

SECONDARY BATTERY USING THE ION-EXCHANGE CARBON FIBER
AND AN AQUEOUS SOLUTION OF NaCl

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New secondary battery having about 2V of the electromotive force was made by placing the ion-exchange carbon cloths as a positive and a negative electrodes in an aqueous solution of NaCl. The capacity of the battery using each 16g of electrodes was 0.46 A·hr in the case of continuous discharge of 0.02 A/dm².

In the course of the investigation on the ion-exchange carbon fiber¹⁾, the author had noticed the following fact. When a saturated solution of NaCl was electrolyzed by using the ion-exchange carbon cloth as the electrodes, the current increased almost linearly along with raising of the applied voltage from 0 to 2.5V and, in the process of lowering the voltage, some counter electric current was observed in the range below 0.5V as is shown in Fig.1. Interest in this fact has led to the suggestion that the secondary battery can be made by use of the ion-exchange carbon electrodes and an aqueous solution of NaCl. Then the battery as is shown schematically in Fig. 2 was made for a preliminary examination. Ion-exchange capacity of the carbon cloth used was 2.1 mequiv/g, and a total apparent surface area and a total weight of the each electrode was 200 cm² and 16g, respectively. First charge was carried out by using a charging current of 0.4A until the charging voltage reaches 2.25V and was continued at this voltage until the current decreases to less than 0.03A. About 20 hours were required to finish the first charge. The voltage of the charged battery decreased gradually on standing as is shown in Fig.3(a). Other curve in Fig. 3 represent the change of the voltage during the continuous discharge. For recharge of the discharged battery, only several hours were required.

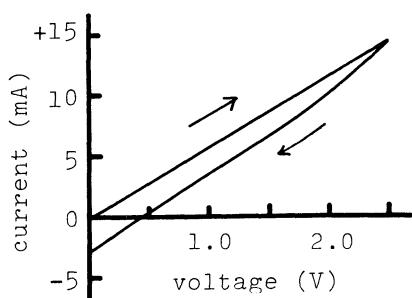


Fig. 1. Relation between a current and a voltage at the electrolysis of a saturated solution of NaCl by using the ion-exchange carbon electrodes

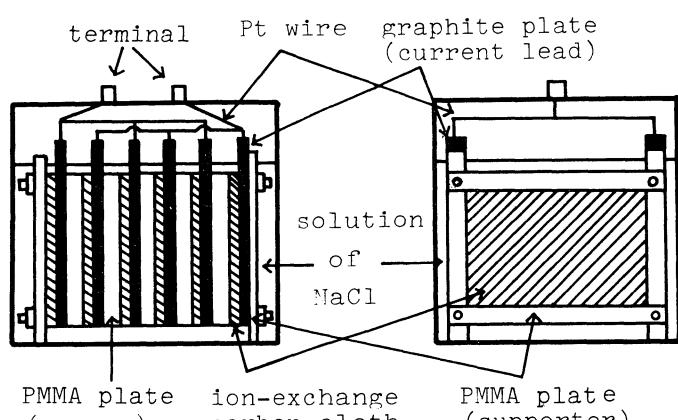


Fig. 2. Schematic structure of the secondary battery

When a cut-off voltage was fixed at 1.0V, a capacity of the battery was about 0.64 A-hr in the case of a continuous discharge at 0.02 A/dm^2 , and watt-hr efficiency was about 65% in continuous discharge at 0.06 A/dm^2 . After the cycles of charge and discharge were repeated 20 times, the capacity decreased in some extent.

Electrode potential and other behaviors concerning the reaction at the both electrodes were measured by using another testing cell having the electrodes of each 2g in weight, 20 cm² in surface area and a glass cloth diaphram. Fig. 4 shows the change of the both electrode potentials during intermittent discharge(150-ohm). At the point of completion of charging, the electrode potentials of the positive and the negative electrodes are +1.35V and -0.90V(SHE) respectively, and the polarization is much remarkable at the positive electrode than at the negative one.

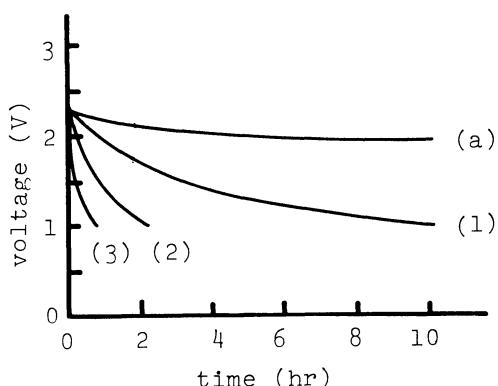


Fig. 3. Change of voltage on standing (a) and during continuous discharge. (1) 0.02 A/dm² (2) 0.06 A/dm² (3) 0.2 A/dm²

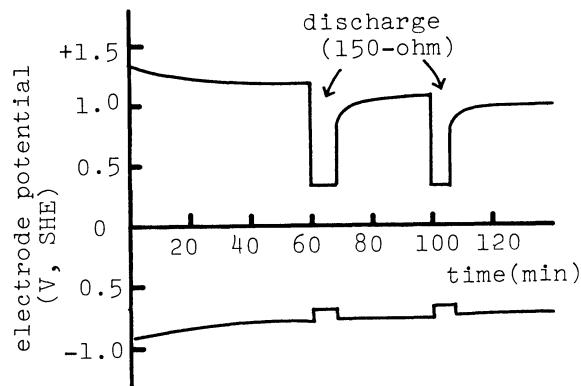
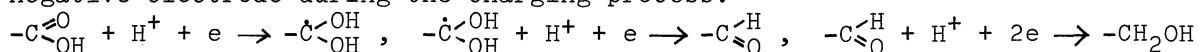


Fig. 4. Change of the electrode potential during the intermittent discharge (150-ohm)

The pH of the electrolytes around the positive and the negative electrodes after charging changed to 1.0-2.0 and 11-12 respectively, and in the cell having no diaphram, the pH of the electrolyte varied in the range of 3 to 4 during the cycle of charge and discharge. In the latter half of the charging process, the formation of fine gas bubbles was observed on the surface of the both electrodes. After several cycles of discharge and recharge, the ion-exchange capacity of the carbon cloth(3.1 mequiv/g before using) used as the positive electrode increased up to 4.2 mequiv/g and that of the negative electrode decreased to 2.3 mequiv/g. Although the reaction mechanism at the electrodes are still uncertain, but it seems most appropriate to consider as follow. From the decrease of the ion-exchange capacity of negative electrode and the change of pH of the electrolyte around the negative electrode, the following reductions of the carboxyl groups which are cause of the ion-exchange property are considered to be main electro-chemical reactions at the negative electrode during the charging process.



The reaction at the positive electrode probably proceeds via the same mechanism as in the case of chlorine gas electrode.

Reference

1) S. Ōtani, M. Tamura, Y. Yoshida and Y. Tsuji, Bull. Chem. Soc. Japan 45, 1908 (1972).

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