—Technical Paper—

A Solubility Study of Prelithiated NiO and Prelithiated Cobaltite as Cathode Materials for MCFC in 62 Li-38 K Eutectic Carbonate Melts

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The solubility of prelithiated NiO and prelithiated cobaltite as cathode materials for MCFC in 62 Li-38 K eutectic carbonate melts was studied with immersion test method. It was found that the solubility of either prelithiated NiO or prelithiated cobaltite was affected by its lithium (Li) content. The higher Li content was, the lower solubility could be in the range of 0~0.25 mole fraction of Li. With the prelithiated NiO at Li content of 0.2 mole fraction, Ni solubility was reduced to $3\sim4\times10^{-6}$ mole fraction, which was only one-third of that of the normal NiO cathode in 30 % CO₂-70 % air at 1 atm. It was obtained that the solubility of prelithiated cobaltite and even LiCoO₂ were higher than the prelithiated NiO in the low O₂ concentration gas. This suggested that even LiCoO₂ was not stable in the O₂ depleting condition, and more soluble than NiO.

Key Words : Solubility, Prelithiated Cathode, MCFC

1 Introduction

The material development represents a key aspect for moving towards the commercialization of molten carbonate fuel cell (MCFC). For this reason, a great attention has been paid in the MOLCARE¹⁾ (MOLten CARbonate Europe) project to find suitable solutions. NiO cathode problem has been selected as one theme of this project, since it is one of material obstacles which limit the lifetime of MCFC to meet its commercial goal of 40,000 h.²⁾

As for the cathode problem of the state-of-art NiO material, it is generally recognized that the dissolved nickel ion diffuses from cathode towards anode by concentration gradient and, is reduced to metallic Ni deposits by dissolved hydrogen from anode side. The accumulative Ni deposits eventually form an electronic conductive chain in the matrix and result in the short-circuit between cathode and anode.

Based on this mechanism, the shorting time of a cell considerably depends on the deposition rate, which is closely related with the solubility of cathode material. Therefore, it is important to study the solubility of cathode materials, and to find a way of reducing the solubility.

In order to suppress the dissolution of the NiO cathode material, alkaline earth metal salts have been added to the carbonate melts^{3,4)} to increase the basicity, and cathode materials of more chemical stability have been developed.^{2,5,6)} Up to now, LiCoO₂ seems to be the best candidate of high stability and comparative cathode performance in the

carbonate melts.

The solubility of LiCoO₂ is only one third of NiO in 1 atm operating pressure.^{2,6)} However, the solubility of LiCoO₂ depends on not only $P_{\text{CO}_2}^{1.55\sim1.7}$ but also $P_{\text{O}_2}^{-0.25}$, while the solubility of NiO almost only depends on $P_{\text{CO}_2}^{1.0}$; that means in case of the depletion of O₂ in cell operation, the solubility of LiCoO₂ could increase. As we know, there are few investigations for the solubility of LiCoO₂ under the lower O₂ concentration condition.

In the LiCoO₂ candidate, high amount of Li is contented. What will be the solubility if the Li content is deficient? Moreover, what will be the solubility of NiO cathode if it is prelithiated at the same Li amount as the prelithiated cobaltite does. The function of lithium content in the NiO-series and in Cobaltite-series cathode materials is worth studying.

In the present paper, the solubility of prelithiated NiO and prelithiated cobaltite at different Li contents under different gas conditions in 62 Li-38 K eutectic carbonate melts was investigated. With this study we try to understand the effect of Li content in these cathode materials and the effect of gas compositions on the solubility of these cathode materials.

2 Experimental

Test materials and their specifications and sources are listed in Table 1. The powder of prelithiated NiO or prelithiated cobalt oxide is prepared by thermal solid reaction from the ball-milled mixture of Ni powder (or Co powder) and Li₂CO₃ powder at the

Table 1 Test materials and their specifications and sources.

Test materials	Specifications	Sources
Ni powder	Type 255, average diameter 5 μm	Inco-Europe LTD, Swansea, UK, SA6 5QR
Co powder	Reagent 99.8 %, <i>ca.</i> 1.6 μm	Johson Matthey GmbH, D-7500 Karlsruhe
Li_2CO_3	extra pure	E. MERCK, D-6100, Germany
K_2CO_3	extra pure	E. MERCK, D-6100, Germany

Table 2 Experimental conditions of the immersion test.

Test conditions :	Gas : $\text{CO}_2 + \text{O}_2 + \text{N}_2$, 1 atm, at 100~200 ml/min Temperature : 650 $^\circ\text{C}$ Immersion period : 250~300 hours
Carbonates :	(Li / K = 62 / 38, mole ratio)
Materials :	Prelithiated NiO ($x = \text{Li} / \text{Ni} = 0, 0.01, 0.10, 0.20$) Prelithiated cobaltite ($x = \text{Li} / \text{Co} = 0.01, 0.10, 0.25$), LiCoO_2

nominated chemical composition. During the calcination, when the temperature reaches to 500 $^\circ\text{C}$, the powder mixture is taken out and each is remilled in an agate mortar for 10 mins, then continues the calcination at 775 $^\circ\text{C}$ for 1 hour in air.

Approximately 1.0 gram of powders is used for the pellet specimen preparation. Each powder is cold pressed into pellets of 10 mm in diameter and about 3 mm in thickness at pressure of $2 \sim 3 \times 10^3 \text{ kg/cm}^2$ for 1 min, then sintered at 900 $^\circ\text{C}$ for 10 hours on a dense alumina plate.

60 g of 62 Li-38 K eutectic carbonate mixture (mixed for 24 hours in an electric shaking mixer) are used for an immersion test. Immersion test condition is listed in Table 2. Immersion time of 250~300 h is adopted in this study based on the Ni or Co solubility equilibrium can be reached at this time scale as many references^{2-3,5-8)} revealed. About 0.2~0.5 g frozen melt is obtained by inserting a cold alumina tube into the testing alumina crucible and then quickly taking out. Ni or Co content in the melt is analyzed by AAS.

3 Results and Discussions

3.1 Effect of lithium content

The effect of Li content in prelithiated NiO and prelithiated cobaltite on their solubility in 30 % CO_2 -15 % O_2 -55 % N_2 is shown in Fig. 1. It can be seen that with the increase of lithium content in the prelithiated NiO and in the prelithiated cobaltite materials, their solubility decreases. It is noticeable that Co solubility is quite high when the Li content is not sufficient in the prelithiated cobaltite, which suggests that the deficiently-prelithiated cobaltite is not chemically stable in the melts.

To date, many solubility data have been obtained on Ni or *ex situ* oxidized NiO as test material. It is supposed that Ni or NiO could be *in situ* lithiated at

some extent during the test. The typical lithium content of the cathode oxidized and lithiated *in situ* from the raw materials (Ni or NiO) is about 0.02~0.04.⁸⁾ Ogura *et. al*⁷⁾ investigated the influence of NiO electrochemically pretreated in LiOH-KOH aqueous solution, and found that the treated NiO with lower solubility than no treated one. They suspected the solubility difference was caused by the difference between the prelithiated NiO surface and the *in situ* formed lithiated NiO surface. Their SEM results revealed that *in situ* lithiated NiO layer easier cracked and exploited from Ni substrate. Compared with the normal NiO, the solubility of prelithiated NiO even at low amount of Li(0.01) is clearly reduced in this test. This may also suggest that the *ex situ* prelithiated NiO layer is relatively more stable than the *in situ* formed lithiated NiO. K. Hatoh *et. al*⁸⁾ studied the influence of different content of lithium in prelithiated NiO ($\text{Li}_x\text{Ni}_{1-x}\text{O}$, $0.05 < x < 0.5$) cathode materials. Their results showed that $\text{Li}_x\text{Ni}_{1-x}\text{O}$ with high Li contents ($0.1 < x < 0.42$) obviously had smaller

Fig. 1 Effect of Li content on the solubility of the prelithiated NiO and the prelithiated cobaltite.

solubility than $\text{Li}_x\text{Ni}_{1-x}\text{O}$ with low lithium contents ($0.02 < x < 0.04$). Under the cathode condition of 30 % CO_2 -70 % air at 1 atm, the former ($\text{Li}_x\text{Ni}_{1-x}\text{O}$, $0.1 < x < 0.42$) is 4.0~2.0 mole ppm, and the later (Ni or NiO, Li: 0.02~0.04) is about 15 mole ppm. Our results of the prelithiated NiO is coordinated with their results.

K. Hatoh *et al.*⁸⁾ based on the variation of lattice parameters calculated from the XRD patterns of the samples before and after immersion tests of 3,000 hours, and found that the change in the x values of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ (even the high prelithiated NiO material) in the carbonates electrolyte was quite slow, that means the prelithiated NiO material is stable in the molten carbonates and the leaching process of lithium to the electrolyte happens slowly. The change of Li content in the tested cathode materials has not been checked in this test. However, the fact of the solubility disparities between different prelithiated specimens itself indirectly indicates that the prelithiated NiO material is relatively stable in the melts. If the Li were quickly leached out, there could not appear a remarkable difference in the solubility of the tested materials.

It is well reported that LiCoO_2 has lower solubility than NiO, especially in the low-pressure atmosphere.^{2,5,6)} However, compared with the solubility data of the prelithiated NiO in our test, this kind of advantage is limited. It is surprising that the prelithiated cobaltite at low Li content is highly soluble. This reveals the formation of LiCoO_2 from low Li-content cobalt oxide is not quickly happened in the test condition. And cobalt oxide with low Li content is easily dissolved into the melt. This explanation is indirectly supported by the high solubility of LiCoO_2 in the lower O_2 concentration gas, which has been normally explained by the chemical decomposition of LiCoO_2 to lithium carbonate and cobalt oxide (see Section 3.3).

As stated above, the effect of Li content in the NiO-series and in Cobaltite-series cathode materials on their solubility in the melts is obvious. In authors' view, the function of lithium content may be explained as:

- (1) A structure modification of NiO or Cobaltite to more stable form by the prelithiation,
- (2) An increase of the local basicity in the interface region between the prelithiated NiO or the prelithiated cobaltite materials and the carbonate melts.

As we know, porous Ni cathode *in situ* takes place a lithiation process during the start-up of MCFC. This phenomenon indicates that the lithiation process of NiO cathode material in the Li-rich melts is a thermodynamically spontaneous process ($\Delta G < 0$). Therefore, the lithiated NiO could be regarded more

stable than NiO form either chemically or structurally (or both). Generally speaking, the lithiated degree, *i.e.*, Li doping concentration in NiO will depend on the surrounding condition. The existence of O_2 will be crucial for the lithiation processes of both NiO and cobaltite. As pointed out by Lundblad *et al.*,⁹⁾ LiCoO_2 could only be prepared in high O_2 content atmosphere from carbonate precursors. No LiCoO_2 could be produced in pure CO_2 and only metallic Co, low valence CoO and Li_2CO_3 were detected in the product. Considered the *in situ* lithiating condition, the melted carbonate is quite possible to flood the NiO surface, and prevent NiO from freely contacting with the gaseous oxygen. This may be a reason of the low lithiated degree of the *in situ* lithiated NiO cathode (Li: 0.02~0.04). Certainly, this amount of Li could not be the upper limit for NiO, since the preparation of LiNiO_2 for Li-ion battery has been succeeded.¹⁰⁾ By now, it is not clear that the prelithiation of NiO to what amount of Li is the most stable and the most benefit for its long-term serve in the cathode condition. However, it is sure that the increment of Li from the *in situ* lithiated amount in the NiO cathode material is possible and will lead to a decrease of Ni solubility. Our data show that with the prelithiated NiO at Li content of 0.2 mole fraction, Ni solubility was reduced to $3 \sim 4 \times 10^{-6}$ mole fraction, which was only one-third of that of the normal NiO cathode in 30 % CO_2 -70 % air at 1 atm. This result is in good agreement with that of Hatoh *et al.*⁸⁾

3. 2 Influence of O_2 concentration

Figure 2 shows the influence of O_2 concentration in 30 % CO_2 gas composition on the solubility of prelithiated NiO and prelithiated cobaltite at Li=0.1. It is obvious that the O_2 concentration almost has no influence on the solubility of the prelithiated NiO, while the prelithiated cobaltite is highly soluble at the low

Fig. 2 Influence of O_2 concentration on the solubility of the prelithiated NiO and the prelithiated cobaltite at Li=0.1.

O₂ concentration. This suggests that the prelithiated NiO is more chemically stable than the prelithiated cobaltite under the low O₂ gas condition.

To further clarify the importance of the existence of O₂, another set of tests in pure CO₂ gas is conducted on the prelithiated cobaltite, LiCoO₂ and the prelithiated NiO as well. It is worth mentioning that the colors of condensed carbonate melts are different. The color of the sampled melt for the prelithiated NiO is pure white, but the colors for both the prelithiated cobaltite and LiCoO₂ are gray-yellow, that directly gives one an impression of high soluble Co inside the melts. Table 3 lists the solubility data. It shows that Co amounts dissolved from the prelithiated cobaltite and LiCoO₂ are 3 to 4 times higher than that of Ni amount from the prelithiated NiO under pure CO₂ condition.

The results of LiCoO₂ in Table 3 ($58 \sim 60 \times 10^{-6}$ mole fraction) are clearly greater than the reported solubility of LiCoO₂ in 68 Li-32 K carbonate electrolyte at 650 °C and 1 atm of 30 % CO₂ + 70 % O₂, which is merely $6.0 \pm (0.2 \text{ wt ppm})^{(6)}$ and 4.2 mole ppm.⁽²⁾ We have tested the prelithiated cobaltite (Li / Co atomic ratio = 0.1) in 30 % CO₂-70 % air, the Co solubility is 6.6 mole ppm (refer to the result of Fig. 2). Therefore, the high solubility of the prelithiated cobaltite and LiCoO₂ in Table 3 could be reasonably attributed to the depletion of O₂ in the experimental atmosphere.

3. 3 Influence of CO₂ concentration

Table 4 shows the influence of CO₂ concentration in 15 % O₂ gas composition on the solubility of prelithiated NiO and prelithiated cobaltite at several Li contents. It can be seen that with the increase of CO₂ concentration the solubility of either prelithiated NiO or prelithiated cobaltite increases. The CO₂-dependence of the prelithiated cobaltite is higher than that of the prelithiated NiO, which is normally explained by following dissolution reactions.⁽²⁾

Table 3 Results of prelithiated NiO, prelithiated cobaltite and LiCoO₂ in pure CO₂ (650 °C, 300 hours, 100 ml/min).

	Prelithiated NiO		Prelithiated cobaltite	
Li : Ni or Li : Co	0.10	0.20	0.10	LiCoO ₂
sample color	Pure white	Pure white	Grey yellow	Grey yellow
Ni or Co content (mole fraction $\times 10^6$)	23.2	19.4	89.6	58 ~ 60

Table 4 Influence of CO₂ concentration on the solubility of the prelithiated NiO and the prelithiated cobaltite (O₂ = 15 %).

		Prelithiated NiO			Prelithiated cobaltite	
Li : Ni or Li : Co		0.01	0.1	0.2	0.1	0.25
Solubility of Ni or Co (mole fraction $\times 10^6$)	30 % CO ₂	9.0	5.8	4.9	6.6	4.1
	85 % CO ₂	28.9	23.8	14.5	27.2	17.7
Calculated α value*		1.12	1.35	1.04	1.37	1.40

* α is the power of P_{CO_2} -dependence of the solubility

As the results mentioned above, the solubility of either prelithiated NiO or prelithiated cobaltite in the carbonate melts is affected not only by the amount of Li content in the material but also by the gas composition. The prelithiated cobaltite even at a relatively low Li content (Li / Co atomic ratio = 0.1) has the similar solubility as LiCoO₂, and the solubility of both prelithiated cobaltite and LiCoO₂ is greatly depended on O₂ content in the gas composition. The question is why the lithiated NiO has less dependence on O₂ content. Does it indicate the prelithiated NiO is more chemically stable than the prelithiated cobaltite and LiCoO₂?

As we know, Li ion can be inserted into the NiO or Cobaltite to form a hexagonal structure, such as LiCoO₂. It has been recognized that Li ion can reversibly intercalate and deintercalate in LiCoO₂ and LiNiO₂, which are cathode materials for Li ion battery. From the charging and discharging behavior, the intercalation and deintercalation process of LiCoO₂ is much easier than that of LiNiO₂, that is why only LiCoO₂ is well applied in the Li-ion battery production though Co is more expensive than Ni. In authors' opinion, the same process may also occur in the molten carbonate condition. Generally, the redox ability of the carbonate melts depends on the O₂ or H₂ content in it. The existence of O₂ and at higher amount means higher redox potential of the melts. Under this condition, the Li ion can enter or steadily exists in the prelithiated cobaltite like charging process. However, if the O₂ content decreases or diminishes the redox potential of molten carbonate decreases, then the former steadily exists Li amount will decrease to match the decrease of its surrounding redox potential and also relieve its O element (as O₂ gas in reaction(1)). Therefore, the relatively lower solubility of Ni than Co at the low O₂ atmosphere might be ascribed to the relatively slower deintercalation of Li from the prelithiated NiO than that from the prelithiated cobaltite, and also the lower solubility of NiO than that of cobaltite.

4 Conclusions

The solubility of prelithiated NiO and prelithiated cobaltite with different Li contents at different gas compositions in 62 Li-38 K eutectic carbonate melts were investigated. From above-stated results and discussions, we draw following conclusions:

- (1) The solubility of prelithiated cobaltite and LiCoO_2 is greatly dependent on the oxygen content in the gas phase. The absence of oxygen will lead to a sharp increase of Co content in melt carbonates. Therefore, even LiCoO_2 is unstable in O_2 -free environment.
- (2) The solubility of either the prelithiated NiO or the prelithiated cobaltite decreases with the increase of Li content in the materials. The solubility of highly prelithiated NiO (Li / Ni atomic ratio=0.2) reduces to one-third of that of normal NiO in 30 % CO_2 + 70 % O_2 at 1 atm.
- (3) The solubility difference between the prelithiated NiO and the prelithiated cobaltite in 30 % CO_2 + 70 % O_2 is not remarkable at Li content > 0.1 mole fraction; but in low O_2 concentration or low Li content (Li / Co atomic ratio=0.01), cobalt oxide is more soluble than nickel one.

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