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# Electrosubstitution at the Metal, Metal Compounds/Na–$\beta''$-$Al_2O_3$ Interface in the SOED Method

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**The electrochemical reaction and electrosubstitution of a metal from the pure metal, its oxide, or its carbonate at the Na–$\beta''$-$Al_2O_3$ interface, which are very important as a cationic source in the solid oxide electrochemical doping (SOED) method, have been studied. $Ag^+$ was easily electrosubstituted for $Na^+$ in Na–$\beta''$-$Al_2O_3$ at a low applied voltage, but not the metal ions from metal oxides because of their strong binding energy. Some cations from their carbonates were substituted for $Na^+$ at a relatively low applied voltage. Consequently, some metal salts as well as pure metals can be useful as the electrode for a cationic source in the SOED method. The mechanism of the electrosubstitution is discussed.** © 1999 Academic Press

***Key Words:*** **Electrochemical doping; $\beta''$-alumina; oxide ceramics; ionic conductor.**

## INTRODUCTION

We have developed a new electrochemical doping method using $\beta''$-$Al_2O_3$, called the solid oxide electrochemical doping (SOED) method (1–4). The SOED method may become very important for developing new oxide materials in the near future, because it could be used for the doping of many kinds of dopants into all oxide ceramics and it allows for microarea doping and the preparation of graded materials.

The anode $M$ is the source of the doping cation $M$ in the SOED method, and the $M$ cation drifts through the $M$–$\beta''$-$Al_2O_3$ solid electrolyte, as shown in Fig. 1A. Therefore, Ag metal together with Ag–$\beta''$-$Al_2O_3$ has been used as the anode when the dopant is Ag. Moreover, Ag metal has been used as the anode even when the dopant is a cation other than Ag (1–4), where Ag is not $M$ in $M$–$\beta''$-$Al_2O_3$. This condition is satisfied when the amount of the needed dopant $M$ is small and the $Ag^+$ ion does not affect the functional properties of the oxide ceramics, because the electrochemical reaction from Ag to $Ag^+$ always occurs at the Ag/$M$–$\beta''$-$Al_2O_3$ interface and trace amounts of $Ag^+$ were doped into the oxide ceramics as well as the dopant $M$ during the electrolysis. The same metal $M$ as the $M$ cation in the $M$–$\beta''$-$Al_2O_3$ must be used as the anode if a relatively large amount of pure $M$ cation needs to be doped into the oxide ceramics. However, the use of a metal as the anode will be difficult when the dopant is an alkaline, alkaline earth, or lanthanide cation. In this case, a metal salt such as carbonate or oxide may be useful as the anode.

In this paper, some metal carbonates, metal oxides, and pure metals were used as an anode, and their electrochemical reactions and electrosubstitutions have been studied at the Na–$\beta''$-$Al_2O_3$ interface.

## EXPERIMENTAL

In the present experiment, Ag and Pt plates (thickness: 0.3 mm for Ag, 0.1 mm for Pt) were used as the metal anode. On the other hand, some carbonates ($K_2CO_3$, $SrCO_3$) and metallic oxides ($TiO_2$, $Fe_2O_3$, CuO, $YBa_2Cu_3O_y$ (YBCO), $La_{0.8}Sr_{0.2}MnO_3$ (LSMO), $Bi_2Sr_2CaCu_2O_y$ (BSCCO)) were used as the compound anode. The pellet samples of the carbonates and oxides (ceramics in (A) and anode in (C) in Fig. 1, thickness: 1.5 mm, surface area: 0.8 $cm^2$) were prepared by pressing the powder at 1000 $Kg/cm^2$ and heating at 800-1250°C. Na–$\beta''$-$Al_2O_3$ (Nihon Tokushu Togyo Co., Ltd., thickness: 2 mm) was used as the solid electrolyte and a Pt plate was used as the cathode. The electrochemical doping was carried out under a constant current density at 400–800°C in air using the experimental setup schematically shown in Fig. 1. The appropriate doping temperatures where no thermal diffusion occurred but where there was electrosubstitution at the interfaces of the metal and metal compounds/Na–$\beta''$-$Al_2O_3$ were selected for all the electrosubstitution tests. The apparent contact area in the anode/Na–$\beta''$-$Al_2O_3$ was 0.10–0.19 $cm^2$. After the electrolysis, the distribution state of the dopants in a cross section of the Na–$\beta''$-$Al_2O_3$ was analyzed using electron probe microanalysis (EPMA).

## RESULTS AND DISCUSSION

### *Metal/Na–$\beta''$-$Al_2O_3$ Interface*

The following reactions for the electrosubstitution occur at the metal anode/Na–$\beta''$-$Al_2O_3$ and Na–$\beta''$-$Al_2O_3$/

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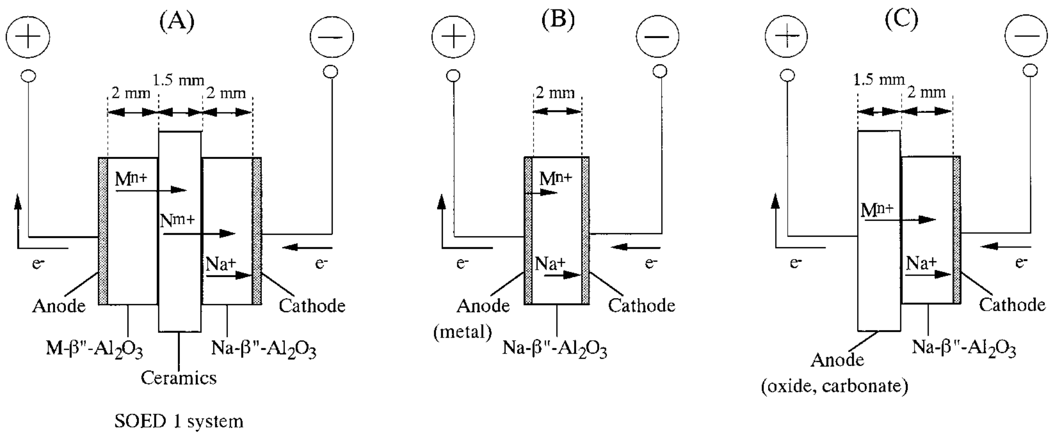

**FIG. 1.** Electrosubstitution systems. (A) SOED 1 system, where $Na^+$ in the Na–$\beta''$-$Al_2O_3$ is substituted for the $N^{m+}$ cation pushed by the injection of the $M^{n+}$ cation. (B) Electrolysis system, where metal cation from pure metal is electrosubstituted for Na in Na–$\beta''$-$Al_2O_3$. (C) Direct injection system, where $M^{n+}$ is directly substituted for $Na^+$.

cathode interfaces in Fig. 1B:

$$M \rightarrow M^{n+}(\text{Na–}\beta''\text{-}Al_2O_3) + ne^- \quad \text{(anode)} \qquad [1]$$

$$Na^+(\text{Na–}\beta''\text{-}Al_2O_3) + e^- \rightarrow Na$$

$$2Na + CO_2(\text{in air}) + (1/2)O_2 \rightarrow Na_2CO_3 \quad \text{(cathode)}. \qquad [2]$$

The production of $Na_2CO_3$ at the Na–$\beta''$-$Al_2O_3$/Pt(cathode) interface was detected by X-ray analysis. However, no reaction occurred when Pt was used as the anode.

The Ag electrosubstitution for Na easily occurred when using the Ag anode. The following reaction occurs at the Ag/Na–$\beta''$-$Al_2O_3$ interface:

$$Ag \rightarrow Ag^+(\text{Na–}\beta''\text{-}Al_2O_3) + e^-. \qquad [3]$$

Figure 2 shows the typical applied voltage as a function of the electrolysis time under 5 mA/cm$^2$ at 400°C in the system shown in Fig. 1B. Figure 3 shows the atomic ratios of Ag/Al and Na/Al in the Ag-substituted Na–$\beta''$-$Al_2O_3$ as a function of the distance from the Ag/Na–$\beta''$-$Al_2O_3$ interface, as analyzed by EPMA. The amount of the substituted Ag is relatively large on the side of the Ag/Na–$\beta''$-$Al_2O_3$ interface, while that of Na is relatively small on the same side. Thus, the present electrosubstitution produces the concentration gradient of the substituted Ag in the Na–$\beta''$-$Al_2O_3$. All the current efficiencies of the Ag electrosubstitution calculated from Eq. [3] and Faraday's law were approximately 100%. This is due to the electrosubstitution but not the thermal diffusion, because doping did not occur under no bias. Figure 4 shows the Ag/Al atomic ratios in the Ag-substituted Na–$\beta''$-$Al_2O_3$ at various distances from the Ag/Na–$\beta''$-$Al_2O_3$ interface as a function of the electrolysis time at 5 mA/cm$^2$. The amount of the substituted Ag was

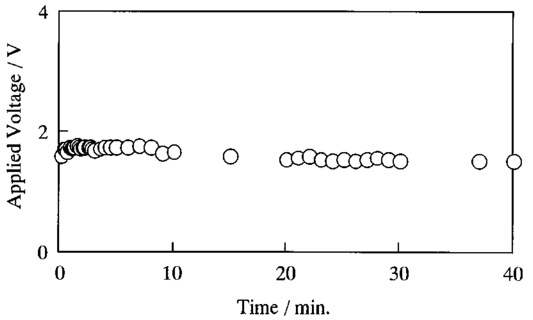

**FIG. 2.** Applied voltage as a function of the electrolysis time for the Ag/Na–$\beta''$-$Al_2O_3$ for a constant current density of 5 mA/cm$^2$ at 400°C in the system shown in Fig. 1B.

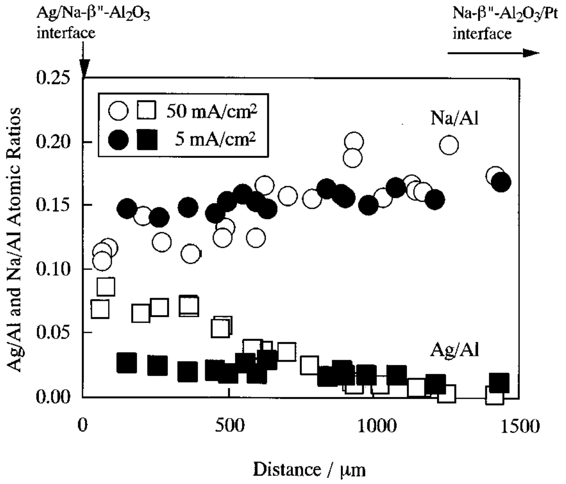

**FIG. 3.** Atomic ratios of Ag/Al and Na/Al in the Ag-substituted Na–$\beta''$-$Al_2O_3$ at 400°C as a function of the distance from the Ag/Na–$\beta''$-$Al_2O_3$ interface.

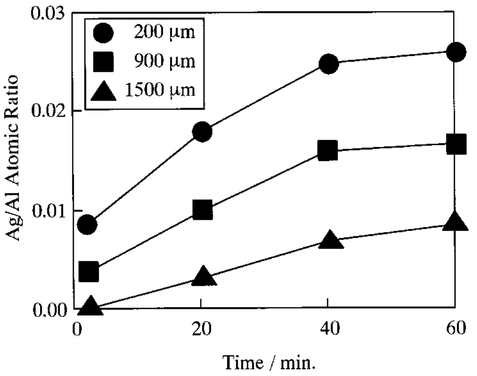

**FIG. 4.** Ag/Al atomic ratios at various distances from the Ag/Na–$\beta''$-$Al_2O_3$ interface in the Ag-substituted Na–$\beta''$-$Al_2O_3$ as a function of the electrolysis time for a constant current density of 5 mA/$cm^2$ at 400°C.

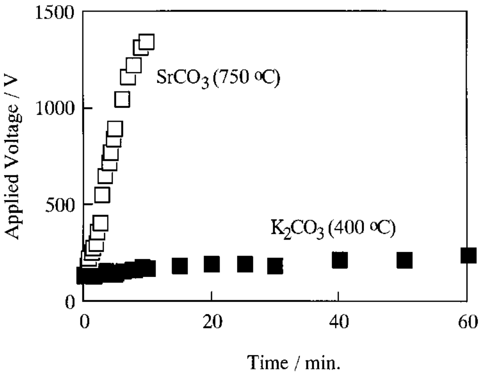

**FIG. 5.** Applied voltages as a function of the electrolysis time for the $K_2CO_3$/Na–$\beta''$-$Al_2O_3$ and $SrCO_3$/Na–$\beta''$-$Al_2O_3$ for a constant current density of 5 mA/$cm^2$ in the system shown in Fig. 1C.

nearly saturated with the increase of time, indicating that some doped $Ag^+$ goes through the Na–$\beta''$-$Al_2O_3$ to the cathode. In fact, Ag metal was detected at the Pt cathode Na–$\beta''$-$Al_2O_3$/cathode interface after 60 min electrolysis. Thus, the electrosubstitution of Ag for Na in the Na-$\beta''$-$Al_2O_3$ was relatively easy and demonstrates its utility as the anode source in the SOED method.

### *Metal Compounds/Na–$\beta''$-$Al_2O_3$ Interface*

The following decomposition reaction probably proceeds at the alkaline metal carbonate anode/Na–$\beta''$-$Al_2O_3$ interface in the system shown in Fig. 1C:

$$M_2CO_3 \rightarrow 2M^+(\text{Na–}\beta''\text{-}Al_2O_3) + CO_2 + (1/2)O_2 + 2e^- \quad \text{(alkaline metal carbonate anode).} \qquad [4]$$

Figure 5 shows the applied voltages for the $K_2CO_3$/Na–$\beta''$-$Al_2O_3$ at 400°C and $SrCO_3$/Na–$\beta''$-$Al_2O_3$ interfaces at 750°C as a function of the electrolysis time. The applied voltage was very large for the latter case, suggesting that the Sr electro-substitution is relatively difficult. In fact, substitution did not occur at 400°C for this case, but did occur at 750°C. Figure 6 shows the atomic ratios of K/Al and Na/Al in the K-substituted Na–$\beta''$-$Al_2O_3$ at 400°C as a function of the distance from the $K_2CO_3$/Na–$\beta''$-$Al_2O_3$ interface which was analyzed by EPMA. The graded substitution, which is similar to the case of Ag/Na–$\beta''$-$Al_2O_3$ (Fig. 3), occurred again as shown in Fig. 6. The current efficiencies for the Sr and K electrosubstitutions calculated from Eq. [4] and Faraday's law were about 100%. These are again due to electrosubstitution but not chemical diffusion, because doping did not occur under no bias at the above temperatures, although the chemical diffusion of $K^+$ ions from $K_2CO_3$ to Na–$\beta''$-$Al_2O_3$ was observed under no bias at 750°C according to the EPMA analysis. In conclusion, some metal carbonates can act as the anode source material for electrosubstitution.

Some oxides were also tested as the anode for electrosubstitution in the system shown in Fig. 1C. In this case, the following reaction will occur at the oxide anode:

$$MO_n \rightarrow xM^{m+}(\text{Na–}\beta''\text{-}Al_2O_3) + xme^- + M_{1-x}O_n. \qquad [5]$$

Reaction [5] will be followed by the decomposition reaction [6], if the cation vacancy, $x$, is large:

$$M_{1-x}O_n \rightarrow M_{1-x}O_{n-m} + (m/2)O_2. \qquad [6]$$

To dope with Cu or Fe, CuO or $Fe_2O_3$ anodes were used at 750°C, but their current efficiencies were less than 10%. No doping ($< 0.1$ at%) occurred for the $TiO_2$ electrode even at 800°C. The complex oxides such as YBCO, LSMO,

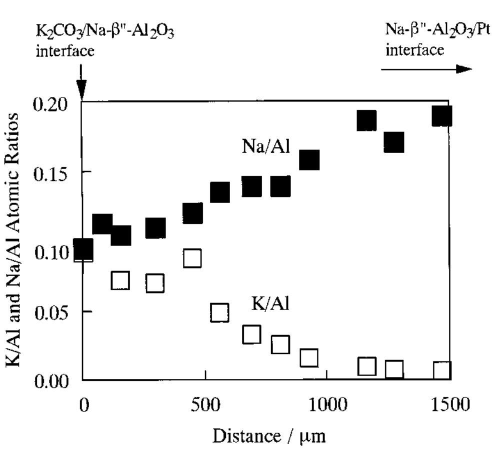

**FIG. 6.** Atomic ratios of K/Al and Na/Al in the K-substituted Na–$\beta''$-$Al_2O_3$ for a constant current density of 5 mA/$cm^2$ at 400°C after 60 min electrolysis as a function of the distance from the $K_2CO_3$/Na–$\beta''$-$Al_2O_3$ interface.

and BSCCO were also tested as anodes. Ba and Ca were mainly doped by using the YBCO or BSCCO, respectively, while La and Sr were doped by using the LSMO. However, their current efficiencies were less than 10%. Thus, electrosubstitution using an oxide anode was difficult. Consequently, the oxide may not be suitable as an anode material.

There are two important factors which affect the electrosubstitution process. One is the cation migration in the Na–$\beta''$-$Al_2O_3$ which occurs after the electrochemical reaction at the anode/Na–$\beta''$-$Al_2O_3$ interface. $Ag^+$ and $K^+$ have a higher conductivity compared to the other cations in $\beta''$-$Al_2O_3$ (5, 6). As a result, electrosubstitution is easier for these cations. On the other hand, electrosubstitution by Pt or Ti does not occur, because these metals do not readily transport in Na–$\beta''$-$Al_2O_3$. The other important factor is the activation energy necessary for the decomposition represented by Eqs. [4] and [6]. In general, metal carbonates decompose more easily than oxides. Therefore, some metal carbonates will satisfactorily act as an anode, but not oxides as already stated.

### *SOED 1-Type Electrosubstitution*

As stated elsewhere (1–4), the $Ba^{2+}$ ion easily migrates from YBCO into Ag–$\beta''$-$Al_2O_3$ in the SOED 1-type system, similar to that shown in Fig. 1A. This is different from the system shown in Fig. 1C, where the direct injection of $Ba^{2+}$ into Na–$\beta''$-$Al_2O_3$ was found to be difficult, as stated in previous sections. The migration of $Ba^{2+}$ from YBCO into Ag–$\beta''$-$Al_2O_3$ in the former case will be promoted by the $M^{n+}$ injection from $M$–$\beta''$-$Al_2O_3$ at the anode side to the YBCO ceramics. This phenomenon was proved by the following test using Na–$\beta''$-$Al_2O_3$ and YBCO ceramics. The Na–$\beta''$-$Al_2O_3$ was analyzed by EPMA after electrolysis in the system shown in Fig. 1A, where $K^+$, $Na^+$, and $Zn^{2+}$ were used as the injection $M$ cation in the $M$–$\beta''$-$Al_2O_3$. Ba was detected (the amount was in the order [Ba] (current efficiency was about 90%) > [Cu] (about 10%)) and its current efficiency was nearly 100%. Moreover, the applied voltage was lower for the system shown in Fig. 1A than for that shown in Fig. 1C. This means that the $Ba^{2+}$ migration from YBCO is promoted by the injection of $K^+$, $Na^+$, and $Zn^{2+}$ cations into YBCO, while the migration of the $Ba^{2+}$ ion is difficult in the system shown in Fig. 1C. The latter system accompanies the decomposition of the YBCO structure, while the former case may not always accompany the same type of reaction.

The same test was carried out using the SOED 1 system shown in Fig. 1A for other complex oxides such as LSMO and BSCCO ceramics, which were used as the ceramics. The injected cations were $Na^+$, $K^+$, $Ag^+$, and $Zn^{2+}$ which acted as the $M^{n+}$ cation in $M$–$\beta''$-$Al_2O_3$ at the anode side. Sr and Ca were detected for the BSCCO, while La and Sr were detected for LSMO in Na–$\beta''$-$Al_2O_3$ after electrolysis. However, the current efficiencies for the injection of these cations from the ceramics to Na–$\beta''$-$Al_2O_3$ were 20–40%, although the efficiencies were higher than in the case of the electrolysis using the system shown in Fig. 1C. The applied voltage was again lower for the system shown in Fig. 1A than for that shown in Fig. 1C ($< 10\%$). Consequently, the cation injection into the ceramics at the anode side interface sometimes brings about the promotion of the cation migration in the ceramics to the Na–$\beta''$-$Al_2O_3$, but its degree strongly depends on the structure of the ceramics.

## REFERENCES

1. Y. Matsumoto, *J. Solid State Chem.* **128,** 93 (1997).
2. Y. Matsumoto, M. Koinuma, H. Yamamoto, and T. Nishimori, *Solid State Ionics* **95,** 309 (1997).
3. Y. Matsumoto, *Solid State Ionics* **100,** 165 (1997).
4. Y. Matsumoto, T. Nishimori, H. Yamamoto, K. Nishimura, K. Kamada, and A. Ogata, *Solid State Ionics* **107,** 41 (1998).
5. J. L. Briant and G. C. Farrington, *J. Solid State Chem.* **33,** 385 (1980).
6. R. Seevers, J. Denuzzio, G. C. Farrington, and B. Dunn, *J. Solid State Chem.* **50,** 146 (1983).