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Solubilities of La and Ni on $LaNiO_3$ in Li/K Carbonate Eutectic with La_2O_3

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The solubilities of La and Ni on $LaNiO_3$ in Li/K carbonate eutectic with La_2O_3 have been investigated. The solubilities of La and Ni were 1.9×10^{-2} (mole fraction) and 1.2×10^{-5} (mole fraction) under CO_2/O_2 of 0.7/0.3 at 923 K. The extraction of Ni from $LaNiO_3$ in molten carbonate saturated with La_2O_3 was almost 57% lower than that from NiO in a molten carbonate without La_2O_3.

Since molten carbonate fuel cells (MCFCs) can directly use various fuels including carbon, have high energy conversion efficiency, and do not use precious metals as a catalyst, they are starting to be used as dispersed power plants.[1] In order to increase their use, the cathode material durability should be improved. There are many materials proposed as an alternative cathode, but NiO is still used as a cathode material for conventional MCFC power plants.[2]

Especially, during high CO_2 pressure operation, the occurrence of an internal short circuit, which is called Ni shorting, is a big problem concerning the lifetime of MCFCs.[3] Since all elemental processes concerning the Ni shorting are related to the Ni^{2+} ion, the reduction of the cathode dissolution would be an essential approach to prevent the Ni shorting. There are two ways to reduce the solubility of Ni; one is to control the activity of nickel in the electrode material. The other is to control the acid–base equilibrium of the melt to decrease the solubility of Ni. In the case of lanthanum nickel compounds, such as $LaNiO_3$, in the Li/Na carbonate eutectic with lanthanum oxide, the concentration of the Ni ion was drastically lower than that in contact with NiO in the Li/Na carbonate eutectic by both effects of the activity of the Ni ion and the acid–base equilibrium of the molten carbonate.[4] However, the extraction of Ni from $LaNiO_3$ by the Li/K carbonate eutectic with La_2O_3 has not been investigated.

In this study, as the Li/K carbonate electrolyte is the conventional electrolyte of MCFCs, the solubilities of La and Ni on $LaNiO_3$ in Li/K carbonate eutectic saturated with La_2O_3 have been investigated.

The $LaNiO_3$ powders were prepared by precipitation.[4] The $LaNiO_3$ pellet ($\phi = 10$ mm) for solubility measurement was prepared by sintering at 1023 K for 40 h in an electric muffle furnace (KM-160, Advantec®, Japan). The sample was identified before and after the immersion in the molten carbonate by X-ray diffraction (XRD; XRD-6000, Shimadzu, Japan).

The Li/K carbonate eutectic with and without La_2O_3 were prepared as follows: Li_2CO_3 (Guaranteed reagent, Junsei Chemical Co., Japan) and K_2CO_3 (Guaranteed reagent, Junsei Chemical Co., Japan) of 62/38 mol% with and without excess amounts of La_2O_3 (99.9%, Kojundo Chemical Laboratory Co., Japan) were mixed in a high-purity alumina crucible in a dry box. The molten carbonate was refined by vacuum drying and CO_2 bubbling.[4,5] The partial pressure of CO_2 (p_{CO_2}) was varied from 0.1 to 0.7 atm while the partial pressure of O_2 (p_{O_2}) and the temperature were kept constant at 0.3 atm and 923 K, respectively. The concentration of La and Ni was determined by ICP-AES (SPS3000, SII, Japan).

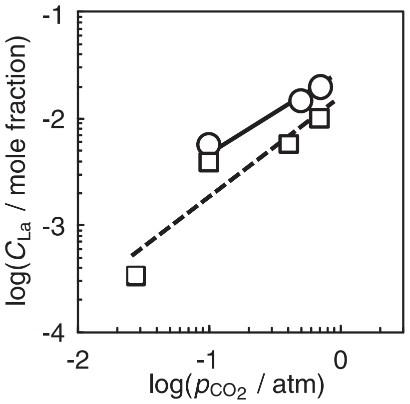

Figure 1. Dependence of C_{La} on p_{CO_2} in Li/K carbonate eutectic without $LaNiO_3$ at 923 K under p_{O_2} of 0.3 atm (○: Li/K, □: Li/Na).

The concentration of La was saturated after 250 h operation at 923 K. The saturated concentration was defined as the solubility of La (C_{La}) in the molten Li/K carbonate. Figure 1 shows the dependence of C_{La} on the p_{CO_2} in the molten Li/K carbonate without $LaNiO_3$ at 923 K. The dependence of C_{La} on the p_{CO_2} in the Li/Na carbonate eutectic is also shown in Figure 1.[4] The C_{La} was 1.9×10^{-2} (mole fraction) in the molten Li/K carbonate at the p_{O_2}/p_{CO_2} of 0.3/0.7, and almost two times greater than that in the molten Li/Na carbonate ($=1.0 \times 10^{-2}$ (mole fraction)). The dependence of C_{La} on the p_{CO_2} in molten Li/K carbonate was almost the same as that in the molten Li/Na carbonate (=1.0). Since the stable phase of the lanthanum oxide was $La_2O_2CO_3$ in both the Li/Na and Li/Na/K carbonate eutectic at the p_{O_2}/p_{CO_2} of 0.3/0.7 at 923 K,[4,6] the dissolution reactions of $La_2O_2CO_3$ in molten Li/Na and Li/Na/K carbonates would be dominated by the acidic dissolution without redox reaction in the high-pressure region. The reaction could be expressed as follows:[4,6]

$$La_2O_2CO_3(s) + 2CO_2(g) \rightleftharpoons 2La^{3+}(l) + 3CO_3{}^{2-}(l) \quad (1)$$

Equation 1 shows that the solubility of La^{3+} is proportional to the p_{CO_2}.

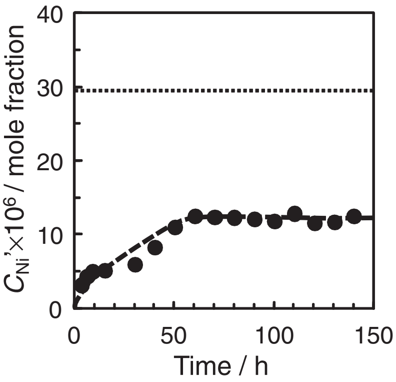

Figure 2. Dissolution curves: C_{Ni}' from $LaNiO_3$ by Li/K carbonate eutectic saturated with La_2O_3 at 923 K under p_{O_2}/p_{CO_2} of 0.3/0.7 (●: $LaNiO_3$, ---: C_{Ni} from NiO in the melt without La_2O_3).

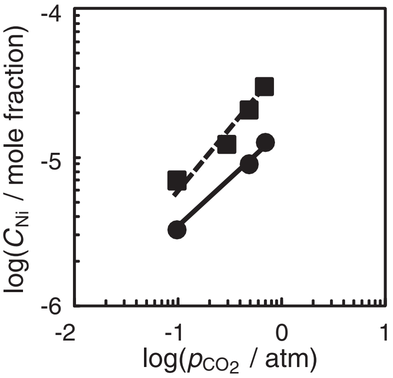

Figure 3. Dependence of C_{Ni} on p_{CO_2} in Li/K carbonate eutectic with and without La_2O_3 at 923 K under p_{O_2} of 0.3 atm (■: NiO in Li/K eut. ●: $LaNiO_3$ in Li/K eut. with La_2O_3).

Figure 2 shows the dissolution curves of Ni; that is, the C_{Ni}' in contact with $LaNiO_3$ in the Li/K carbonate eutectic with La_2O_3 for the p_{O_2}/p_{CO_2} of 0.3/0.7 at 923 K as a function of time. C_{Ni} in contact with NiO in the Li/K carbonate eutectic is also shown in Figure 2.[5] The C_{Ni}' in contact with $LaNiO_3$ showed a steady value of 1.3×10^{-5} (mole fraction) over 100 h. Though the C_{Ni} in contact with $LaNiO_3$ in Li/Na carbonate eutectic saturated with La_2O_3 was 90% lower that in contact with NiO ($=1.2 \times 10^{-5}$ (mole fraction)) under the same conditions,[7] it was 57% lower than that in contact with NiO ($=3.0 \times 10^{-5}$ (mole fraction)). As the melt became basic by the addition of La_2O_3, the C_{Ni} in contact with $LaNiO_3$ decreased more than that in contact with NiO. Since the dissolution of Ni in molten carbonate follows the acid dissolution,[5] the Ni concentration would become low when the molten carbonate becomes basic. Besides, the activity of Ni in $LaNiO_3$ was also different from that in NiO.

Figure 3 shows the dependence of C_{Ni} in contact with $LaNiO_3$ on the p_{CO_2} in the Li/K carbonate eutectic saturated with La_2O_3 at 923 K. The dependence of the C_{Ni} of NiO on the p_{CO_2} in the Li/K carbonate eutectic is also shown in Figure 3.[6] The C_{La} in saturated La_2O_3 adding molten Li/K carbonates with $LaNiO_3$ was also the same as that without $LaNiO_3$ in saturated La_2O_3 adding Li/K in molten carbonates as shown in the Figure 1. The slope of the $\log C_{Ni}$ in contact with $LaNiO_3$ on the $\log p_{CO_2}$ was 0.75 in Figure 3, and it was different from the C_{Ni} in contact with NiO on the p_{CO_2} in the molten Li/K carbonate without La_2O_3. The slope of the $\log C_{Ni}$ in contact with NiO was 1.0. Since the slope of the $\log C_{Ni}$ in Li/Na carbonate eutectic with La_2O_3 was also 1.0,[6,7] the molten Li/K carbonates might be more effective than molten Li/Na carbonates to reduce the C_{Ni} under high CO_2 pressure opreation.

In the high p_{CO_2} region, the dissolution mechanism of NiO in the molten carbonate was dominated by the acidic dissolution as follows:

$$NiO(s) + CO_2(g) \rightleftharpoons Ni^{2+}(l) + CO_3{}^{2-}(l) \qquad (2)$$

Equation 2 shows that the C_{Ni} is proportional to the p_{CO_2}. Equation 2 was divided into the following equations:

$$NiO(s) \rightleftharpoons Ni^{2+}(l) + O^{2-}(l) \qquad (3)$$

$$CO_2(g) + O^{2-}(l) \rightleftharpoons CO_3{}^{2-}(l) \qquad (4)$$

For $LaNiO_3$, the C_{Ni} was obviously depended on the p_{CO_2}, but its slope was different from that for NiO. If the stable phase of nickel on $LaNiO_3$ would be the same as that on NiO as Ni^{2+} in the molten carbonate with La_2O_3, the dissolution reaction of $LaNiO_3$ could be described by the following equation.

$$\begin{aligned}&4LaNiO_3(s) + 10CO_2(g)\\&\quad \rightleftharpoons 4La^{3+}(l) + 4Ni^{2+}(l) + 10CO_3{}^{2-}(l) + O_2(g)\end{aligned} \qquad (5)$$

Since the C_{La} might be proportional to the p_{CO_2} in the Li/K carbonate eutectic as shown in eq 1, the activity of La^{3+}: $[La^{3+}]$ would be expressed by the following equation:

$$[La^{3+}] = K_1 \cdot p_{CO_2} \qquad (6)$$

where K_1 is the equilibrium constant of eq 1. On the other hand, the activity of Ni^{2+}: $[Ni^{2+}]$ in eq 5 would be described by the following equation:

$$[Ni^{2+}] = K_5 \cdot p_{O_2}{}^{-1/4} \cdot p_{CO_2}{}^{5/2} \cdot [La^{3+}]^{-1} \qquad (7)$$

where K_5 is the equilibrium constant of eq 5. Since the C_{La} in this melt was almost same as the C_{La} in the melt without $LaNiO_3$ as shown in Figure 1, eq 6 was substituted into eq 7, and then eq 8 was obtained as follows:

$$[Ni^{2+}] = K_3 \cdot K_1{}^{-1} \cdot p_{O_2}{}^{-1/4} \cdot p_{CO_2}{}^{3/2} \qquad (8)$$

The slope of $\log C_{Ni}$ in contact with $LaNiO_3$ vs. the $\log p_{CO_2}$ should be 1.5 if the eq 8 reaction occurs under this condition. However, in this study, the slope of $\log C_{Ni}$ in contact with $LaNiO_3$ was 0.75; therefore, it was difficult to explain the dissolution mechanism of $LaNiO_3$ in the Li/K carbonate eutectic with La_2O_3 at 923 K. It might be implied that the $LaNiO_3$ was dissolved into the molten carbonate as a cation of the oxynickel ion.[7–9]

Since the cationic mole fraction of Ni in $LaNiO_3$ is 0.5, we could expect that the reduction of the Ni solubility is 50% that is very close to our result.[3] The reduction of C_{Ni} in contact with $LaNiO_3$ might be caused by the reduction of the Ni activity in a solid.

Figure 4 shows the XRD patterns of $LaNiO_3$ before and after immersion. Si powder was also contained in order to calculate the lattice constant of $LaNiO_3$. Most peaks were identified as $LaNiO_3$ after immersion for 2000 h, and the lattice constants of

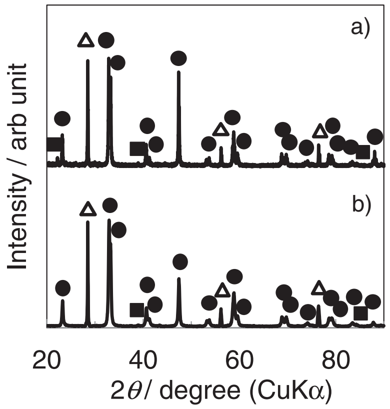

Figure 4. XRD patterns of $LaNiO_3$ before immersion in molten carbonates (●: $LaNiO_3$, ■: NiO, △: Si) (a: after immersion, b: before immersion).

the $LaNiO_3$ before and after the immersion were 3.86 and 3.82 Å, respectively. The lithiation of the $LaNiO_3$ would occur during the immersion for 2000 h in the molten carbonate, and the lattice constant might slightly decrease during the immersion.

Overall, since the solubilities of the Ni ion was 57% lower than that on NiO, the $LaNiO_3$ with La_2O_3 addition might be a promising alternative material as the cathode of MCFCs.

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