much higher than that of the EDLC cell.

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