

FUNDAMENTAL STUDIES OF URANIUM AND NEPTUNIUM REDOX FLOW BATTERIES (II)

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The atomic power generation entails production of so-called minor actinides and accumulation of depleted uranium. The theoretical and experimental investigations are underway to transmute minor actinides for minimizing the long-term radiotoxicity and reducing the radioactive waste. The utilization, however, would be alternative means. The actinide redox couples, An(VI)/An(V) and An(IV)/An(III), have excellent properties as battery active materials. Here, the uranium and neptunium redox flow batteries for the electric power storage are discussed from the electrochemical properties of U, Np, Pu and Am [1,2].

One of the required properties for the batteries for electric power storage is high energy efficiency, which is defined by the ratio of the discharge energy to the charge energy. These energies are dependent on the rapidness of kinetics in the electrode reactions, namely the standard rate constants and also the internal resistance of the battery.

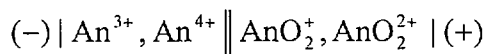
The current density j due to the electrode reaction $O + ne^- \leftrightarrow R$ in the well-stirred solution is given by the Butler-Volmer equation, using the exchange current density $j_o = nFk^oC_O^{1-\alpha}C_R^\alpha$ and the overpotential $\eta = E - E_{eq}$,

$$j = j_o [e^{-\alpha n f \eta} - e^{(1-\alpha) n f \eta}] \quad (1)$$

where α the transfer coefficient, $f = F/RT$, k^o the standard rate constant, C_O and C_R the bulk concentrations of O and R, E electrode potential and E_{eq} equilibrium potential. In the eq.(1), the first and second terms describes the reduction and the oxidation reaction, respectively.

Fig. 1 shows the relationship between the current density and the overpotential in eq. (1). The overpotential is negative for the reduction and positive for the oxidation.

The actinide battery is written by



The discharge voltage V_d of the battery at the constant current density j_d is written by

$$V_d = (E_+ + \eta_{d+}) - (E_- + \eta_{d-}) - j_d R = (E_+ - E_-) + (\eta_{d+} - \eta_{d-}) - j_d R \quad (2)$$

where E_+ and E_- are the positive and negative electrode potentials, η_{d+} and η_{d-} are overpotentials, R is internal resistance and $(E_+ - E_-)$ is the open circuit voltage. In the discharge process, both electrode reactions are written by

$$j_d = j_{o+} [e^{-\alpha n f \eta_{d+}} - e^{(1-\alpha) n f \eta_{d+}}] \quad \text{for positive electrodes} \quad (3)$$

$$j_d = -j_{o-} [e^{-\alpha n f \eta_{d-}} - e^{(1-\alpha) n f \eta_{d-}}] \quad \text{for negative electrodes} \quad (4)$$

because the positive electrode reaction is cathodic and the negative one is anodic. As is shown in Fig. 1, since the overpotential η_{d+} is negative and η_{d-} is positive,

$$V_d < (E_+ - E_-) - j_d R \quad (5)$$

Thus, the discharge voltage is lower than the open circuit voltage $(E_+ - E_-)$.

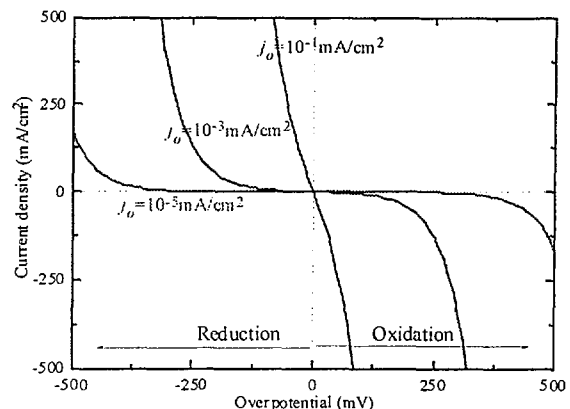


Fig.1 Current-overpotential curves for $O + e^- \leftrightarrow R$



Similarly, the charge voltage and current are written by

$$V_c = (E_+ + \eta_{c+}) - (E_- + \eta_{c-}) + j_c R = (E_+ - E_-) + (\eta_{c+} - \eta_{c-}) + j_c R \quad (6)$$

$$j_c = -j_{o+} [e^{-\alpha n f \eta_{c+}} - e^{(1-\alpha) n f \eta_{c+}}] \quad (7)$$

$$j_c = j_{o-} [e^{-\alpha n f \eta_{c-}} - e^{(1-\alpha) n f \eta_{c-}}] \quad (8)$$

$$V_c > (E_+ - E_-) + j_c R \quad (9)$$

because of $\eta_{c+} > 0$ and $\eta_{c-} < 0$. For the charge discharge process by constant current density, the charge and discharge energies, E_c and E_d , are written by

$$E_c = j_c \times \int V_c dt \quad \text{and} \quad E_d = j_d \times \int V_d dt \quad (10)$$

Then, the energy efficiency ε of the secondary battery is written by

$$\varepsilon = E_d / E_c \quad (11)$$

Fig. 1 shows calculated charge-discharge curves for the constant current density of 75 mA/cm^2 , where K_p and K_n are standard rate constants of the positive and negative electrode reactions, respectively, where the internal resistance is assumed to be zero. The charge and discharge voltages depends on the rapidness of electrode reactions and the difference in the two voltages become larger as the reactions become slower.

The relationships between the standard rate constants of both electrodes and the current density are shown in Fig. 2. These figures shows show the energy efficiency is strongly dependent on the standard rate constants and the internal resistance.

From these qualitative considerations, it is found that there is no significant difference in the energy efficiency between $k_p/k_n=10^{-1}/10^{-1}$ and $10^{-2}/10^{-2}$ in the charge and discharge current densities up to 200 mA/cm^2 .

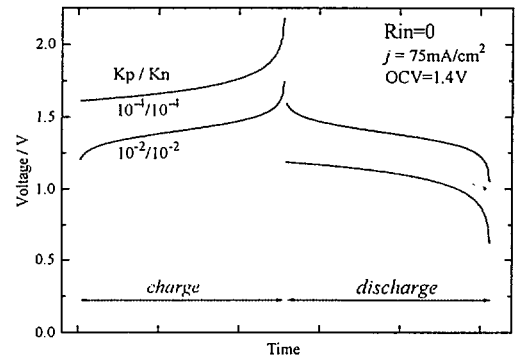


Fig. 1. Dependence of charge-discharge curves on the standard rate constants of both electrode reactions at the internal resistance $R=0$.

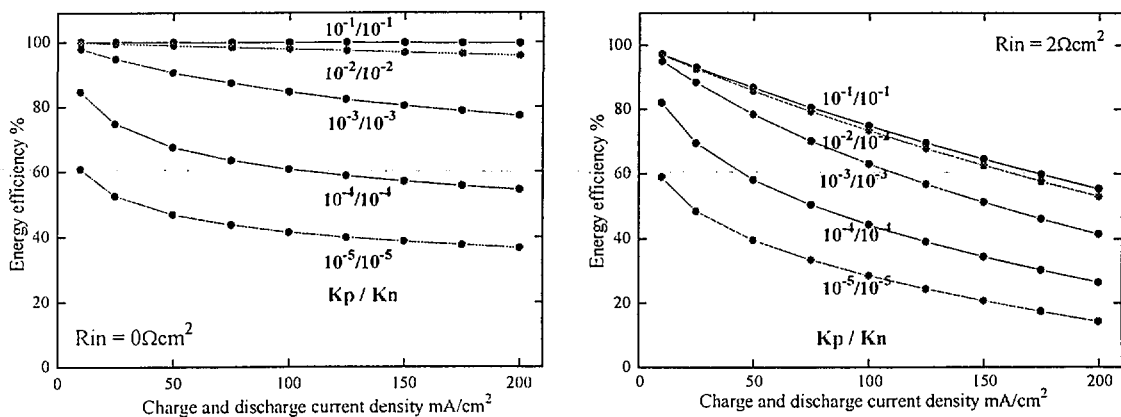


Fig. 2. The dependence of energy efficiencies on the standard rate constants of both electrodes and the inner resistance of the battery.

References

- [1] Y. Shiokawa, H. Yamana, and H. Moriyama, J. Nucl. Sci. Tech. 37 (2000) 253.
- [2] L. H. Thaller, NASA TMX-71540, NASA, USA Dept. of Energy, 1974, USA Patent 3996064.