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Electrochemical Behavior of High Transition Temperature Superconducting Oxides

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Typical high transition temperature (high-T_c) superconducting oxides were used as electrodes in order to investigate their electrochemical behavior at room temperature. Chemical stability of these materials in various solutions was also tested. These superconducting oxides were stable in nonaqueous solutions, but is was very difficult to protect electrical contacts from the solvents because of porous structures of these oxides. These materials were rather stable in highly concentrated alkaline solutions while unstable in neutral and acid solutions. Electrochemical experiments were carried out in alkaline solutions, and the following results were obtained: (1) All of the high-T_c superconducting oxides were unstable at cathodic polarization. (2) Oxygen evolution was observed under anodic polarization. (3) These oxides behaved like p-type semiconductros though no photocurrents were detected. (4) $[Fe(CN)_6]^{3-/4-}$ served as a redox couple for all of these high-T_c oxides.

Since a high-T_c superconducting oxide La–Ba(Sr)–Cu–O systm was discovered in 1986, various kinds of high-Tc oxides have been reported.[1–5] Recently the study for practical use and the understanding of the mechanism of superconductivity have shown much progress, and electrochemistry has played an important role in these studies.[6–13] These electrochemical studies reported so far are summarized as follows.

a) **Chemical and electrochemical corrosion of the oxides;** the corrosion potentials of these materials were more positive than oxygen evolution potential.[6] At open circuit, Cu, Y, and Ba contained in $YBa_2Cu_3O_{7-\delta}$ (YBCO) were dissolved in the acid solutions at the rate controlled by proton transport while no film was formed.[6,7] On the other hand, Ba was selectively dissolved at anodic polarization in neutral solutions, and a film containing Cu and Y was formed.[7] Furthermore, possibility of the reduction of Cu(III) in YBCO was pointed out in an alkaline solution,[8] and oxygen within YBCO was reduced more easily than that within $Bi_4Ca_{1.34}Sr_{4.66}Cu_4O_x$ in a nonaqueous solution;[9] both of the observations were shown by using cyclic voltammetry.

b) **Deposition on the surface;** in order to protect the surface of high-T_c oxides, electrochemical deposition was tried; Ag and Hg were successfully deposited onto YBCO from neutral aqueous solutions containing Ag^+ and Hg^+, respectively.[10] Some conducting polymers like polypyrrole were also deposited electrochemically on YBCO.[11]

c) **Redox selectivity;** some redox couples such as $[Co(bpy)_3]^{2+/3+}$ did not show electrochemical responses on the YBCO electrode.[9,12,13] This may be due to slow electron-transfer rates of heterogeneous reactions of these redox couples.[13] It is also possible that the electron state densities of the superconductors affect electrochemical responses.[13]

d) **Low temperature experiments;** there have been a lot of interests in the electrochemical behavior of high-T_c oxides at a temperature where these oxides show superconductivity. However, the lowest temperature employed for superconductor electrochemistry so far was 183 K in CH_2Cl_2.[13]

In this work, typical high-T_c superconducting oxides, $(La_{0.98}Sr_{0.02})_2CuO_{4-\delta}$ (LSCO), YBCO and $Bi_2Sr_2CaCu_2O_8$ (BSCC) were examined from chemical and electrochemical point of view. First, chemical stability of these materials was investigated in various electrolytes. Next, current–potential characteristics, capacitance–potential characteristics and photoelectrochemical properties of these materials were examined. In particular, we discuss the oxygen evolution reaction in alkaline solutions and activity of the redox couple ($[Fe(CN)_6])^{3-/4-}$) at the high-T_c oxide electrodes.

Experimental

Samples. LSCO, YBCO, and BSCC samples were prepared from the raw oxides by the standard solid state procedures, and were made into pellets (10 mm in diameter and 1 mm thick). LSCO and YBCO pellets used were in single phase. BSCC pellets mostly had 80 K phase, though they also contained a slight 20 K phase.

Chemical Stability. The chemical stability of high-T_c superconductors was investigated as follows. First, two-point surface resistance of the pellets was measured before they were immersed in the solutions. Indium was used as a contact material. Two-point surface resistance of the pellets was measured again after immersing them in various solutions for two hours. The chemical stability was judged from changes in the two-point surface resistance, changes in the color of the surface, and changes in the color of the solutions before and after immersing pellets in the solutions. In order to know the elements dissolved in solutions, the solutions after the immersion of LSCO and BSCC pellets were analyzed with a X-ray fluorometer.

Electrochemical Experiments. The pellets of these materials were fabricated into electrodes. Molten indium or indium–gallium was used as an electrical contact material. Molten paraffin was used in order to fill porous voids.

Electrochemical experiments were performed with three electrodes; a high-T_c oxide working electrode, a Pt coil counter electrode, a saturated calomel electrode (SCE) or a silver/silver chloride electrode (Ag/AgCl) reference electrode. Electrolytes used were concentrated alkaline solutions in which pellets were not so easily decomposed. A Pt plate (1×1 cm^2) was also used as a working electrode in order to compare activity of oxygen evolution. The oxygen evolution potential was determined from current–potential characteristics. The acceptor density and the flatband potential were determined from the potential dependence of the capacitance. A high pressure mercury lamp (500 W) was used to test photoactivity of the electrodes.

Results and Discussion

Chemical Stability. Surface resistance showed only a small change when LSCO pellets were immersed in each solution as shown in Table 1. On the other hand, the surface color changed clearly in some of those solutions. Therefore, it is expected that the observation of surface color change is useful to investigate the chemical stability. Surface color of LSCO turned brown from black after LSCO was immersed in acid and neutral solutions. This indicates that LSCO was corroded in these solutions. The substrate was stable in alkaline solutions with concentration lower than 10 M (1 M=1 mol dm^{-3}). However, it was corroded in a 12 M alkaline solution. We found Sr and Cu, but no La using a X-ray fluorometer in 15 M NaOH after two-hour immersion. In nonaqueous solutions such as acetonitrile and DMF, no change was observed in the surface resistance, surface color of LSCO and the color of the solution before and after two-hour immersion.

For YBCO the surface resistance increased considerably in acid and neutral solutions. This is summarized in Table 2. This result indicates that YBCO is easily decomposed in these solutions. In particular, YBCO was dissolved completely in concentrated acid. This observation agrees with dissolution process of YBCO in the presence of proton reported as follows.[6]

$$14H^+ + YBa_2Cu_3O_7 \longrightarrow 2Ba^{2+} + Y^{3+} + 2Cu^{2+} + Cu^{3+} + 7H_2O, \quad (1)$$

$$Cu^{3+} + 1/2H_2O \longrightarrow H^+ + 1/4O_2 + Cu^{2+}. \quad (2)$$

After YBCO was dissolved in acid and neutral solutions, a part of the surface of YBCO changed from black to white. A needle-like white compound was observed in the white part of YBCO with SEM. Besides the Eqs. 1 and 2, following dissolution process is known in hot water.[14]

$$2YBa_2Cu_3O_7 + 3H_2O \longrightarrow Y_2BaCuO_5 + 3Ba(OH)_2 + 5CuO + 1/2O_2, \quad (3)$$

$$Ba(OH)_2 + CO_2 \longrightarrow BaCO_3 + H_2O. \quad (4)$$

Table 1. Stability of LSCO in Various Solutions

Solution	Resistance change (Ω) after 2 h immersion	Surface change	Solution change
Acetonitrile	2→ 2	—[a]	—
Water	2→ 5	Brown	White
0.2 M Na_2SO_4	5→ 4	—	White
0.1 M $HClO_4$	3→ 2	Brown	White
0.01 M NaOH	5→ 5	—	—
0.1 M NaOH	5→ 5	—	—
1 M NaOH	8→ 8	—	—
10 M NaOH	8→ 8	—	—
12 M NaOH	8→32	Brown	—
15 M NaOH	10→10	Brown	—

a) "—" means "no change."

Table 2. Stability of YBCO in Various Solutions

Solution	Resistance change (Ω) after 2 h immersion	Surface change	Solution change
Acetonitrile	2→ 2	—	—
Water	2→ 8	White	White
0.1 M $HClO_4$	1→300[a]	White	White
1 M NaOH	1→ 5	White	White
6 MNaOH	2→ 5	White	White
8 M NaOH	1→ 1	White	White
10 M NaOH	1→ 2	—	—
12 M NaOH	1→ 4	—	—

a) The value after 20 min immersion (completely dissolved after 2 h).

Table 3. Stability of BSCC in Various Solutions

Solution	Resistance change (Ω) after 2 h immersion	Surface change	Solution change
Acetonitrile	2→ 2	—	—
Water	1→ 2	—	—
0.1 M Na_2SO_4	2→ 2	—	—
0.1 M $NaClO_4$	2→ 2	—	—
0.1 M $HClO_4$	2→70	Yellow	Yellow
0.1 M NaOH	1→ 2	—	—
1 M NaOH	1→ 3	—	—
2 M NaOH	2→ 2	—	Blue
4 M NaOH	2→10	—	Blue
8 M NaOH	2→ 4	—	Dark blue
12 M NaOH	1→ 9	—	Dark blue

Therefore the white compound may be the needle polycrystal of $BaCO_3$ produced by reactions (3) and (4).[15] As alkaline concentration became higher, the surface change became smaller. The surface did not change in alkaline solutions with concentration larger than 10 M. YBCO was stable in nonaqueous solutions presumably because there is no proton in nonaqueous solutions.

As shown in Table 3, surface resistance increased considerably when a BSCC pellet was immersed in acid solution. It also increased in alkaline solutions with concentration higher than 1 M. The color of the acid solution turned yellow and that of the alkaline solutions turned blue after BSCC was immersed. This indicates that decomposition process of BSCC in alkaline solutions is different from that of BSCC in acid solution. All metals composing BSCC were detected in the acid solution using a X-ray fluorometer after the two-hour immersion test. Sr was dissolved in water though BSCC has been believed to be stable in water. All metals were dissolved when neutral salt like Na_2SO_4 was added to water. As alkaline concentration increased, the degree of decomposition of BSCC seemed to increase. This similarity to LSCO indicates that BSCC has a decomposition process similar to LSCO. BSCC was stable in nonaqueous solutions.

Electrochemical Characteristics. Concentrations of electrolyte solutions were chosen based on the results in the previous section; 0.1—8 M NaOH, 10—16 M NaOH and 0.1 M NaOH were used for LSCO, YBCO and BSCC, respectively.

Current-Potential Characteristics: Current-potential curves and Mott-Schottky plots are shown for LSCO, YBCO and BSCC in Figs. 1, 2, and 3, respectively. It was determined that the cathodic limit of potential sweep range was more positive than −0.5 V vs. SCE or Ag/AgCl in order to obtain stable current-potential curves; all of high-T_c oxides were decomposed at cathodic polarization. An anodic current was observed, and oxygen evolution was observed along with anodic current at LSCO, YBCO and BSCC. Photocurrent was not observed at all kinds of the electrodes.

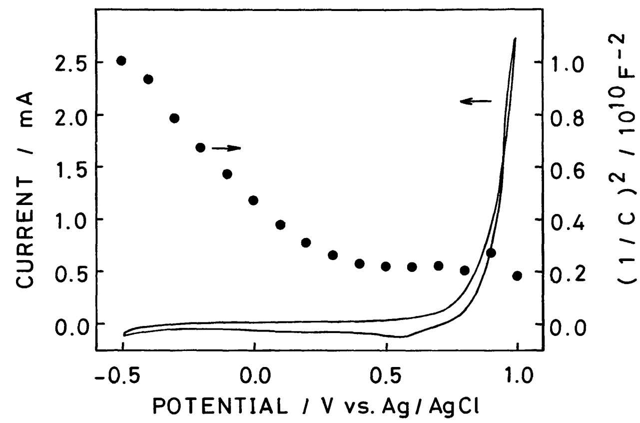

Fig. 1. Cyclic voltammetry and Mott-Schottky plot in 1 M NaOH at LSCO.

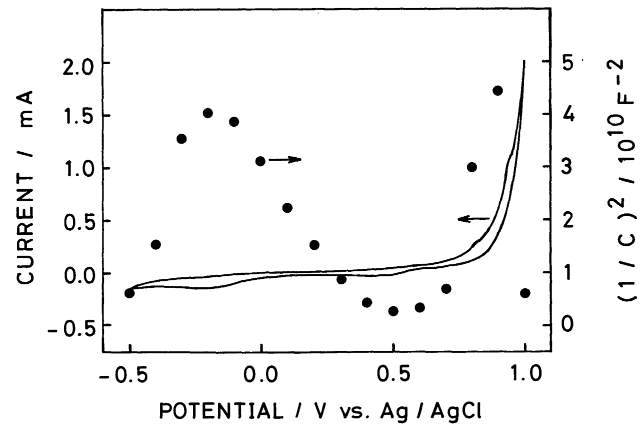

Fig. 2. Cyclic voltammetry and Mott-Schottky plot in 10 M NaOH at YBCO.

Characteristics of Capacitance of the Electrodes: The slopes of the main region of Mott-Schottky plots were negative at LSCO, YBCO, and BSCC. Therefore it is concluded that these superconductors are p-type semiconductors. The acceptor densities N_A of LSCO,

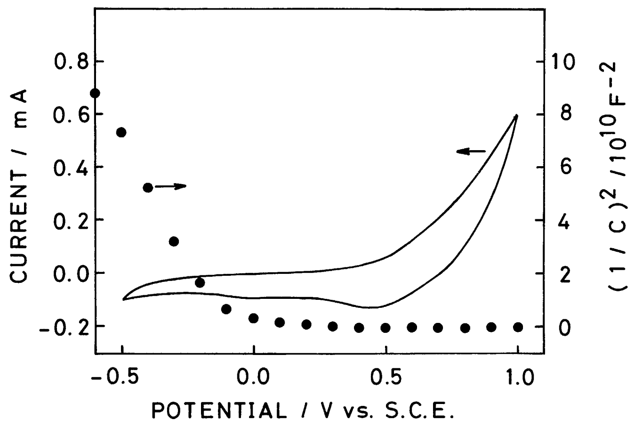

Fig. 3. Cyclic voltammetry and Mott-Schottky plot in 0.1 M NaOH at BSCC.

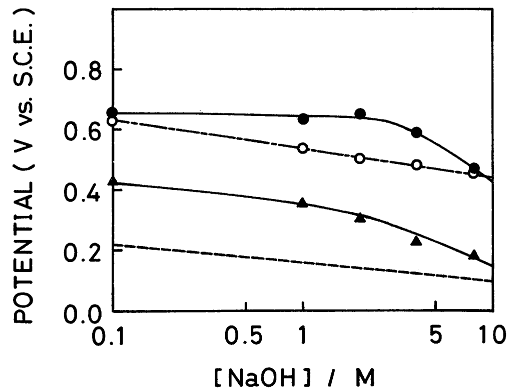

Fig. 4. O_2 evolution potential (V_{O2}) and flatband potential (V_{fb}) as a function of alkaline concentration [NaOH]. —●—: V_{O2} for LSCO, ---○---: V_{O2} for Pt, -----: theoretical V_{O2}, —▲—: V_{fb} for LSCO.

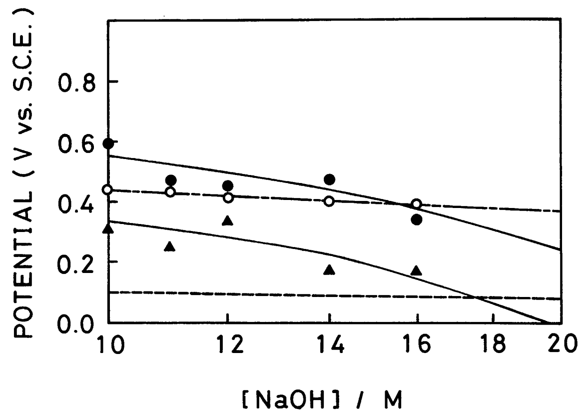

Fig. 5. O_2 evolution potential (V_{O2}) and flatband potential (V_{fb}) as a function of alkaline concentration [NaOH]. —●—: V_{O2} for YBCO, ---○---: V_{O2} for Pt, -----: theoretical V_{O2}, —▲—: V_{fb} for YBCO.

YBCO, and BSCC were calculated to be 4—20$\times$10^{21} cm^{-3}, 0.3—4$\times$10^{21} cm^{-3}, and 5$\times$10^{21} cm^{-3}, respectively, based on the following equation

$$N_A = 2/(q\varepsilon\varepsilon_0 S^2 A). \qquad (5)$$

The above equation is deduced from the Mott-Schotkky equation[16)]

$$(S/C)^2 = 2/(\varepsilon\varepsilon_0 q N_A)(V - V_{fb} - kT/q). \qquad (6)$$

Here S is electrode area, C is capacitance of electrical double layer, ε is dielectric constant, ε_0 is permittivity of vacuum, q is unit charge, V is electrode potential, V_{fb} is flatband potential, k is Boltzmann constant, T is absolute temperature, and A is the slope of the main straight region of the Mott-Schottky plot. ε is assumed to be 10. The apparent electrode area was used for S in order to calculate carrier densities. These calculated acceptor densities agree well with that obtained from Hall coefficient (2—5$\times$10^{21} cm^{-3}). The scatter in N_A values is probably due to the different roughness factor of various electrodes and/or the different electrode stability in various electrolytes.

Activity in Oxygen Evolution Reaction: The current-potential characteristics of Pt was also measured in order to observe the difference in activity in oxygen evolution between high-T_c oxides and Pt in the same electrolyte. Oxygen evolution potential at Pt electrode ($V_{O2,Pt}$) was defined as follows; the potential where an excess current of 0.1 mA flowed as compared with the capacitance current due to the double layer region. Because the electrode area of each oxide pellet was not constant due to its porous structure, the value of the current at LSCO electrodes was corrected. Corrected current values were obtained, assuming that carrier density of each sample is constant, and also using the fact that apparent capacitance and current are in proportion to the electrode area. Oxygen evolution potential at LSCO ($V_{O2,LSCO}$) was defined in a similar manner to Pt, except that currents corrected as above were used. Though this correction may not give exact comparison between LSCO and Pt, it is possible to make qualitative discussion. Figure 4 shows alkaline concentration dependence on $V_{O2,LSCO}$, V_{fb} of LSCO and $V_{O2,Pt}$. $V_{O2,LSCO}$ was shifted to more cathodic potential with increasing alkaline concentration in a similar manner to $V_{O2,Pt}$. Though apparent electrode area of LSCO was smaller than that of Pt, activity of oxygen evolution was almost the same. This is either because real electrode area of LSCO pellets was bigger apparent one, or activity of electrochemical catalysis of LSCO was higher than Pt.

V_{fb} was also shifted to cathodic direction with increasing alkaline concentration. This is due to dissociation equilibrium of H$^+$ and OH$^-$ on the electrode surface of the oxides.[18)]

Figure 5 shows the dependence of $V_{O2,YBCO}$, V_{fb} of YBCO and $V_{O2,Pt}$ on alkaline concentration. The

Table 4. Changes of LSCO Electrodes during the Electrochemical Reaction

Solution	Resistance change (Ω)	Surface change	Solution change
0.1 M NaOH	4→18	Gray	—
1 M NaOH	3→23	Gray	—
2 M NaOH	2→ 9	Gray	—
4 M NaOH	2→22	Gray	—
8 M NaOH	2→ 8	Gray	—

Table 5. Changes of YBCO Electrodes during the Electrochemical Reaction

Solution	Resistance change (Ω)	Surface change	Solution change
12 M NaOH	42→100	Brown	Brown
15 M NaOH	0→130	Brown (Partially white)	Brown

current values were corrected by using the fact that double layer capacitance C is in proportion to the electrode area; since the form of the Mott–Schottky plot of YBCO was complicated, we employed the above method instead of the way $V_{02,\mathrm{LSCO}}$ was determined. Maximum value of capacitance on the Mott–Schottky plot was used in this correction. $V_{02,\mathrm{YBCO}}$ was also shifted to a cathodic region with increasing alkaline concentration. Oxygen evolution of YBCO is as active as that of LSCO. The observation that V_{fb} showed a tendency similar to $V_{02,\mathrm{YBCO}}$ indicates that some kind of dissociation equilibrium of H^+ and OH^- was achieved on the electrode surface.

Stability for Electrochemical Reaction: The change in surface resistance of LSCO before and after electrochemical measurement was very small as shown in Table 4. This indicates that LSCO is rather stable against electrochemical reactions.

In the case of YBCO, surface resistance and surface condition showed considerable changes as a result of electrochemical reaction as shown in Table 5. This observation indicates that the electrodes were degraded owing to large current flow.

Behavior of Oxidation and Reduction: Oxidation and reduction properties of LSCO, YBCO and BSCC were observed in 0.1 M NaOH, 12 M NaOH and 0.1 M NaOH, respectively, containing 10 mM $[Fe(CN)_6]^{3-/4-}$ as a redox couple. The results of LSCO, YBCO, and BSCC measurements are shown in Figs. 6, 7, and 8, respectively. Peaks of oxidation and reduction were observed at all substrates. This result indicates that acceptor density is high in all three high-T_c oxides. Oxidation peaks were smaller than reduction peaks at LSCO and YBCO; oxidation did not catch up with reduction. Peaks of both oxidation and reduction at BSCC were the smallest among those high-T_c oxides.

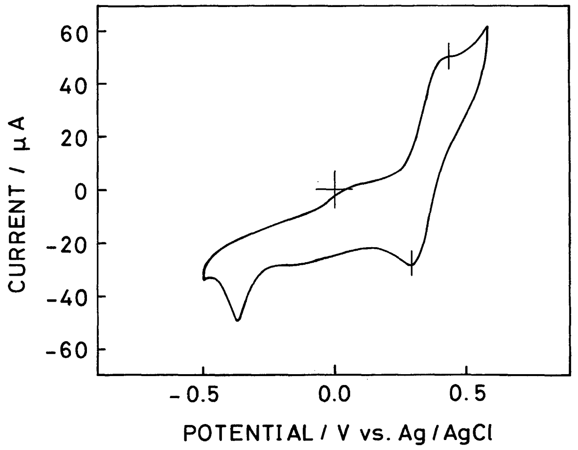

Fig. 6. Cyclic voltammetry in 0.1 M NaOH of 10 mM $[Fe(CN)_6]^{3-/4-}$ at LSCO.

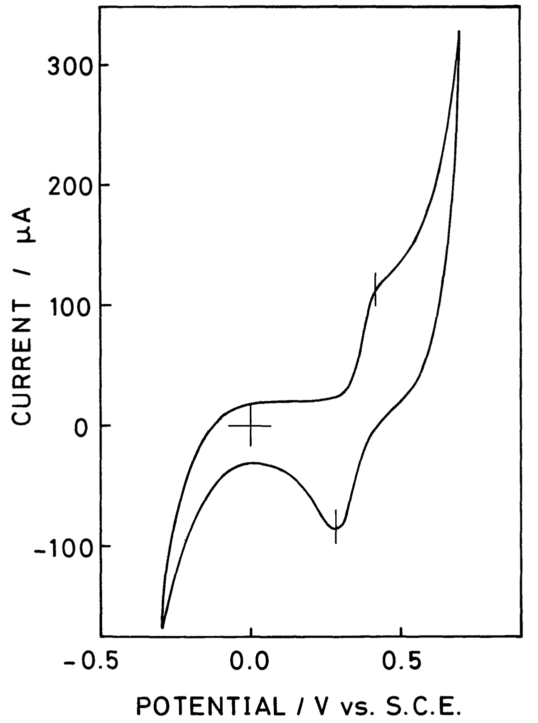

Fig. 7. Cyclic voltammetry in 12 M NaOH of 10 mM $[Fe(CN)_6]^{3-/4-}$ at YBCO.

Half wave potentials ($E_{1/2}$) of LSCO and BSCC were not so different from that of Pt, but that of YBCO was slightly different from that of Pt. Peak separations of LSCO (122 mV), YBCO (142 mV) and BSCC (220 mV) were all larger than that of Pt (60 mV). This result leads the conclusion that electrochemical reaction rates of $[Fe(CN)_6]^{3-/4-}$ on the high-T_c oxides are slower than on Pt.

Improvement of the Quality of Superconductivity with Electrochemical Treatments: As shown above very active oxygen evolution was observed in high-T_c oxides. Since T_c is closely related to oxygen quantity

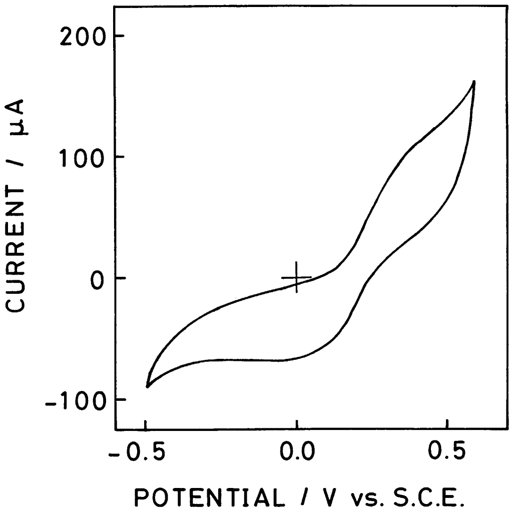

Fig. 8. Cyclic voltammetry in 0.1 M NaOH of 10 mM $[Fe(CN)_6]^{3-/4-}$ at BSCC.

contained in high-T_c oxides, there is a possibility to improve the quality of superconductivity by oxygen evolution on the substrate in electrochemical reaction. Therefore we tried a simple electrochemical experiment; a YBCO pellet quenched from 900 °C, and thus having low critical temperature (T_c=70.5 K), was polarized at +1 V vs. Ag/AgCl for 10 minutes in 12 M NaOH. However, T_c of the YBCO sample did not change. Surface color of the sample was changed to brown, which indicates that the electrode was decomposed. Although this preliminary experiment did not improve T_c, it is desirable to find optimum conditions which minimize decomposition of electrodes and improve T_c values.

Conclusion

LSCO, YBCO, and BSCC were stable in nonaqueous solutions. The stability generally increased as pH increased in aqueous solutions. However, LSCO and BSCC were decomposed in highly concentrated alkaline solutions.

For the electrochemical reactions, all of the high-T_c oxides used here were unstable at cathodic polarization, while they were relatively stable at anodic polarization. Oxygen evolution was observed along with anodic current and the high-T_c oxides were almost as active as Pt.

Negative slope of the straight line region in Mott–Schottky plots showed that these high-T_c oxides are highly doped p-type semiconductors ($N_A \simeq 10^{21}\ \mathrm{cm}^{-3}$). No photocurrent was observed. These high-T_c oxides were active for $[Fe(CN)_6]^{3-/4-}$ redox couple.

The electrochemical rate constants for $[Fe(CN)_6]^{3-/4-}$ couple on these oxides were smaller than that on Pt. The chemical and electrochemical stabilities of the high-T_c oxides are the following order; LSCO> BSCC>YBCO.

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