

Short Communication

In situ NiO dissolution behavior in (Li + Na)CO₃ melts under pressurized oxidant gas atmospheres

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Abstract

The dissolution behavior of in situ oxidized NiO is investigated under pressurized oxidant gas conditions as a function of pressure, temperature and lithium content in (Li + Na)CO₃ melts. For the measurement of NiO solubility, a high performance liquid chromatography (HPLC) method was employed. It is found that NiO solubility is proportional to CO₂ partial pressure (0.1 ≤ *p*CO₂ ≤ 3.6 atm at *p*O₂ = 0.9 atm) but not to the O₂ partial pressure (0.1 ≤ *p*O₂ ≤ 3.6 atm at *p*CO₂ = 0.9 atm). This indicates that NiO dissolution under pressurized condition follows the acidic dissolution mechanism. On increasing temperature from 823 to 973 K under a total pressure of 5 atm with an air/CO₂ mixture results in decreasing NiO dissolution because the melts shifted to more basic media. Similarly, increasing the lithium content from 40 to 70 mol% increases the basicity of the carbonate melt. This also resulted in decreasing NiO solubility.

Keywords: Nitrogen oxide dissolution; Pressurized conditions; Molten carbonate fuel cells

1. Introduction

The reaction of the cathodic gas electrode in molten carbonate fuel cells (MCFCs) is considered as a bottleneck for the practical use of those devices. The electrode has considerable concentration polarization and comparatively low reaction rates compared with the anodic side [1]. For the commercialization of MCFCs, the enhancement of cathodic performance is necessary. Some approaches have been attempted such as the development of alternative cathode materials and the searching for optimum operation conditions.

As alternatives to NiO cathode materials, LiFeO₂ [2], Li₂MnO₃ [2] and LiCoO₂ [3,4] have been mainly investigated. Since the MCFC is operated at high temperature, the electrocatalytic differences among these alternative materials are not so appreciable [5,6]. Therefore, NiO is the most appropriate and, hence, most commonly employed cathode material in terms of electric conductivity and stability. Pressurized operation is employed as this increases output power density and reduces the concentration polarization of the cathode electrode. Such an approach, however, brings about serious dissolution of NiO due to the increased *p*CO₂. This significantly limits the life of MCFCs. It has been reported [7] that the dissolution of NiO is proportional to the *p*CO₂ under atmospheric conditions except at an extremely low

*p*CO₂. Therefore, NiO dissolution in carbonate melts follows an acidic dissolution mechanism under the standard conditions of MCFC (70% air:30% CO₂) and is affected by the basicity of carbonate melts



Recently, Maru et al. [8] have suggested that an (Li + Na) carbonate melt should be more appropriate than an (Li + K) carbonate melt from the point of view of long MCFC life. It has also been shown [9] that the NiO solubility in (Li + Na)CO₃ was about half of that in (Li + K)CO₃ under atmospheric conditions.

In the present work, in situ NiO dissolution has been investigated under pressurized oxidant gas conditions in (Li + Na)CO₃ melts as a function of oxidant gas partial pressure, temperature and lithium content in carbonate melts.

2. Experimental

The (Li + Na)CO₃ melts were used as solvents and were prepared by AR grade anhydrous reagents (Waco Pure Chemical Co.). The purification process for the carbonate melts and the pressure cell assembly were identical to those described in Ref. [10].

The pO_2 was changed in the range of 0.1–3.6 atm keeping $pCO_2 = 0.9$ atm at 923 K in a (53+47) mol% (Li+Na) CO_3 melt. In the same way, the pCO_2 were changed in the range of 0.1–3.6 atm keeping $pO_2 = 0.9$ atm under the same conditions mentioned above. The temperature was raised from 823 to 973 K while maintaining the total pressure at 5 atm with air: $CO_2 = 70:30$ and 90:10 mol%. The (Li+Na) CO_3 melt compositions were changed from Li:Na = 40:60 to 70:30 mol% under total pressure of 5 atm of $pO_2:pCO_2 = 10:90$ mol%.

The porous nickel plaque (5 mm×15 mm×0.75 mm thickness) made of Inco-123 and Inco-287 (33:67 wt.%) was partially immersed in the carbonate melts to contact the gas phase, then oxidized under $pO_2:pCO_2 = 0.5:4.5$ and 0.1:0.9 atm. The in situ oxidized NiO thus obtained was left in the melts; the melt was sampled at a given interval. The Ni^{2+} concentration in the melt sample was determined by an HPLC method in which the pyridine-2-aldehydebenzoylhydrazone (PAB) was used as the ligand. The details of sampling under pressurized conditions, as well as the measurement procedures and equipment were the same as used previously [10].

3. Results and discussion

The time dependence of in situ NiO solubility under atmospheric conditions is given in Fig. 1. The background level of the nickel concentration in the pure melt was about 2×10^{-6} mole fraction. The in situ NiO solubility reached an equilibrium value about 6 h after immersion of the nickel plaque in carbonate melt as shown in Fig. 1. By contrast, this required about 20 h in the case of ex situ NiO pellets [9]. The difference may be attributed to the fact that the nickel plaque employed in this study is porous with a quite large surface area. Therefore, the oxidation and dissolution of NiO proceeds rapidly. According to this result, it is regarded that the equilibrium NiO solubility is achieved at least 12 h after immersion of the nickel plaque in the carbonate melts. The equilibrium NiO solubility is about 20 ppm, as shown in Fig. 1. This corresponds to the other results that have been [9] reported with ex situ NiO by atomic absorption spectroscopy.

The effect of pCO_2 on equilibrium solubility under pO_2 fixed at 0.9 atm is given in Fig. 2. The NiO solubility is proportional to the pCO_2 . The dependence of the NiO solubility on pO_2 under a fixed pCO_2 at 0.9 atm is given in Fig. 3. It is found that the equilibrium NiO solubility is not dependent on pO_2 up to 3.6 atm. Apparently the NiO dissolution is strongly affected by pCO_2 but not by pO_2 of the oxidant gas. This indicates that the NiO dissolution into the (Li+Na) CO_3 melts under pressurized conditions follows the acidic dissolution mechanism as given in Eq. (1).

Fig. 4 shows the temperature dependence of the equilibrium solubility under a total pressure of 5 atm at air: $CO_2 = 70:30$ and 90:10%. Since the melt basicity (pO^{2-}) depends on temperature [11], the equilibrium solubility

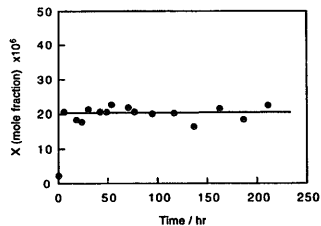


Fig. 1. Time dependence of NiO solubility at 923 K in (53+47) mol% (Li+Na) CO_3 ; $pO_2 = 0.1$ and $pCO_2 = 0.9$ atm.

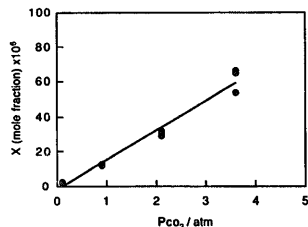


Fig. 2. Effect of pCO_2 on NiO solubility at 923 K in (53+47) mol% (Li+Na) CO_3 ; $pO_2 = 0.9$ atm.

decreases versus increasing temperature at both of the oxidant gas compositions, as shown in Fig. 4. The enthalpy change of NiO dissolution was about -28 kJ/mol.

Based on these results, it is possible to establish the empirical equation of NiO solubility in terms of pCO_2 and temperature. The dissociation constant of Eq. (1) can be expressed as follows

$$K_d = \frac{[Ni^{2+}][CO_3^{2-}]}{[NiO]pCO_2} = \frac{[Ni^{2+}]}{pCO_2} \quad (2)$$

where $[Ni^{2+}]$, $[CO_3^{2-}]$ and $[NiO]$ denote the activity of Ni^{2+} , carbonate ion and NiO, respectively. The activity of carbonate ion and NiO can be considered as unity. From the relationship between temperature (T) and $[Ni^{2+}]$ of Fig. 4, Eq. (2) can be expressed as follows

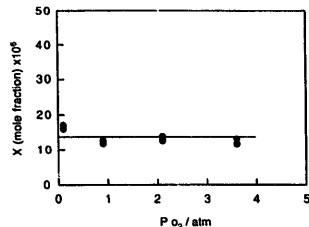


Fig. 3. Effect of pO_2 on NiO solubility in (53+47) mol% (Li+Na) CO_3 at 923 K, $pCO_2 = 0.9$ atm.

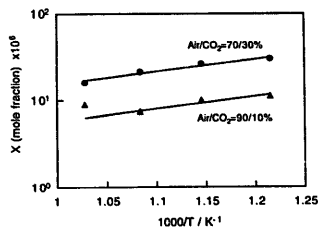


Fig. 4. Effect of temperature on NiO solubility in (53+47)mol% (Li+Na)CO₃ under total pressure of 5 atm with air:CO₂=70:30 and 90:10%.

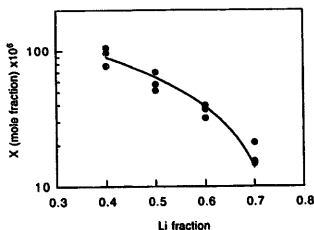


Fig. 5. Effect of lithium fraction on NiO solubility at 923 K in (Li+Na)CO₃ under total pressure of 5 atm with pO₂:pCO₂=10:90%.

$$\log(K_0) = -6.465 + 1474/T \quad (3)$$

Provided that the mole fraction of Ni, (X), is equal to [Ni²⁺], the following relationship can be written

$$\log(X) = [\log(p\text{CO}_2) - 6.465] + 1474/T \quad (4)$$

The effect of the lithium fraction on the equilibrium solubility under a total pressure of 5 atm at pO₂:pCO₂=10:90% is displayed in Fig. 5. The equilibrium solubility decreases with increasing lithium content due to the increased basicity of the carbonate melts.

4. Conclusions

The NiO dissolution in an (Li+Na)CO₃ melt under pressurized condition is investigated as a function of pressure,

temperature and lithium content of the carbonate melt. The equilibrium solubility is proportional to pCO₂ up to 3.6 atm but not to pO₂. This suggests that the NiO dissolution behavior under pressurized conditions follows an acidic dissolution mechanism. The NiO solubility decreases with increasing temperature due to the basicity (pO²⁻) change of the melt as a function of temperature. The NiO solubility also decreases with increasing lithium content of the (Li+Na)CO₃ melt. From the proportionality of NiO solubility to pCO₂, the following experimental relation was obtained

$$\log(X) = [\log(p\text{CO}_2 - 6.465) + 1474/T] \quad (5)$$

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