Porous and Electrically Conducting Clay–Carbon Composite as Positive Electrodes of Zinc–Oxygen Primary Cells and Zinc–Iodine Secondary Cells

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Preparation and utilization of various porous electrode materials have been reported [1–3]. We now report use of a new porous and electrically conducting clay–carbon composite, which is prepared by sintering mixtures of clay and porous carbon, as excellent positive electrodes of zinc–oxygen primary cells and zinc–iodine secondary cells. Although clay-modified electrodes have been recently reported to show interesting electrochemical properties [4–9], use of clay-based porous materials as electrodes of primary and secondary cells has no precedent.

The clay–carbon composite was prepared by sintering mixtures of clay (kibushi clay (locality = Sanage, Aichi prefecture, Japan) mainly composed of kaolinite) and one of the two carbons shown in Table I.

TABLE I. Clay Data

Name (code)	Supplier	Surface area (m^2/g)	Density (g/cm^3)
Ketjen black EC (KBEC)	Lion Corp.	930	0.60
Ketjen black EC-DJ600 (ECDJ600)	Lion Corp.	1270	0.35

When a 85:15 mixture of the clay and porous carbon was sintered at 800 °C for 1 h, the obtained composite showed high mechanical strength of about 200 kg cm^{-2}, good electrical conductivity (*ca.* 1 S cm^{-1}), large surface area of 160–210 m^2 g^{-1} (measured by BET method and the value depended on the kind of the carbon powder), bulk density of about 0.9 g cm^{-3}, and high porosity of about 60%. The mechanical strength of the composite was higher than that (130 kg cm^{-2}) of a commercialized porous carbon plate (Nippon carbon #P140), although the

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composite had higher porosity than that (50%) of the commercialized porous carbon plate. Because of its high porosity, high mechanical strength, large surface area and good electrical conductivity, the composite is suitable for positive electrodes of zinc–oxygen primary cells and zinc–iodine secondary cells. Since the composite shows high affinity toward water due to the hydrophilic property of the sintered clay, it is especially useful for electrodes in aqueous media. Carbon is widely used as a good material for electrodes, however use of porous carbon is sometimes restricted because of its water-repelling nature. Increase in the carbon content gave a composite with higher surface area and higher porosity, but it showed lower mechanical strength (compressive strength = 100 kg cm^{-2}) and the composite with 15–20 wt% of carbon seemed to be best suitable for preparation of the electrode.

Scanning electron microscopy indicated that the porous composite contains many micropores with an approximate diameter of 1 μm. Since the diameter of the micropores is considerably small, the rate of flow of gas through the composite is rather slow (but the rate of flow is enough for the positive electrode of the zinc–oxygen cell). When a composite with a diameter of 5 mm and thickness of 2 mm was used and oxygen flowed through the composite along a direction perpendicular to the surface of the composite, the rate of flow of oxygen changed with change of applied pressure of oxygen (as shown in Fig. 2). If we apply the Hagen–Poiseuilli law,

$$\text{rate of flow} = \frac{\pi R^4}{8\eta L} \times P \tag{1}$$

(R: diameter of micropore, η: viscosity, L: length of micropore, P: applied pressure)

and assume that the micropore has a structure shown in Fig. 1 and the composite has the porosity of 50%, we obtain the broken line in Fig. 2 for the calculated rate of flow of oxygen. The rough agreement of the observed and calculated values supports the validity of the model shown in Fig. 1. Water also can move through the composite, but the rate of flow of water was considerably low due to its high viscosity. Since gases can pass through the composite at an appropriate rate of flow and the passage of electrolytic solutions is negligible, the composite is suited for electrodes of cells using gases (e.g., fuel cells, zinc–O_2 cell, zinc–Cl_2 cell, etc.); a gas–liquid–solid ternary system favored for cell reactions [10] is formed in the composite, whereas leak of the electrolytic solution through the composite is prevented.

Figure 3 shows the structure of a Zn|KOH (8 M) aq|O_2 primary cell. Figure 4 shows the discharging
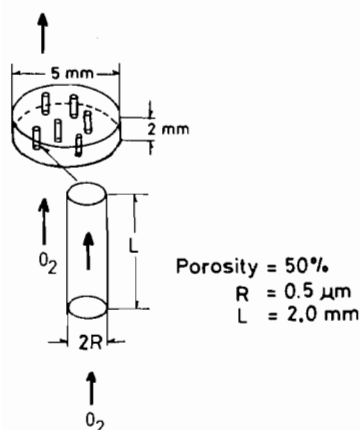
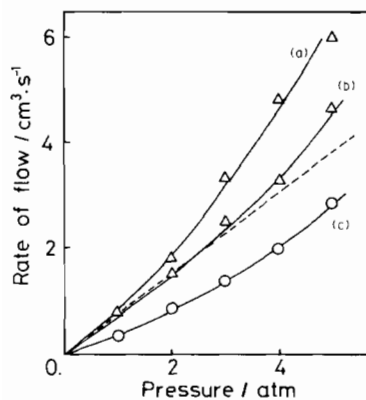Fig. 1. Model for the flow of oxygen through the composite.

Fig. 2. Rate of flow of oxygen through the composite at room temperature. Carbon powder in the composite: (a) ECDJ600 (20.5 wt%), (b) ECDJ600 (15.6 wt%), or (c) KBEC (19.0 wt%).

Fig. 3. Structure of $Zn|KOH$ (8 M) $aq|O_2$ cell using the porous composite as the positive electrode. A: positive electrode disk, B: Tube made of stainless steel, C: Tube made of silicon resin, D: Tube made of glass, E: zinc plate (negative electrode), and F: packing. An aqueous solution of KOH (8 M) was introduced into the inside of B and D. Side face of the positive electrode disk was connected to B with electrically conducting resin (electrodag + 301).

Fig. 4. Discharging curves of the $Zn|KOH$ (8 M) $aq|O_2$ cell shown in Fig. 3 at constant electric current (2, 4, 6, 8, and 10 mA) at room temperature. Values in parentheses indicate electric current per surface area of the positive electrode disk (ϕ = 5 mm, area = 0.196 cm^2).

curves of the cell at constant electric currents. As shown in Fig. 4, the cell shows a stable flat discharging voltage even at a large current density of 51 mA/cm^2.

Although porous carbon plates and carbon filter felts have been used as the positive electrode of the zinc—oxygen or zinc—air galvanic cell, the carbon-based electrode usually contains catalysts such as Pt, Pd [11] and metal complexes [12] for activation of oxygen. In the present cell, however, the positive electrode containing no metal catalyst gave the stable current even at the high current density. This is presumably due to the large active surface area of the composite. Due to the high activity of the clay—carbon composite as the gas-electrode, the composite may be useful also as electrodes of fuel cells.

In addition to the usability as the electrode of zinc—oxygen cells, the clay—carbon composite showed good usability as a positive electrode of zinc—iodine secondary cells. As we previously reported [13, 14], the zin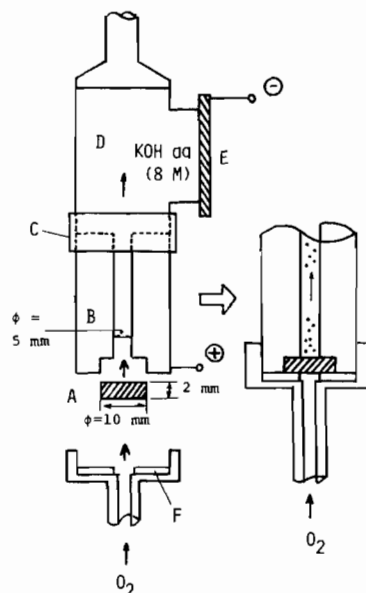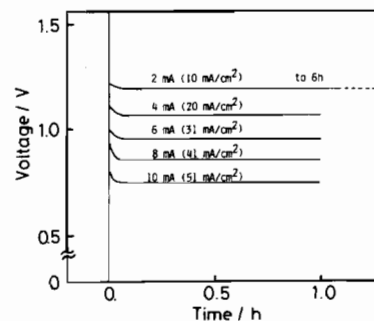c—iodine secondary cell using a cation exchanging membrane as a separator showed good rechargeability with current efficiency of 100%. In our previous report, we used nylon-6-carbon composite as the electrode. Use of the porous clay—carbon described above as the electrode of the zinc—iodine secondary cell also gave good rechargeability with 100% current efficiency as shown in Fig. 5. In the experiment to obtain the results shown in Fig. 5, we used a cell similar to that reported in our previous papers [13, 14]; the clay—carbon composite was employed instead of the nylon-6-carbon composite
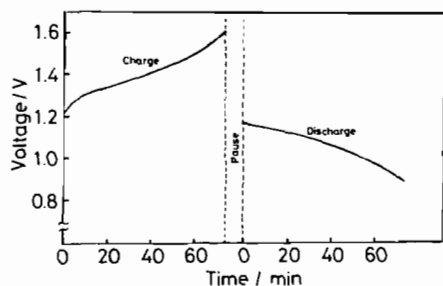
Fig. 5. Charging and discharging curves of the $Zn|ZnI_2$ (2.5 M) + NH_4Cl (5 M)|cation exchange membrane|ZnI_2 (2.5 M) + NH_4Cl (5 M)|iodine + clay—carbon composite cell at 40th charge—discharge cycle at room temperature. At 10 mA constant electric current. Diameter of the cell = 1.0 cm. Amounts of the electrolytic solution in the anode compartment and cathode compartment are 160 μl, respectively.

and the electrolytic solution was modified from an aqueous solution of ZnI_2 (0.5—1.0 M) to an aqueous solution containing ZnI_2 (2.5 M) and NH_4Cl (5 M). Both the anode and cathode compartments contained 160 μl of the electrolytic solution, and about 2/3 of the electrolytic solution in the anode compartment was absorbed by the porous clay—carbon composite.

As shown in Fig. 5, the cell is rechargeable with almost 100% current efficiency even in the charging and discharging at considerably large electric current (12.7 mA/cm^2 of the positive and negative electrodes).

In the present secondary cell, most of the positive electrode reaction,

$$2I^- \underset{\text{charge}}{\rightleftharpoons} I_2 + 2e \qquad (2)$$

is considered to occur in the porous clay—carbon composite impregnated with the electrolytic solution. Iodine formed in the charging seems to stay in the porous composite and part of the iodine seems to form complexes with clay and carbon in the composite. The capacity of the secondary cell was about 30 mA h/(cm^3 of inner volume of cell) in the charge—discharge cycle at 10 mA constant electric current, and the cell was rechargeable more than 250 cycles. Since the porous and electrically conducting clay—carbon composite is easily prepared and has commercial advantages, and handling of the composite is easy due to its high mechanical strength, cells using the composite may find practical use.

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