CHEMISTRY LETTERS, pp. 1339-1340, 1981.

THE CONTRIBUTION OF LATTICE OXYGEN ATOMS OF PRASEODYMIUM OXIDE TO ITS CATHODIC PERFORMANCE

Yoshio TAKASU*, Yoshiharu MATSUDA, and Katsumi YAMASHITA
Faculty of Engineering, Yamaguchi University, Tokiwadai, Ube 755

The cathodic performance of praseodymium oxide systems ($PrO_{2.0}$, $PrO_{1.83}$, and $PrO_{1.71}$) was examined galvanostatically in a mixed solvent of propylene carbonate and 1,2-dimethoxyethane containing $LiClO_4$ at 25 °C. The cathode potential becomes more positive and decays more slowly for the praseodymium oxide with higher oxygen contents.

Whilst various oxide cathodes such as MnO_2, CuO, CrO_3, V_2O_5, MoO_3, AgO, PbO_2, TiO_2, and Bi_2O_3 have been reported for the high energy density batteries with non-aqueous organic solvents,[1-6] the role of lattice oxygen atoms of the oxides for their cathodic characteristics has not adequately been elucidated. Praseodymium oxide is a typical non-stoichiometric oxide, and some of its lattice oxygen atoms could easily be removed by heating it in vacuo above 350 °C.[7,8] Since several metastable states of this oxide can be prepared with little change in surface area, this system is suitable for examining the contribution of the lattice oxygen atoms to the characteristics of oxide cathodes.

Praseodymium oxide, $PrO_{1.83}$ (Pr_6O_{11}), was prepared by calcining the oxalate in air at 800 °C for 6 h. The surface area was 2.3 $m^2\ g^{-1}$. When this oxide was exposed to O_2 (400 Torr, 1 Torr = 133.3 $N\ m^{-2}$) at 300 °C for 1 h after being heated in vacuo at 750 °C for 1 h, $PrO_{2.0}$ was obtained. $PrO_{1.71}$ (Pr_7O_{12}) was prepared by heating $PrO_{1.83}$ in vacuo at 580 °C for 1 h. These oxides were identified with the X-ray diffraction analysis.

The press-molded (400 kg cm^{-2}) PrO_x tablet cathode (13 mm in diameter, 1 mm in thickness) was composed of the mixture of PrO_x (296 mg), graphite (80 mg), acetylene black (4 mg) and polyethylene powder (20 mg). The tablet was mounted on a frame made of poly-tetrafluoroethylene, and the electrical contact was made with a platinum plate (13 mm in diameter) connected to a platinum spring wire. This platinum plate was brought into contact with the tablet cathode. Since the geometric area of the cathode faced to the electrolyte solution was 0.95 cm^2 (corresponding to 71% of the cross section of the tablet cathode), about 212 mg of PrO_x would be effective as the active cathode material. The electrolytic cell was a glass beaker filled with 100 ml of an electrolyte solution composed of a mixture of propylene carbonate (PC) and 1,2-dimethoxyethane (DME) in volume ratio of 1 : 1 containing 1.0 mol dm^{-3} of $LiClO_4$. The counter electrode and the reference electrode were a platinum plate (2 x 3 cm^2) and an SCE, respectively. Prior to the electrical measurements, the electrolyte solution was deoxygenated with high purity nitrogen. The electrolytic cell was thermostated at 25 °C.

Figure 1 shows the discharge curves of the praseodymium oxide cathodes at a

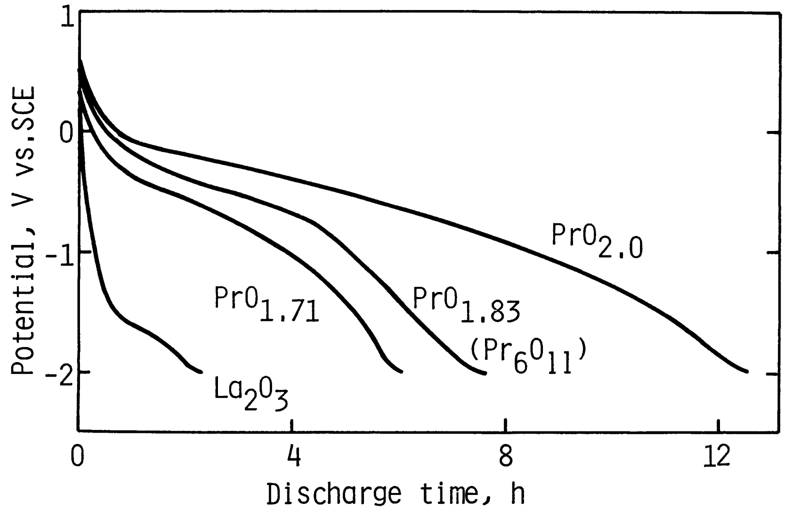

Fig.1. Discharge characteristics of PrO_x cahtodes.

Effective amount of oxide, 212 mg; solvent, PC + DME (1 : 1); solute, $LiClO_4$ (1.0 mol dm^{-3}); current density, 0.53 mA cm^{-2}; temp., 25 °C. Rest potential: E ($PrO_{2.0}$) = 0.59 V, E ($PrO_{1.83}$) = 0.52 V, E ($PrO_{1.71}$) = 0.34 V, E (La_2O_3) = 0.20 V.

constant current density, 0.53 mA cm^{-2}. The discharge curve of a La_2O_3 cathode was also presented for comparison. As is evident from Fig.1, the praseodymium oxide cathodes show remarkably better performance (the electrode potentials remain higher and longer) than the lanthanum oxide cathode. Interestingly, the potential becomes higher and decays slower when the oxygen content of the praseodymium oxide systems increases. Since these electrodes have practically the same surface area, the main factor of the effect must be the presence of the unstable lattice oxygen atoms.

In the X-ray diffraction analysis of the $PrO_{2.0}$ cathode, the peak intensities of $PrO_{2.0}$ [fcc, a (lattice constant) = 5.39 Å] decreased with discharge, while the diffraction lines of $PrO_{1.83}$ [fcc, a = 5.466 Å] began to appear and their intensities increased with discharge. In the case of the $PrO_{1.83}$ cathode, the intensities of the diffraction peaks of $PrO_{1.83}$ decreased with discharge, but neither any new peak nor peak shift was observed on the diffraction spectra. Similar behavior was observed for the $PrO_{1.71}$ [rhombohedral, a = 5.516 Å] cathode. During the discharge of the $PrO_{2.0}$ cathode, therefore, the oxide is probably reduced to PrO_x ($x \leqq 1.83$) via $PrO_{1.83}$ liberating the unstable lattice oxygen atoms, and the liberated oxygen atoms will be consumed to form Li_2O. Thus the conversion of $PrO_{2.0}$ into $PrO_{1.83}$ can be represented by $6\ PrO_2 + 2\ Li^+ + 2\ e^- = Pr_6O_{11} + Li_2O$; but no diffraction line of Li_2O was observed, presumably owing to its low degree of crystallization. The reduction of both $PrO_{1.83}$ and $PrO_{1.79}$ will also involve the liberation of the lattice oxygen atoms, though the definite evidence is not available at present.

References

1) R. Jasinski, J. Electroanal. Chem., 26, 189 (1970).
2) H. Ikeda, T. Saito, and H. Tamura, DENKI KAGAKU, 45, 314 (1977).
3) Y. Matsuda, K. Teraji, and Y. Takasu, ibid. 44, 363 (1976).
4) H. Knapp, Power Source Conference, 19, 94, (1965).
5) N. Margalit, J. Electrochem. Soc., 121, 1460 (1974).
6) T. Ohzuku, Z. Takehara, and S. Yoshizawa, DENKI KAGAKU, 46, 407, 411 (1978).
7) Y. Takasu, M. Matsui, H. Tamura, S. Kawamura, Y. Matsuda, and I. Toyoshima, J. Catal., 69, 51 (1981).
8) P. Kunzmann and L. Eyring, J. Solid State Chem., 14, 229 (1975).

(Received June 29, 1981)