JOURNAL OF APPLIED ELECTROCHEMISTRY 12 (1982) 275–280

Properties of $SrMO_{3-\delta}$ (M=Fe, Co) as oxygen electrodes in alkaline solution

Y. TAKEDA, R. KANNO, T. KONDO, O. YAMAMOTO
Department of Chemistry, Faculty of Engineering, Mie University, Tsu, 514, Japan

H. TAGUCHI
Osaka Prefectural Industrial Research Institute, Nishi-ku, Osaka 550, Japan

M. SHIMADA, M. KOIZUMI
The Institute of Scientific and Industrial Research, Osaka University, Osaka 565, Japan

Received 24 July 1981

Strontium ferrates and cobaltates with compositions $SrFeO_{3-\delta}$ ($0.06 \leqslant \delta \leqslant 0.40$) and $SrCoO_{3-\delta}$ ($0.04 \leqslant \delta \leqslant 0.30$) were synthesized. The dependence of the oxygen electrode properties on the δ value was examined in 1 mol dm^{-3} KOH solution. In the $SrFeO_{3-\delta}$ series, the samples with $0.24 < \delta < 0.29$, showed the highest activity in both oxygen evolution and reduction reactions. In contrast, no strong dependence on the δ value was observed in $SrCoO_{3-\delta}$, which also showed a high catalytic activity for oxygen evolution.

---

1. Introduction

During the last decade, many compounds with the perovskite structure have been found to exhibit high electrical conductivity and good catalytic activity for oxygen evolution and the reduction of oxygen [1]. The general formula for perovskites is ABO_3. The A ion may be a large cation and the B ion, a small transition metal cation. Many authors have reported on the effect on the electrode properties of partial substitution of the A site ions with another cation or the B site ions with another transition metal [2–4]. The $La_xSr_{1-x}MO_{3-\delta}$ (M = Mn, Fe, Co) systems in particular have been studied because of their high catalytic activity. It is well known that perovskite-type oxides containing alkaline earth metals have a nonstoichiometric composition and that the measure of the nonstoichiometry of the compound, δ, which corresponds to the concentration of the oxygen ion vacancies, depends on the preparation conditions, e.g. oxygen pressure and annealing temperature. The stoichiometric compounds, ABO_3 (A = alkaline earth metal, B = Fe or Co), were obtained only under a high oxygen pressure. The relationships between δ and the magnetic properties and between δ and the electrical properties of these compounds have been studied extensively [5]. However, no detailed report on the dependence of the catalytic properties of the oxygen electrodes on the value of δ has been presented. Kudo *et al.* [6] have reported the electrode potentials of $Nd_{1-x}Sr_xCoO_{3-\delta}$ in a KOH solution as a function of δ, where δ is reversibly changed by the electrochemical reaction. Further, Bronoel *et al.* [7] suggested that the catalytic activity of $La_{1-x}Sr_xFeO_{3-\delta}$ for the oxygen electrodes increases as the fraction of oxygen vacancies increases.

In this study, $SrFeO_{3-\delta}$ and $SrCoO_{3-\delta}$, with various values of δ, were prepared under different conditions (oxygen pressure and temperature). The electrode characteristics of these compounds in KOH solution were examined as a function of δ.

2. Experimental procedure

Well dried reagent grade $SrCO_3$ and α-Fe_2O_3 or $SrCO_3$ and $CoCO_3$ were weighed in equimolar ratios and mixed in an agate mortar. After the

0021-891X/82/030275-06$03.22/0

mixtures were prefired at 900° C for 2 h in Pt crucibles in air, they were ground, pelleted, and fired at 1300° C for 24 h in air for $SrFeO_{3-\delta}$, and at 1000° C for 24 h in a flow of oxygen gas for $SrCoO_{3-\delta}$. Then, they were quenched to room temperature. The products obtained were ground thoroughly and pressed under a pressure of 50 MPa into a pellet before being refired at 1300° C in air ($SrFeO_{3-\delta}$) or at 1000° C in a flow of oxygen gas ($SrCoO_{3-\delta}$) for 24 h. $SrFeO_{3-\delta}$ samples were annealed under an oxygen pressure of 20 kPa–120 MPa at 500–1300° C for 10–96 h, and $SrCoO_{3-\delta}$ samples were annealed under an oxygen pressure of 10–120 MPa at 300° C for 72–168 h.

The products were identified by X-ray powder diffractometry using nickel filtered Cu*Kα* or iron filtered Co*Kα* radiation. The lattice parameter was obtained at a slow scan rate of 0.25°/min using silicon powder as an internal standard. The oxygen content in the samples was determined by chemical analysis using the oxidation–reduction method, which was presented by Mori *et al.* [8] for $SrFeO_{3-\delta}$ and by Gushee *et al.* [9] for $SrCoO_{3-\delta}$. The electrical conductivity was measured by a four-terminal method with direct current. The electrochemical measurements were carried out in an H-type Pyrex cell. The electrolyte solutions were 1 mol dm^{-3} KOH. An Hg/HgO electrode was used as the reference electrode and a graphite bar as the counter electrode. The working electrodes were sintered $SrFeO_{3-\delta}$ and $SrCoO_{3-\delta}$. The electrode surfaces were previously polished with No. 1000 emery papers, and an electrical lead was connected via silver paste on one side of the electrode surface. The specimen was then mounted in a paper tube with polyester resin. The *IR*-free potentials were obtained as a function of the current by means of a current interrupter. The current was increased in a stepwise manner and the electrode potentials at each current point were considered as the quasi steady-state potentials when the deviation of the measured potentials was within 5 mV for 2 min. There were no significant differences in the polarization curves when measured several times provided a high current was not passed through the electrodes. The curves in the figures indicate the initial values. At higher current densities, significant gas evolution and decomposition of the electrodes were observed, and the electrode potentials increased with time. Such a current density region is shown by the dotted line in the polarization curves. During the measurements, oxygen gas was bubbled through the electrolyte. All measurements were made at room temperature.

3. Results and discussion

In Tables 1 and 2, the δ values for $SrFeO_{3-\delta}$ and $SrCoO_{3-\delta}$ obtained by annealing at various oxygen pressures and various temperatures are shown. The δ values of the strontium ferrates $SrFeO_{3-\delta}$ quenched from 1300° C in air are in the range 0.34–0.40, and those slowly cooled in the furnace from 1300° C are in the range 0.24–0.31, depending on the annealing period: δ decreases with increasing annealing period. However, the samples with δ values lower than 0.24 were not obtained in air. In order to prepare the less oxygen deficient specimens, the samples were annealed in an oxygen gas flow. The lowest value of δ, 0.13, was found for samples annealed at

Table 1. δ values in $SrFeO_{3-\delta}$

Annealing conditions			*Cooling conditions*	δ
Temperature (° C)	*Time* (h)	*Atmosphere*		
1300	16	Air	Quenched	0.40
1300	7	Air	Quenched	0.34
1300	15	Air	Slow	0.31
1000	12	Air	Quenched	0.30
1200	16	Air	Slow	0.27
1300	12	Air	Slow	0.24
1000	12	O_2	Slow	0.14
1300	24	O_2	Slow	0.13
500	96	O_2 (14 MPa)	Slow	0.06

Table 2. δ values in $SrCoO_{3-\delta}$

Annealing conditions			δ
Temperature (° C)	*Oxygen pressure* (MPa)	*Time* (h)	
300	10	168	0.30
300	30	168	0.15
300	60	168	0.07
300	80	72	0.16
300	100	72	0.08
300	120	168	0.04

1300° C in an oxygen gas flow and then cooled slowly. Further, for samples annealed under a high oxygen pressure such as 14 MPa, the δ value reaches 0.06 as shown in Table 1. In the case of strontium cobaltates $SrCoO_{3-\delta}$, samples with δ values less than 0.35 were not obtained in an oxygen gas flow or air. The samples were annealed under high oxygen pressures, where the annealing temperature was 300° C, because at higher temperatures the perovskite phase changes to a hexagonal $BaCoO_3$-type phase [10].

In Fig. 1, the lattice constants and the electrical conductivities of the $SrFeO_{3-\delta}$ series at room temperature are shown as a function of the δ value. MacChesney *et al.* [11] reported that the stoichiometric composition $SrFeO_3$ exhibits a simple cubic perovskite structure (a = 3.850 Å) and with increasing oxygen deficiency, $SrFeO_{3-\delta}$ shows increased cell constants and eventually tetragonal distortion. The oxygen deficient $SrFeO_{3-\delta}$ prepared in this study was indexed by tetragonal symmetry. The slight split in X-ray powder patterns caused by transition from a cubic form to a tetragonal form made the precise determination of the cell constant very difficult, and the values of the cell constants were accurate to within ± 0.005 Å. The samples of $SrFeO_{3-\delta}$ with $\delta \leqq 0.26$ have high electrical conductivities of 1 S cm^{-1} or more, and the conductivity was almost independent of temperature. The highly oxygen deficient $SrFeO_{3-\delta}$ ($\delta \geqslant 0.40$) shows an electrical conductivity as low as 10^{-3} S cm^{-1} or less at room temperature, and this decreases strongly with increasing δ value. The cell constants and the electrical conductivities of $SrCoO_{3-\delta}$ were measured as a function of δ by Taguchi *et al.* [10, 12]. $SrCoO_{3-\delta}$ showed the cubic perovskite structure over the range $0.05 \leqslant \delta \leqslant 0.26$, and in this range the cell constants increased monotonously with increasing δ. The electrical conductivity of $SrCoO_{3-\delta}$ at room temperature increased with increasing δ, from 5.6 S cm^{-1} at δ = 0.04 to 1.0 S cm^{-1} at δ = 0.30, and the conduction was metallic.

Fig. 2 shows typical polarization curves for the oxygen evolution reaction for $SrFeO_{3-\delta}$ in 1 mol dm^{-3} KOH. The open circuit voltage of $SrFeO_{3-\delta}$ was dependent on the value of δ: it decreased from 0.29 ± 0.05 V (δ = 0.13) to 0.13 ± 0.05 V (δ = 0.4). A similar dependency was found in $Nd_{0.5}Sr_{0.5}CoO_{3-\delta}$ by Kudo *et al.* [6]. The following potential determining reaction was postulated:

$$O^{2-}(\text{lattice}) + 2Co^{4+} + H_2O + 2e \rightleftarrows V_{O^{2-}} + 2Co^{3+} + 2OH^-$$

where $V_{O^{2-}}$ is the oxygen ion vacancies. The electrode potential became nobler as the Co^{4+} concentration increased. In the case of $SrFeO_{2.73}$ the linear relationship between the logarithm of the current density and the overpotential, η_a, is

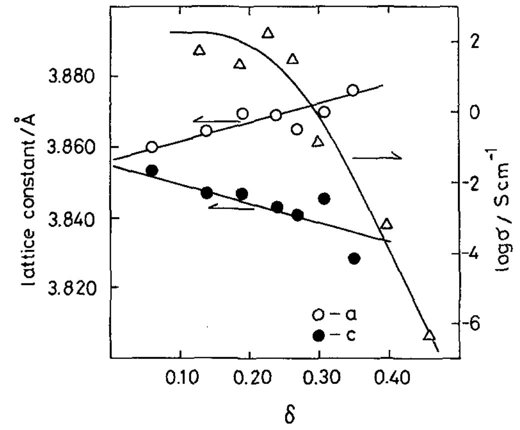

Fig. 1. Lattice constant and electrical conductivity σ as a function of δ in $SrFeO_{3-\delta}$ at 25° C.

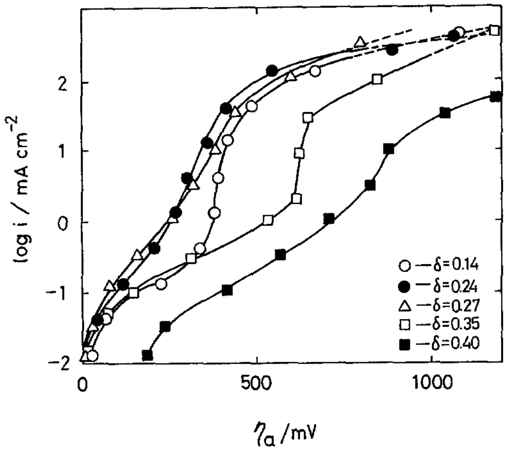

Fig. 2. Anodic polarization curves for $SrFeO_{3-\delta}$ in 1 mol dm^{-3} KOH.

observed in the current range 0.5 to 20 mA cm^{-2}, where rapid oxygen evolution was observed. At higher current density, greater than 100 mA cm^{-2}, the overpotential increased drastically with the period of electrolysis, and the electrode decomposed to hematite and strontium hydroxide. A similar polarization curve is found for $SrFeO_{2.86}$. The activity for the oxygen evolution reaction on this electrode is less than that on $SrFeO_{2.73}$. The more oxygen deficient specimens such as $SrFeO_{2.65}$ and $SrFeO_{2.60}$ are less active than $SrFeO_{2.73}$. The relationship between δ and the anodic current density at $\eta_a = 0.45$ V is shown in Fig. 3. Masumoto *et al.* [13] reported an anodic polarization of 380 mV at 10 mA cm^{-2} for $SrFeO_{3-\delta}$. Although they did not measure the δ value, the composition is considered to be close to $SrFeO_{2.75}$ from the preparation method reported. Our result is comparable to that of Matsumoto *et al.* It is interesting that the $SrFeO_{3-\delta}$ series shows the highest activity at $\delta = 0.24$–0.27. Tofield *et al.* [14] proposed that the oxygen vacancies are distributed in an ordered form at or near the composition $SrFeO_{2.75}$, and our electrical conductivity results showed that the sample with a δ value of 0.30 or more exhibited extremely low conductivity. So, it could be supposed that the activity for the oxygen evolution reaction on $SrFeO_{3-\delta}$ is related to the concentration of oxygen ion vacancies and the distribution form, as well as the value of the electrical conductivity.

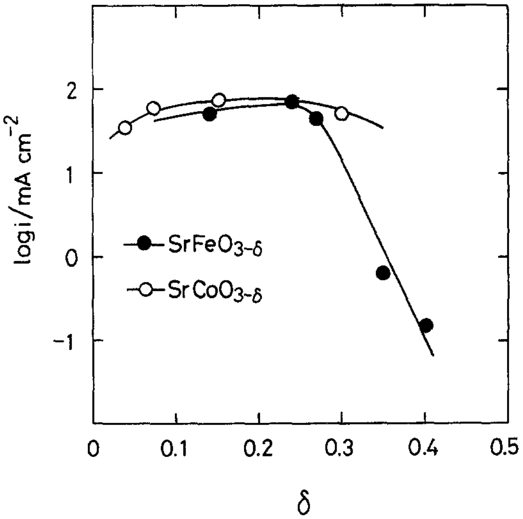

Fig. 3. The relationship between anodic current at η_a = 0.45 V and the δ value in $SrFeO_{3-\delta}$ and $SrCoO_{3-\delta}$.

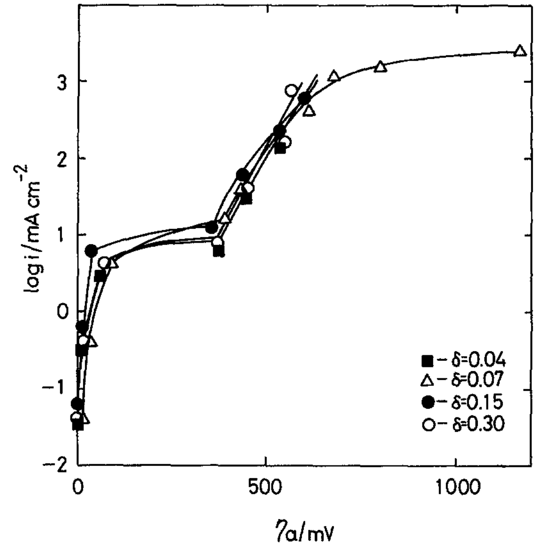

Fig. 4. Anodic polarization curves for $SrCoO_{3-\delta}$ in 1 mol dm^{-3} KOH.

Fig. 4 shows the anodic polarization curves for $SrCoO_{3-\delta}$. The open-circuit voltages of this series were about 0.27 V and almost independent of the δ value. At lower current densities (< 10 mA cm^{-2}), the electrode potentials were less than 0.4 V vs Hg/HgO, the value of which is lower than that of the oxygen evolution potential of the cell, about 0.51 V [6], and no oxygen evolution was observed. The plateaus in the overvoltage range between 0.1 and 0.35 V may be due to the anodic oxidation of the electrode. At 10 mA cm^{-2} or more, the potential was greater than 0.6 V and oxygen evolution was observed. No significant

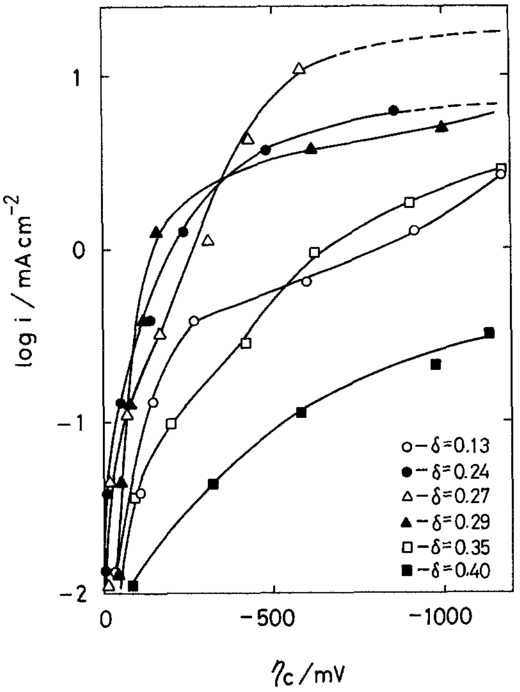

Fig. 5. Cathodic polarization curves for $SrFeO_{3-\delta}$ in 1 mol dm^{-3} KOH.

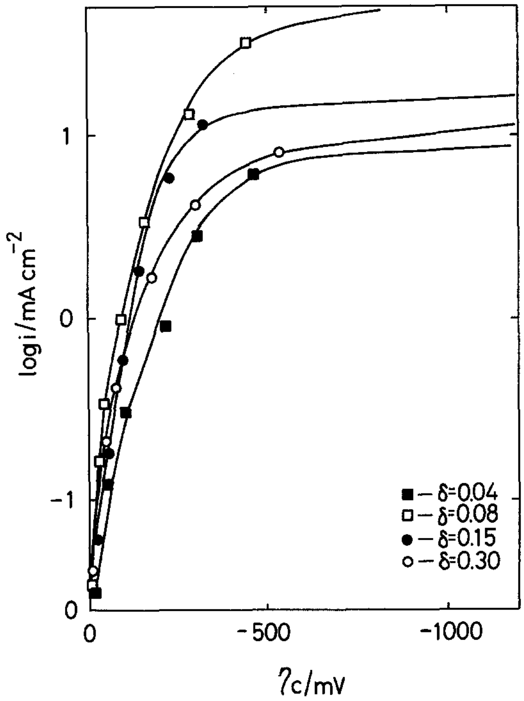

Fig. 6. Cathodic polarization curves for $SrCoO_{3-\delta}$ in 1 mol dm^{-3} KOH.

difference in the electrode activity is observed in the $SrCoO_{3-\delta}$ series. The dependence of the current density at $\eta_a = 0.45$ V on the δ value is shown in Fig. 3 also. The activity of $SrCoO_{3-\delta}$ for the oxygen evolution reaction is comparable to that of the highest active samples in the $SrFeO_{3-\delta}$ series.

Figs 5 and 6 show the cathodic polarization curves for $SrFeO_{3-\delta}$ and $SrCoO_{3-\delta}$, respectively. The catalytic activity for oxygen reduction on the $SrFeO_{3-\delta}$ series depends strongly on the δ value, and the cathodic current densities at $\eta_c = 0.3$ V are shown as a function of δ in Fig. 7. For $SrFeO_{3-\delta}$, the highest activity is found for δ between 0.24 and 0.29. Bronoel *et al.* [7] reported that for $La_{0.33}Sr_{0.67}FeO_{3-\delta}$ ($0.06 \leq \delta \leq 0.27$), the catalytic activity for oxygen reduction was related to the fraction of vacancies existing in the compound: the activity increases with increasing δ value. However, they have not reported the polarization behaviour of highly oxygen deficient samples such as $La_{0.33}Sr_{0.67}FeO_{2.65}$. They found that $La_{1-x}Sr_xFeO_{3-\delta}$ compounds undergo reduction at the same time as the reduction of oxygen. The cathodic polarization curves of $SrFeO_{2.87}$ and $SrFeO_{2.76}$ were examined under nitrogen. No significant difference between the activity under a nitrogen atmosphere and that under an oxygen atmosphere was observed for the $SrFeO_{2.87}$ electrode, whose activity is relatively low (see Fig. 7). On the other hand, for $SrFeO_{2.76}$, whose activity

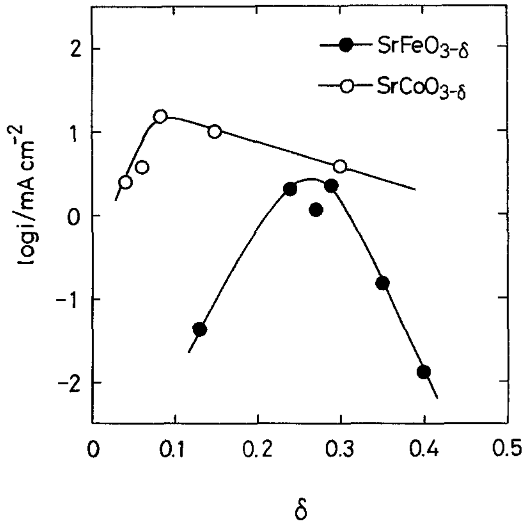

Fig. 7. The relationship between cathodic current at $\eta_c = 0.3$ V and the δ value in $SrFeO_{3-\delta}$ and $SrCoO_{3-\delta}$.

is comparably high, the overpotentials under a nitrogen atmosphere were 100 mV greater than those under an oxygen atmosphere. These results suggest that the low activity $SrFeO_{3-\delta}$ is reduced (probably Fe^{4+} to Fe^{3+}) in the cathodic polarization and on the highly active one, there is a reduction of the compound along with the reduction of oxygen.

The series $SrCoO_{3-\delta}$ shows high activity for oxygen reduction compared with that of the $SrFeO_{3-\delta}$ series. The highest activity was found for $SrCoO_{2.92}$: the reduction current can reach 30 mA cm^{-2} at 0.4 V overpotential. At a higher overpotential such as 0.5 V, a rapid increase of the overpotential with time was observed, and hydrogen gas began to evolve. In Fig. 7, the relationship between δ and the reduction current density at $\eta_c = 0.30$ V is shown. For $SrCoO_{3-\delta}$, the dependence of composition on the reduction current is not so marked as that for $SrFeO_{3-\delta}$. The overpotential under a nitrogen gas flow was comparable to that under an oxygen gas flow. The time dependence of the overpotential at the cathodic current density at 4 mA cm^{-2} was measured for $SrCoO_{2.93}$. The overpotential increased gradually from 0.32 to 0.55 V over a period of 20 h, and then increased suddenly to 1.9 V. On the other hand, no change in overpotential of the oxygen evolution reaction for $SrCoO_{2.93}$ was observed at a current density as high as 30 mA cm^{-2} for several hundred hours. These results suggest that reduction of the compound may be predominant in all of the cathodic region.

Consequently, it can be concluded that the $SrFeO_{3-\delta}$ series shows a dependence of the anodic and cathodic polarization on the δ value (the concentration of the oxygen ion vacancies) and the $SrCoO_{3-\delta}$ series does not show such a dependence. The previously reported oxides having good catalytic activity show a current density for oxygen evolution of about 20–100 mA cm^{-2} at an overpotential of 0.45 V. $SrCoO_{3-\delta}$ is considered to have a high catalytic activity for the oxygen evolution reaction, comparable to or higher than that of other oxides, although there is a problem in comparing them directly because of the different methods of measurement.

References

[1] H. Tamura, H. Yoneyama and Y. Matsumoto, 'Electrodes of Conductive Metal Oxides' (edited by S. Trasatti), Elsevier Scientific Publishing, Amsterdam (1980) p. 261.
[2] D. B. Meadowcroft, *Nature* **226** (1970) 847.
[3] Y. Matsumoto, H. Yoneyama and H. Tamura, *J. Electroanal. Chem.* **83** (1977) 115.
[4] Y. Matsumoto, H. Yoneyama and H. Tamura, *J. Electroanal. Chem.* **79** (1977) 319.
[5] P. K. Gallagher, J. B. MacChesney and D. N. E. Bachanan, *J. Chem. Phys.* **41** (1964) 2429.
[6] T. Kudo, H. Obayashi and T. Geji, *J. Electrochem. Soc.* **122** (1975) 159.
[7] G. Bronoel, J. C. Grenier and J. Reby, *Electrochim. Acta* **25** (1980) 1015.
[8] S. Mori, H. Hirata and Y. Tonooka, *Nippon Bunseki Kagaku* **16** (1967) 1340.
[9] B. E. Gushee, L. Katz and R. Ward, *J. Amer. Chem. Soc.* **5** (1957) 5601.
[10] H. Taguchi, M. Shimada and M. Koizumi, *J. Sol. Stat. Chem.* **29** (1979) 221.
[11] J. B. MacChesney, R. C. Sherwood and J. F. Potter, *J. Chem. Phys.* **43** (1965) 1907.
[12] H. Taguchi, M. Shimada and M. Koizumi, *Mater. Res. Bull.* **15** (1980) 165.
[13] Y. Matsumoto, J. Kurimoto and E. Sato, *J. Electroanal. Chem.* **102** (1979) 77.
[14] B. C. Tofield, C. Greaves and B. E. F. Fender, *Mater. Res. Bull.* **10** (1975) 737.