CHARACTERIZATION OF NICKEL OXIDE IN MOLTEN CARBONATE
II. *IN SITU* X-RAY DIFFRACTION OF HIGHER NICKEL OXIDE
IN MOLTEN CARBONATE

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Summary

A special apparatus for *in situ* X-ray diffraction measurements has been designed to investigate unstable intermediates that are formed during the anodic oxidation of nickel in molten $Li_2CO_3-K_2CO_3$, and can exist only under certain conditions. In preliminary experiments, the anodic oxidation of copper, which is well understood, has been used to test the apparatus. The result demonstrated that the *in situ* X-ray diffraction apparatus functions effectively. Using this apparatus, the mechanism of anodic oxidation of nickel in molten $Li_2CO_3-K_2CO_3$ has been investigated, and the higher nickel oxide earlier inferred from transient electrochemical measurements has been confirmed as Ni_2O_3.

Introduction

There are still many problems to be solved in achieving the practical application of the molten carbonate fuel cell (MCFC). At present, nickel oxide (lithiated NiO) is used for MCFC electrodes. Dissolution of the NiO cathode of the MCFC is, however, one of the major problems hindering the development of this power source. In an earlier paper [1] the anodic oxidation of nickel has been investigated. The results indicate that in addition to normal NiO, a unstable higher nickel oxide (Ni_2O_3) appears to be formed at −400 mV. The formation of a higher nickel oxide may have important implications for the dissolution of the NiO cathode in the MCFC. At present, it is believed that NiO dissolves into molten alkali metal carbonate, M_2CO_3 (M denotes Li, Na, K, or Rb), in one of two modes: acidic dissolution or basic dissolution. Acidic dissolution is defined as:

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$$NiO + CO_2 = NiCO_3 \qquad (1)$$

while the basic mode is:

$$NiO + M_2CO_3 = M_2NiO_2 + CO_2 \qquad (2)$$

Several studies on these modes of NiO dissolution have been published [2 - 5].

From the results of earlier work in the author's laboratories [1], it appears that there is also a possibility for the nickel oxide electrode to transform into higher nickel oxide Ni_2O_3 under cell operating conditions. This kind of higher nickel oxide is rather unstable. Thus, the degradation of the MCFC cathode may be explained not as a direct dissolution, as mentioned above, but by an indirect process, i.e., the NiO is first oxidized into Ni_2O_3 and then decomposed into NiO again while some of the newly formed NiO dissolves into the electrolyte. Because of the compound's instability, Ni_2O_3 is quite difficult to detect by the usual ex situ surface analysis methods. In view of this situation, a special in situ X-ray diffraction (XRD) apparatus has been developed. This apparatus is applicable not only in aqueous systems but also in high temperature systems, such as molten Li_2CO_3–K_2CO_3 (62 mol% + 38 mol%).

Experimental

A schematic of the apparatus is shown in Fig. 1, and a photograph of the actual equipment is presented in Fig. 2. The set-up consists of a special electrolysis cell and a gas-tight pyrex glass cap; this allows the atmosphere inside the pyrex cap to be controlled. The melt container (100 ml capacity), the protection tube for the thermocouple, and the reference electrode compartment were all made of pure alumina. A standard oxygen gas reference electrode (denoted as 1:2 $O_2/CO_2/Au$) was used. The counter electrode was a nickel rod. The working electrode was a disc that was fixed in a horizontal shaft by a set-screw and, therefore, could be rotated by a motor. The upper part of the disc and the shaft were exposed to the atmosphere, but a part of
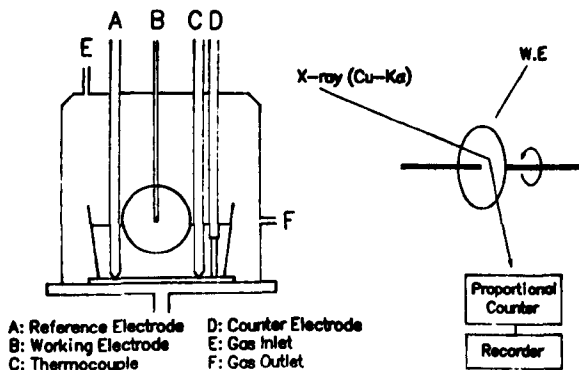

A: Reference Electrode   D: Counter Electrode
B: Working Electrode   E: Gas Inlet
C: Thermocouple   F: Gas Outlet

Fig. 1. Schematic diagram of in situ XRD apparatus.

Fig. 2. Photograph of *in situ* XRD apparatus.

the disc was immersed in the electrolyte contained in the small crucible. Since the disc was wetted very well by the electrolyte, and by virtue of its rotation, the whole disc was covered by a thin film of molten carbonate. The latter was thin enough not to obstruct the XRD measurement and effectively caused the surface of the upper part of the disc to be in almost the same environment as the bulk electrolyte. Two windows were made in the side of the pyrex glass cap and sealed by thin aluminium foils (30 μm). The incident and diffractive X-rays were able to penetrate the pyrex glass cover easily through these windows. The X-ray beam was allowed to fall upon the upper part of the disc that was not immersed directly in the electrolyte. The XRD measurement could thus be carried out *in situ* while electrolysis was in progress.

The temperature of the experiment was controlled by a heater coiled around the crucible. Because of the limited power of the heater, the maximum temperature of the apparatus was 600 °C instead of 650 °C, the usual operating temperature of the MCFC. The purification process of the carbonate was the same as described previously [1].

Results and discussion

A preliminary experiment on copper was executed to determine the effectiveness of the apparatus. Figure 3 shows the voltammogram for a

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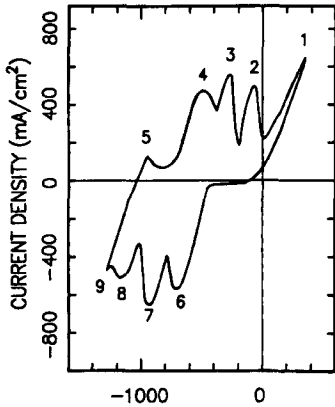
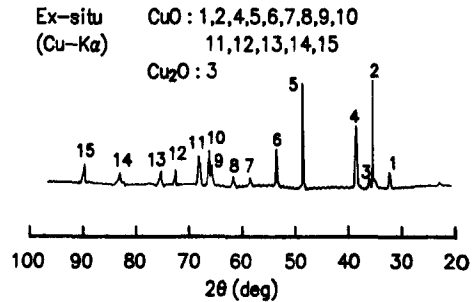Fig. 3. Voltammogram of copper electrode under P_{Ar}/P_{CO_2} = 0.9/0.1 atm.; scan rate = 100 mV s^{-1}.

Fig. 4. XRD pattern of copper electrode prepared at −100 mV under P_{Ar}/P_{CO_2} = 0.9/0.1 atm.

copper electrode in molten eutectic Li_2CO_3–K_2CO_3 at 650 °C under an atmosphere of P_{Ar}/P_{CO_2} =0.9/0.1 atm. The XRD study revealed that peaks 2 and 3 corresponded to the formation of CuO and Cu_2O, respectively (see Figs. 4 and 5). Using the apparatus, the mechanism of copper oxidation was investigated further. Figure 6 gives the XRD pattern of a copper electrode taken after potentiostatic electrolysis at −500 mV in molten Li_2CO_3–K_2CO_3 under the same atmosphere as used above. The results indicate that the surface of the electrode was oxidized to Cu_2O, as well as a small amount of CuO. The XRD pattern taken at −100 mV under the same atmosphere is presented in Fig. 7. It was found that most of the Cu_2O had been further oxidized to CuO. These results were in agreement with those obtained from *ex situ* measurements, as had been expected. This confirmed the applicability of the XRD apparatus to *in situ* studies in molten electrolytes.
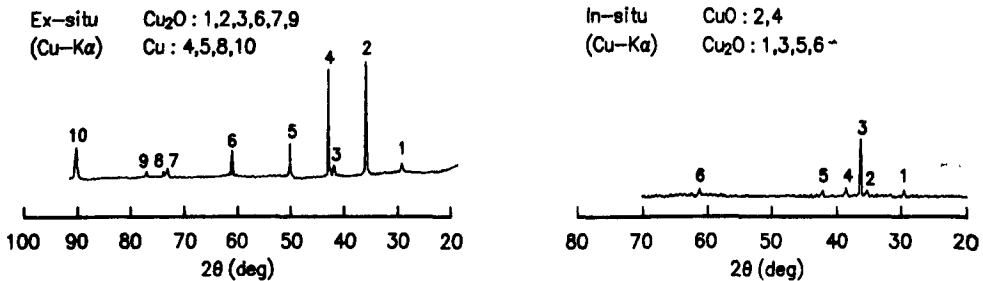

Fig. 5. XRD pattern of copper electrode perpared at −500 mV under P_{Ar}/P_{CO_2} = 0.9/01 atm. for 20 h.

Fig. 6. *In situ* XRD pattern of copper electrode at −500 mV under P_{Ar}/P_{CO_2} = 0.9/0.1 atm.

In situ examination of the anodic behavior of a nickel electrode was carried out under two kinds of atmosphere: $P_{Ar}/P_{CO_2} = 0.99/0.01$ atm and $P_{Ar}/P_{CO_2}/P_{O_2} = 0.25/0.25/0.5$ atm. The results of *in situ* XRD under the former atmosphere at applied potentials of -500 and -100 mV are shown in Figs. 8 and 9, respectively. According to previous findings [1], NiO and Ni_2O_3 are expected to form at -500 and -100 mV, respectively. The XRD pattern at -500 mV revealed definitely the existence of NiO, but that at -100 mV indicated the presence of only normal NiO. No significant changes were detected in the XRD pattern after an increase in the period of electrolysis at -100 mV (Fig. 10). Two explanations can be offered for this [1]: (i) the film of higher oxide (Ni_2O_3) on the electrode surface was too thin to be detected by XRD due to instability of the oxide, even under *in situ* conditions; (ii) the crystal lattice of the higher oxide is so similar to that of normal NiO that the XRD patterns of these two oxides are indistinguishable. If the first explanation is correct, then the problem of identifying the higher oxide can be solved by suppressing the decomposition of the oxide. In this case, the higher oxide becomes detectable by increasing the atmosphere in
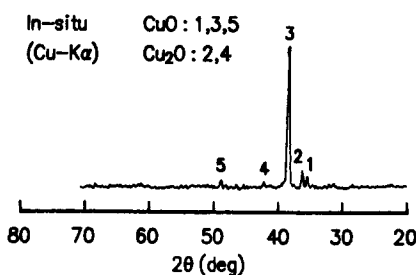

Fig. 7. *In situ* XRD pattern of copper electrode at -100 mV under $P_{Ar}/P_{CO_2} = 0.9/0.1$ atm.
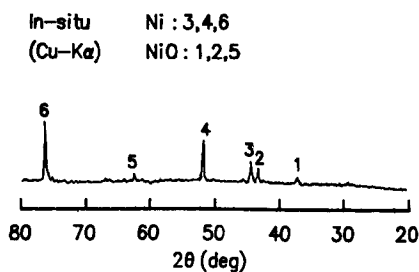
Fig. 8. *In situ* XRD pattern of nickel electrode at -500 mV under $P_{Ar}/P_{CO_2} = 0.99/0.01$ atm.
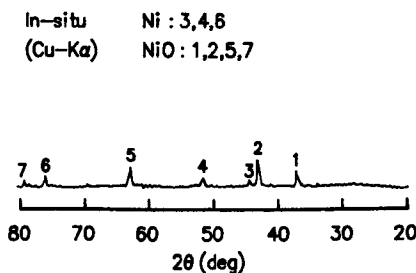

Fig. 9. *In situ* XRD pattern of nickel electrode at -100 mV under $P_{Ar}/P_{CO_2} = 0.99/0.01$ atm.
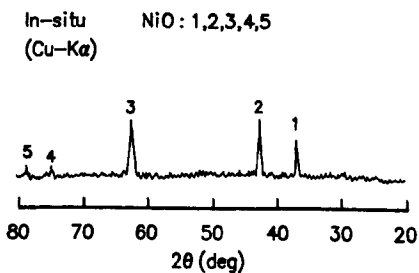
Fig. 10. *In situ* XRD pattern of nickel electrode at -100 mV under $P_{Ar}/P_{CO_2} = 0.99/0.01$ atm. after a longer period of potentiostatic electrolysis.

oxygen partial pressure, as concluded in earlier studies [1]. If the second explanation is correct, the problem is more complicated. In this situation, the crystal lattice of the higher oxide will have a subtle difference from that of normal NiO, caused by the change of chemical state of nickel ion from bivalence to trivalence. The problem is whether the diversity is large enough to be detectable. It seems that assumption (i) is more amenable to investigation.

In situ XRD measurements of a nickel electrode under an oxygen atmosphere were carried out. Contrary to expectation, in most of the measurements only NiO was detected. Only in one case were several new peaks observed (Fig. 11). In addition to the peaks corresponding to Ni and NiO, peaks appeared at $2\theta = 27.2°$, $33.2°$ and $38.9°$. The most likely explanation is that these three peaks correspond to Ni_2O_3 ($2\theta = 27.6°$, $31.9°$, $39.1°$, $44.8°$, $51.6°$ and $56.8°$ [6]). In addition, peaks 6 and 7 can be considered as belonging to Ni_2O_3, since at these positions peaks corresponding to both Ni_2O_3 and Ni ($2\theta = 44.6°$, $51.9°$ and $76.1°$) appear. It is rather difficult to tell whether these peaks originate from Ni_2O_3 or Ni. As discussed previously [1], Ni_2O_3 can be considered as a kind of surface-defect structure of NiO. It has almost the same lattice structure as NiO, so the XRD of Ni_2O_3 cannot be detected easily. If there exists an optimum environment suitable for the growth of Ni_2O_3, a Ni_2O_3 film which possesses its own crystal-lattice structure (hexagonal) should be formed. This may explain the XRD pattern given in Fig. 9. In future work, it is intended to determine the conditions under which this pattern can be produced in a consistent manner. Furthermore, the experimental angle of $33.2°$ is rather different from the literature value of $31.9°$. It is well known that the formation of NiO is accompanied by lithiation, and thus it is equally reasonable to suppose that the formation of Ni_2O_3 is also accompanied by lithiation. If such is the case, then lithiation could account for the discrepancies in the positions of the XRD peaks. In addition, because the measurements were carried out *in situ* , the high temperature may cause considerable distortion of the crystal lattice. There have been few published studies of lithiation and thus its mechanism is not well understood. At present, it is impossible to calculate quantitatively the effect of lithiation on the crystal structure of Ni_2O_3. Further investigation of the dependence of the stability of Ni_2O_3 on atmosphere is also required.
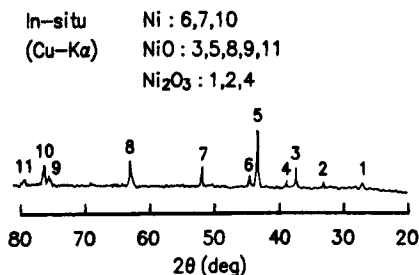

Fig. 11. *In situ* XRD pattern of nickel electrode at -100 mV under $P_{Ar}/P_{CO_2}/P_{O_2} = 0.25/0.25/0.5$ atm.

Conclusions

The principal results of the present study are as follows.

(1) The applicability of *in situ* XRD studies to investigating molten carbonate systems has been demonstrated.

(2) The anodic behaviour of copper in molten carbonate has been confirmed by *in situ* XRD measurements.

(3) More evidence has been obtained that a higher nickel oxide is formed at -400 mV, and that it is an unstable, surface-defect structure of NiO.

Acknowledgements

References

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