

Short communication

## The solubility of Ni in molten $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3$ (52/48) in $\text{H}_2/\text{H}_2\text{O}/\text{CO}_2$ atmosphere

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### Abstract

In this work the solubility of a Ni–Al anode for MCFC has been studied at atmospheric pressure and two different temperatures using various gas compositions containing  $\text{H}_2/\text{H}_2\text{O}/\text{CO}_2$ . It is well known that nickel is dissolved at cathode conditions in an MCFC. However, the results in this study show that nickel can be dissolved also at the anode, indicating that the solubility increases with increasing  $\text{CO}_2$  partial pressure of the inlet gas and decreasing with increasing temperature. This agrees with the results found by other authors concerning the solubility of NiO at cathode conditions. The dissolution of Ni into the melt can proceed in two ways, either by the reduction of water or by the reduction of carbon dioxide. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Nickel solubility; MCFC; Fuel cells

### 1. Introduction

The molten carbonate fuel cell (MCFC) is a promising power technology for converting renewable fuels into electric power and heat. Today the MCFC technology may be divided into two groups: atmospheric systems with internal reforming of natural gas, like the systems from FuelCell Energy (FCE) in USA and MTU CFC Solutions in Germany, and the pressurised systems with external reforming, being developed by Ishikawajima-Harami Heavy Industry (IHI) in Japan and Ansaldo Fuel Cells in Italy. Both techniques have their advantages and disadvantages. The main life-time limiting factor of the atmospheric systems is loss of electrolyte [1,2], whereas Ni-shorting is the main factor for the pressurised systems [3]. The dissolution at the cathode side of NiO of various kinds has been studied in different molten alkali carbonate mixtures, mainly Li/K and Li/Na, at different temperatures and oxidising gas composition containing  $\text{O}_2$  and  $\text{CO}_2$  [4–17]. The solubility of NiO depends on temperature and electrolyte composition, but mainly on the partial pressure of carbon dioxide. Studies of addition of rare-earth metals to the

Li/Na electrolyte have been made and it has been concluded that the solubility of NiO may be lowered [14,16,17].

The dissolution of nickel has always been investigated in oxidising atmosphere. However, in this work the solubility of a Ni–Al anode for MCFC has been studied at atmospheric pressure and two different temperatures with various gas compositions containing  $\text{H}_2/\text{H}_2\text{O}/\text{CO}_2$ .

### 2. Experimental

#### 2.1. Experimental setup

A mixture of 52/48 mol% of  $\text{Li}_2\text{CO}_3$  (Kanto Kagaku, 99.95%  $\text{Li}_2\text{CO}_3$ ) and  $\text{Na}_2\text{CO}_3$  (Kanto Kagaku, 99.5%  $\text{Na}_2\text{CO}_3$ ) was mixed from pure dry salts and about 150 g of the salt mixture was put in an alumina crucible. About 1 g of a porous Ni–Al anode made by AIST was divided in, small millimeter-sized, pieces and put into the salt mixture. The pot was placed at the bottom of a Pyrex vessel and sealed with a glass top. The Pyrex vessel was placed in an oven and thermal insulation was placed at the top and bottom. Nitrogen was supplied to the free space between the Pyrex vessel and the oven wall to protect the latter from the reactant gas. The temperature of the oven was manually controlled. The temperature of the melt was monitored

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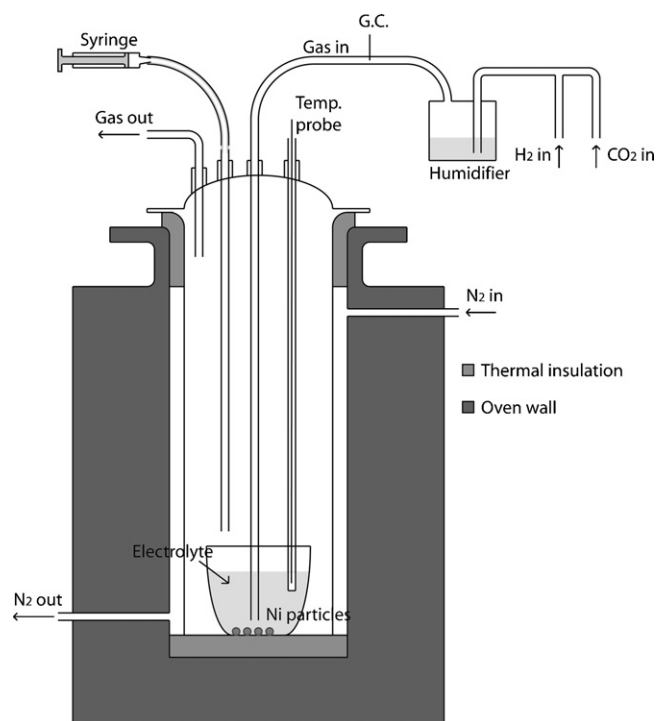


Fig. 1. Experimental setup.

with a thermal probe in an alumina tube submerged into the electrolyte. A mixture of  $H_2$  and  $CO_2$ , supplied individually and mixed, was humidified at about  $48^\circ C$ . In the case of pure  $CO_2$  no water was added. The gas composition after humidification was measured with a gas chromatograph (model M200 from Agilent). The humidified gas mixture was supplied into the electrolyte through an alumina piping. During the start up procedure dry  $CO_2$  was supplied, until the starting temperature of each experiment was reached. The experimental setup can be seen in Fig. 1.

### 2.2. Nickel content measurement procedure

The temperature of the furnace was set to a constant value for each experiment and monitored separately with the temperature probe. For each experiment the flow rate of  $H_2$  and  $CO_2$  was controlled individually and varied between 0 and  $5\text{ ml min}^{-1}$  of each, dry basis. Each gas mixture was supplied for 10 h before a sample of the electrolyte was taken. Every time a sample was taken, two droplets of electrolyte were taken from the melt using an alumina pipe and a syringe. Each droplet was placed in an alumina crucible. After solidification of the droplet it was weighed and placed in a test tube. The droplet was dissolved in  $1\text{ M HNO}_3$

(Kanto Kagaku), at a ratio of  $1\text{ ml HNO}_3$  for each  $10\text{ mg}$  of electrolyte. When the droplet had been dissolved the sample was placed in an ultrasonic bath for 10 min or until bubbles no longer were formed. The nickel content in each sample was measured using ICP-AES, an ICPS-7500 from Shimadzu Corporation. To compare the results from different ICP measurement days eight reference samples were measured each time, to check the reproducibility and to get a practical detection limit. The Ni content in the reference samples varied between  $1.0 \times 10^{-5}$  and  $1.0\text{ mg ml}^{-1}$ . The measured weight fraction was recalculated to mole Ni per total amount of moles of salt and Ni.

## 3. Results and discussion

### 3.1. Nickel dissolution

For Test-1, see Table 1, the mole fraction of Ni was measured by the ICP twice, the first time only some of the samples were tested, in reality to ascertain the functionality of the equipment, calibration solutions and reference samples (date 1). The second measurement included all the samples from Test-1 and a measurement of the Al content (date 2). Fig. 2 shows the mole fraction of Ni obtained in the electrolyte. It can be seen that the solubility of Ni increases with the partial pressure of carbon dioxide. At lower carbon dioxide contents the detection limit of the ICP equipment limits the analysis. The solubility increases about two orders of magnitude, when going from a low carbon dioxide content to a high.

Test-3 was performed at a higher temperature than Test-1, closer to the operating temperature of the MCFC. As can be seen in Fig. 3 the mole fraction Ni is mainly in the range of  $(5\text{--}10) \times 10^{-7}$  for a gas composition containing less than 60% carbon dioxide, and for higher contents of carbon dioxide the mole fraction of Ni seems to be higher. If comparing Figs. 2 and 3 it can be seen that the solubility of Ni is lower for Test-3, i.e. higher temperature, at gas compositions of carbon dioxide above 40%. This shows the same tendency for experimental solubility data of NiO in oxidising atmosphere obtained by Ota et al. [15]. For both Test-1 and Test-3 the data are scattered but a trend may be seen: an increased solubility with an increased fraction of carbon dioxide. However, since the Ni mole fraction is close to the detection limit for a carbon dioxide in the gas of less than 60% for Test-3, it is difficult to draw any conclusion about whether the Ni mole fraction continues to decrease with the decrease of the carbon dioxide in the gas.

The values found for the solubility of Ni in reducing atmosphere may be compared with those found for the dissolution of NiO in oxidising atmosphere at various contents of carbon dioxide. Fig. 4 shows a comparison of the solubility of the Ni–Al

Table 1  
Conditions for the different tests

Experiment	Gas composition	Humid temperature ( $^\circ C$ )	Temperature ( $^\circ C$ )	Addition to the electrolyte	Measured contents
Test-1	0–100% $CO_2$ balanced with $H_2$	48	560–580	Ni–Al alloy	Ni and Al
Test-2	100% $CO_2$	–	570	–	Al
Test-3	0–100% $CO_2$ balanced with $H_2$	48	609–611	Ni–Al alloy	Ni

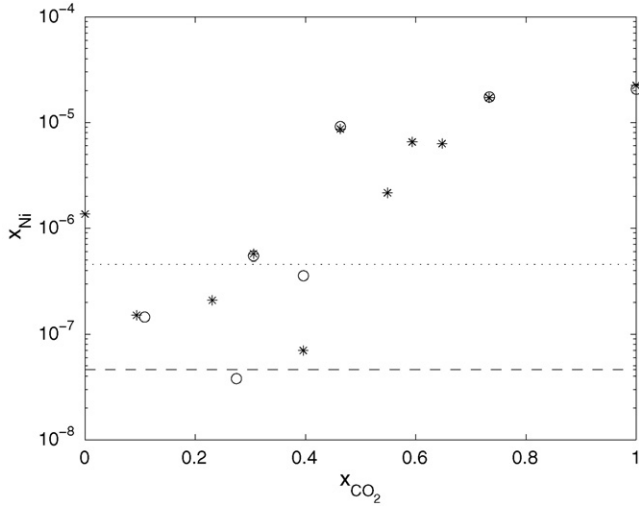


Fig. 2. Mole fraction of dissolved Ni from Test-1: (○) ICP measurement date 1, (\*) ICP measurement date 2, (- - -) detection limit for ICP measurement date 1, and (· · ·) detection limit for ICP measurement date 2.

alloy used in this study and the solubility of NiO in oxidising atmosphere found by others [6,11,14,15] at various contents of carbon dioxide. The solubility of Ni is lower in  $H_2/H_2O/CO_2$  atmosphere, at both 570 and 610 °C, than that of NiO in oxidising atmosphere at 650 °C. However, the solubility of Ni for Test-1 is in the same range as for NiO at a higher content of carbon dioxide.

For the oxidation of Ni:



the following two different reduction reactions are proposed. The first with  $CO_2$  as oxidant:

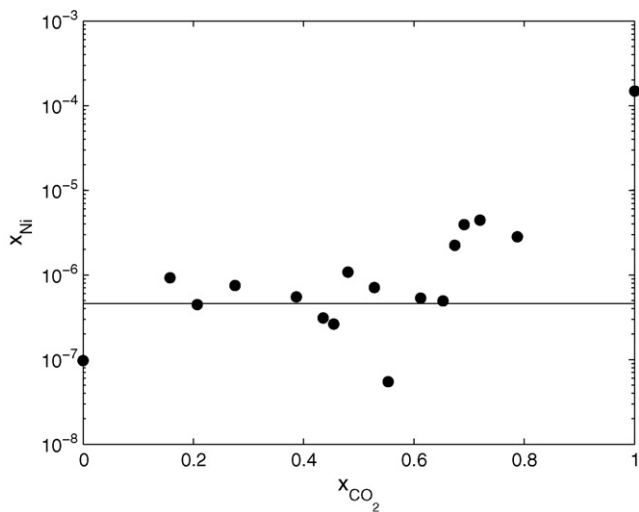
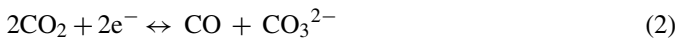


Fig. 3. Mole fraction of dissolved Ni from Test-3: (●) measured Ni mole fraction at various contents of carbon dioxide in gas and (—) detection limit for ICP measurement.

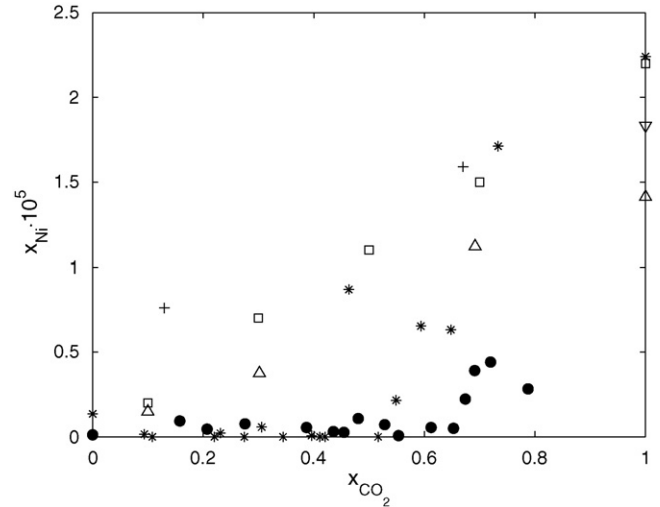
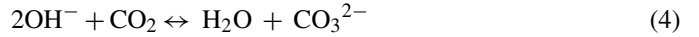


Fig. 4. Mole fraction of dissolved Ni for various mole fractions of carbon dioxide: (\*) Test-1, (●) Test-3, (□) NiO at 923 K [15], (Δ) NiO at 923 K [14], (+) NiO at 873 K [11], and (∇) NiO at 923 K [6].

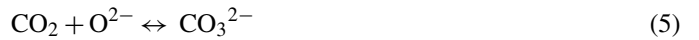
or the reduction of water:



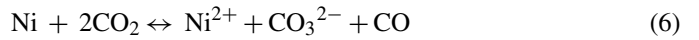
followed by the equilibrium reaction:



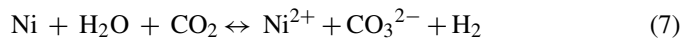
If the Ni is in dissolved state in the melt, as  $Ni^{2+}$ , or in solid form, as NiO, depends on the basicity of the melt given by the equilibrium of the following reaction:



It has been found that Ni can be oxidised by  $CO_2$  in an atmosphere of pure  $CO_2$  [8,9] by the sum of reactions (1) and (2):



In the case of a humidified mixture of  $H_2$  and  $CO_2$  the following reaction is possible for the dissolution, which is the reverse reaction of that proposed for Ni-shortening:



The equilibrium constant, assuming unit activity for Ni and the dissolved  $NiCO_3$ , may be written as

$$x_{Ni^{2+}} = S \frac{x_{H_2}}{x_{H_2O} \cdot x_{CO_2}} \quad (8)$$

The anode gas is usually a mixture containing hydrogen, water, carbon monoxide and carbon dioxide. The gas mixture has a thermodynamic equilibrium composition according to the water–gas shift reaction:



The inlet gas mixture may either be in equilibrium or in a non-equilibrium composition. The solubility constant may be calculated for the equilibrium gas composition according to the

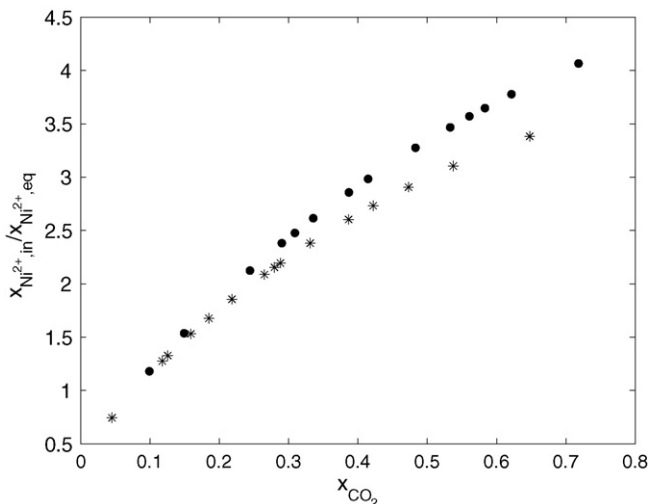


Fig. 5. The ratio between the reaction constant for reaction (7) if the gas is in equilibrium or at non-shifted inlet gas composition: (\*) Test-1 and (●) Test-3.

water–gas shift reaction for each inlet gas composition,  $x_{Ni^{2+},eq}$ , and for the actual measured (non-equilibrium) inlet gas compositions,  $x_{Ni^{2+},in}$ . Fig. 5 shows the ratio between the solubility constants for the actual inlet gas composition and for the equilibrium composition of the inlet gas, respectively.

As may be seen in Fig. 5 the solubility of Ni should be different if the inlet gas is in non-equilibrium according to the water–gas shift reaction compared to a gas mixture in equilibrium. If the gas is humidified the most probable reaction path for the dissolution of Ni–Al is through reactions (1), (3) and (4) rather than (1) and (2) due to the faster kinetics for the hydrogen reduction/oxidation than for the carbon monoxide reaction.

### 3.2. Aluminium dissolution

In Test-1 aluminium was found in the samples of electrolyte. The aluminium content is shown in Fig. 6 as a function of

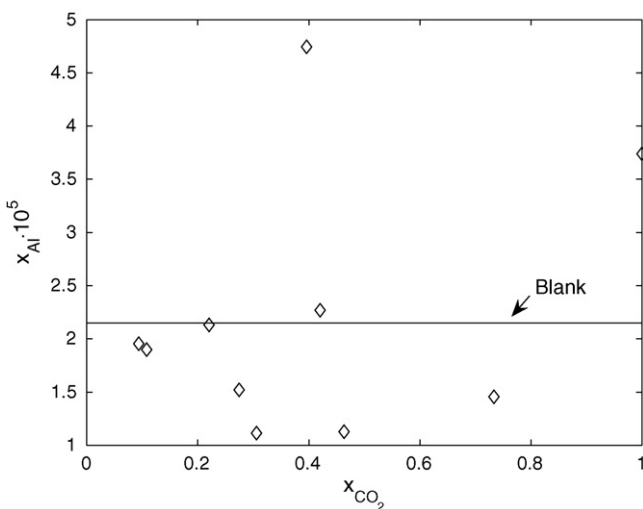


Fig. 6. Mole fraction of Al: (◇) the mole fraction of Al measured in Test-1 at various carbon dioxide contents of gas of and (—) the mole fraction of Al in Test-2.

the content of carbon dioxide in the gas. It was surprising to find since the content of Al in the electrode is low. In Fig. 6 the content of Al in the blank experiment, i.e. no Ni–Al alloy electrode was put into the melt, Test-2, is shown. Thus, this shows that if some of the aluminium dissolves from the electrode it cannot be distinguished from that originating from the crucible.

## 4. Conclusions

In this study the solubility of Ni at anode conditions in molten lithium/sodium carbonate has been studied experimentally. The results show that nickel can be dissolved also at the anode, indicating that the nickel solubility increases with increasing  $CO_2$  partial pressure of the inlet gas and decreases with increasing temperature. This shows the same tendency with the results found by other authors of the solubility of NiO at cathode conditions.

The dissolution of Ni into the melt can proceed in two ways, either by the reduction of water or the reduction of carbon dioxide. The most probable reaction mechanism is the reduction of water in mixed gas compositions due to much faster kinetics, due to the involvement of hydrogen.

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