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Electrode kinetics of the NiO porous electrode for oxygen production in the molten carbonate electrolysis cell (MCEC)

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The performance of a molten carbonate electrolysis cell (MCEC) is to a great extent determined by the anode, *i.e.* the oxygen production reaction at the porous NiO electrode. In this study, stationary polarization curves for the NiO electrode were measured under varying gas compositions and temperatures. The exchange current densities were calculated numerically from the slopes at low overpotential. Positive dependency on the exchange current density was found for the partial pressure of oxygen. When the temperature was increased in the range 600–650 °C, the reaction order of oxygen decreased from 0.97 to 0.80. However, there are two different cases for the partial pressure dependency of carbon dioxide within this temperature range: positive values, 0.09–0.30, for the reaction order at lower CO₂ concentration, and negative values, –0.26–0.01, with increasing CO₂ content. A comparison of theoretically obtained data indicates that the oxygen-producing reaction in MCEC could be reasonably satisfied by the reverse of oxygen reduction by the oxygen mechanism I, an $n = 4$ electron reaction, assuming a low coverage of oxide ions at high CO₂ content and an intermediate coverage for a low CO₂ concentration.

Introduction

There is a growing interest in high-temperature electrolysis cell technology for producing hydrogen and/or syngas, since these fuels are considered important for future energy systems. Electrolysis in molten carbonate salts at high temperature (typically 650 °C) is a promising option, especially when in combination with renewable electricity resources such as wind power and/or solar energy. Some researchers have evidenced the possibility of electrolysis in molten carbonates, but mainly by converting CO₂ into CO.^{1–4} However, most experiments were performed on flag electrodes, which differ from porous electrodes with regards to the electrode surface and mass-transport properties. Our previous study⁵ showed that it is feasible to run the molten carbonate fuel cell reversibly with conventional Ni-

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based porous electrodes at 650 °C. A lower polarization loss has been found for the electrolysis cell compared to the fuel cell, mainly due to the NiO electrode performing much better as an anode in MCEC mode.⁵ The activity of the NiO electrode provides a dominant contribution to the performance of the cell, regardless of fuel cell or electrolyzer operation. Thus, it is essential to elucidate the kinetics at the NiO porous electrode for oxygen reduction in the fuel cell, as well as for oxygen production in the electrolysis cell.

However, the kinetics and reaction mechanism at the NiO porous anode for oxygen production in MCEC mode are still unknown. A feasible path to overcome this is to understand whether the reversed process of oxygen reduction takes place at the NiO electrode or whether there are some other electrochemical/chemical reaction pathways in the electrolysis operation. Several reaction mechanisms for the oxygen reduction reaction in fuel cell mode have been discussed in the literature,^{6–12} see Table 1. The corresponding reaction orders of oxygen and carbon dioxide for these five mechanisms have been reported by Makkus¹³ for varying rate-determining steps (rds). According to Appleby and Nicholson,^{6–8} the peroxide (O_2^{2-}) mechanism was suggested for oxygen reduction in pure lithium

Table 1 Reaction mechanisms reported in the literature for oxygen reduction^{6–12}

The peroxide mechanism: $n = 2$

The superoxide mechanism: $n = 3$

The peroxycarbonate mechanism: $n = 2$

Oxygen mechanism I: $n = 4$

Oxygen mechanism II: $n = 2$

and lithium rich melts, while the superoxide (O_2^-) path seemed to be involved in sodium and potassium-rich melts. Dunks and Stelman⁹ and Takahashi¹⁰ proposed a mechanism based on the peroxycarbonate (CO_4^{2-}) ion. Kunz *et al.*¹¹ suggested oxygen mechanism I to evaluate the concept of the homogeneous/agglomerate model. Makkus *et al.*¹² discussed oxygen mechanism II for the thin-film model. All proposed mechanisms consist of two or more single electron transfer reactions. All five of these reaction mechanisms show the same final recombination step:

Kunz and Murphy,¹⁴ Lu and Selman,¹⁵ and Peelen *et al.*¹⁶ suggested that this recombination reaction is possibly the rate-determining step at the porous electrodes under MCFC conditions, due to the slow reaction rate.

In MCEC mode, the main electrochemical reaction taking place at the NiO porous electrode for oxygen production is the electrolysis of the carbonate ion (CO_3^{2-}).

Sugiura *et al.*¹⁷ suggested separation of CO_2 in a molten carbonate fuel cell (MCFC) device. One of the options suggested was to use reaction (2) as the anode reaction in the device.

This paper aims to study the kinetics and reaction mechanism at the NiO porous electrode for oxygen production in MCEC operation. For this purpose the general procedure is to determine the reaction orders of oxygen and carbon dioxide. Thus, steady-state polarization data are investigated for varying gas compositions and operating temperatures. The exchange current densities, which differ with the concentration of the electroactive species and the temperature, are calculated numerically from the slopes of the polarization curves at low overpotential. Based on this, the partial pressure dependencies of oxygen and carbon dioxide could be evaluated. Meanwhile, a possible reaction mechanism for oxygen production at the NiO porous electrode in MCEC mode is proposed.

Experimental

The cell set-up used in this study was identical to that described in a previous study.⁵ Experimental data were obtained from the laboratory cell unit with a geometrical area of 3 cm^2 , where the cell components were provided by Ansaldo Fuel Cells in Italy. The cell has a porous Ni anode, oxidized and lithiated *in situ*, and a porous Ni–Cr alloy as the cathode. The electrodes are separated by a porous LiAlO_2 matrix, which also supports the electrolyte, a eutectic mixture of 62/38 mol % $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$. The current collectors used on the NiO and Ni electrode sides are made of stainless steel SS316 and nickel, respectively. Two current collector probes each separately measure the current and the potential. Two reference electrodes, consisting of Au wires in equilibrium with a gas mixture of 33/67% O_2/CO_2 , are placed in separate chambers filled with the same electrolyte as that in the

Table 2 The inlet gas compositions, by percentage

Gas no.	O ₂ /%	CO ₂ /%	N ₂ /%
(1) Changing O₂			
1.1	1.5	30	68.5
1.2	2.5	30	67.5
1.3	5	30	65
1.4	10	30	60
1.5 ^a	15	30	55
1.6	20	30	50
1.7	25	30	45
1.8	30	30	40
(2) Changing CO₂			
2.1	15	2.5	82.5
2.2	15	5	80
2.3	15	10	75
2.4	15	15	70
2.5	15	20	65
2.6	15	25	60
2.7 ^a	15	30	55
2.8	15	35	50
2.9	15	40	45

^a The standard inlet gas, 15/30/55% O₂/CO₂/N₂.

cell. These chambers are connected to the cell through a capillary with a gold plug.

The cell is operated at three different temperatures, 600, 625 and 650 °C. The inlet fuel gas mixture consisting of 25/25/25/25% H₂/CO₂/H₂O/N₂ is introduced to the Ni electrode. The concentration of H₂O in the fuel gas is controlled by the temperature of the water in the humidifier, 65 °C. The different gas mixtures of O₂/CO₂/N₂ for the NiO electrode are shown in Table 2. The concentrations of oxygen and carbon dioxide are varied separately in group 1 and group 2. The O₂ and CO₂ partial pressures increase in the ranges 1.5–30% and 2.5–40%, respectively. In order to reduce the effects of mass-transfer limitations in the gaseous phase, the flow rates of the inlet gases for the NiO porous electrode are held at as high as approximately 250 ml min⁻¹. The gas flow rate for the Ni electrode is also about 250 ml min⁻¹, while the reference gas has a flow rate of 20 ml min⁻¹. All of the gases used in the experiments are certified gas mixtures from AGA Gas AB, Sweden.

The polarization curves are measured using a Solartron Interface SI1287 supported by CorrWare software. The current-interrupt technique is used to separate the ohmic loss from other types of polarization. In this paper, the negative current density refers to the electrolysis mode, as shown in the figures below.

Theory

Elucidating the kinetics and mechanism of reaction (2) is generally done by determining the partial pressure dependencies of oxygen and carbon dioxide. The

same method was used to understand the hydrogen production on the cathode side, the Ni electrode.¹⁸ When analyzing kinetic data it is important to consider the current distribution along the depth of the NiO electrode due to its porous characteristics.¹⁹ The current distribution is determined by a combination of the intrinsic electrode activity, its specific surface area, the effective diffusion path lengths of the electroactive species, and the effective conductivities of the electrolyte and electrode. In the present study the polarization data are analyzed only at a low overpotential range, where the electrode is assumed to be mainly under charge-transfer limitation and the influence of mass-transfer limitation is negligible. According to Lagergren and Simonsson,²⁰ in order to take the current distribution into account when analyzing data, the expression for the total polarization resistance is

$$\frac{d\eta}{di} = \frac{L}{k_1 + k_2} + \frac{L}{\sqrt{a}} \frac{1}{k_1 + k_2} \left[\frac{2}{\sinh \sqrt{a}} + \left(\frac{k_1}{k_2} + \frac{k_2}{k_1} \right) \coth \sqrt{a} \right] \quad (3)$$

where

$$a = \frac{nFL^2 Si_0}{RT} \left(\frac{1}{k_1} + \frac{1}{k_2} \right) \quad (4)$$

L is the electrode thickness and k_1 and k_2 are the effective conductivities in the electrode and electrolyte phases, respectively. S is the exterior agglomerate surface area.

There are two limiting cases of eqn (3), in which a approaches either zero or infinity. These two cases refer to uniform and uneven current distributions, respectively.

According to eqn (3), the ohmic loss, $\frac{L}{k_1 + k_2}$, due to the finite conductivities of the electrolyte and electrodes, is included in the total polarization resistance. In this study the current-interrupt technique is used to correct the iR drop, and therefore the experimentally obtained polarization data does not contain the ohmic contribution.

The partial pressure dependencies of oxygen and carbon dioxide can be expressed as

$$i_0 = i_0^0 (p_{O_2})^x (p_{CO_2})^y \quad (5)$$

where i_0^0 is the standard exchange current density, and x and y denote the reaction orders of oxygen and carbon dioxide, respectively.

Results and discussion

The iR -corrected polarization curves for different gas compositions at 650 °C are shown in Fig. 1. The blue curves in the figure correspond to the performance of the NiO electrode with the standard inlet gas 15/30/55% O₂/CO₂/N₂ in the electrolysis operation. The red symbols refer to gases with lower content than the standard level when changing O₂ and CO₂ partial pressures separately, while the green symbols refer to gases with higher concentrations. In Fig. 1(a) the polarization loss of the NiO electrode decreases gradually when increasing the

Fig. 1 iR-corrected polarization curves for the NiO electrode in electrolysis mode at 650 °C for different gas compositions, changing (a) O₂ and (b) CO₂ partial pressures.

concentration of O₂ from 1.5 to 30%. The polarization curves show a tendency to bend downward at high current densities, and under lower O₂ content that bending is observed even at low current density. It seems that mass-transfer limitation does not take place at high current density, as otherwise the curves would be bending upward. When increasing the CO₂ content in the range 2.5–20%, the activity of the NiO electrode shows a slow improvement in oxygen production at 650 °C, as shown in Fig. 1(b). However, with an increase in CO₂ content from 20 to 40%, only a very small impact on the polarization loss of the NiO electrode is observed also at high current density.

In order to more thoroughly analyze the polarization data, the electrochemical performance of the NiO electrode was investigated within a low overpotential range, <45 mV, at 600–650 °C. Varying the concentration of O₂ within the range 1.5–30% gives the quasi-linear characteristics of the iR-corrected curves at all measured temperatures, as visualized in Fig. 2. Increases in O₂ content improve the NiO electrode polarization performance for oxygen production in the electrolysis operation. However, the impact of CO₂ concentration on the polarization performance of the NiO electrode is strongly dependent on temperature, as shown in Fig. 3. At 600 °C, increasing the CO₂ content from 2.5 to 10% gives only a small improvement in the performance of the NiO electrode; in contrast, upon

Fig. 2 iR-corrected polarization curves at low overpotential for the NiO electrode in electrolysis mode for different percentages of O₂: (a) 600 °C, (b) 625 °C and (c) 650 °C.

increasing the CO₂ content to 40%, increasingly poorer behavior is observed for the electrode. In Fig. 3(b) the polarization loss of the NiO electrode decreases gradually as the CO₂ concentration rises from 2.5 to 15%, and it then shows very small increases in the electrode polarization with increasing CO₂ content in the range 15–40% at 625 °C. When reaching 650 °C, the NiO electrode has an improved activity for oxygen production in the range 2.5–20% CO₂ content, and

Fig. 3 iR-corrected polarization curves at low overpotential for the NiO electrode in electrolysis mode for different percentages of CO_2 : (a) $600\text{ }^\circ\text{C}$, (b) $625\text{ }^\circ\text{C}$ and (c) $650\text{ }^\circ\text{C}$.

the electrode performance remains almost stable within the partial pressure range 20–40%, as seen in Fig. 3(c). The carbon dioxide content affecting the performance of the NiO electrode for oxygen production varies with the temperature. It is assumed that in this low overpotential range the electrode is under kinetic control as it is not necessary to take mass-transfer limitations into consideration. All of the measured polarization curves are quasi-linear, and the

polarization resistances, $d\eta/di$, could thus be evaluated from the slopes of these curves by linear regression analysis.

The exchange current densities for each gas composition and temperature could be obtained by solving eqn (3). Parameter values used for solving eqn (3) are listed in Table 3. It is assumed that the NiO electrode has a pseudo-homogeneous structure and that the electrode reaction takes place mainly at the exterior surface of the agglomerates.¹⁹ Assuming that the agglomerates are spherical and have a radius of 5 μm , the external agglomerate area, S , is estimated to be $3 \times 10^5 \text{ m}^{-1}$.¹⁹ The effective conductivity of the porous NiO electrode is in the order of 1000 S m^{-1} .^{20,21} The effective conductivity in the pore electrolyte was measured to be $0.9\text{--}2.2 \text{ S m}^{-1}$ at 650°C .²² Thus, in this work the effective electrolyte conductivity at 650°C was set to be 2.0 S m^{-1} , from which values of 1.7 S m^{-1} and 1.8 S m^{-1} were calculated for 600 and 625°C , respectively, using the Arrhenius equation.²³ The exchange current density i_0 for the standard inlet gas, $15/30/55\% \text{ O}_2/\text{CO}_2/\text{N}_2$ (1.5^* and 2.7^* in Table 4), shows an increase from 4.0 to 22.7 A m^{-2} when the temperature is raised from 600 to 650°C . The value of i_0 for oxygen production in the electrolysis cell is in the same order of magnitude as that for oxygen reduction at the NiO porous electrode in fuel cell mode (22.4 A m^{-2} at 650°C).¹⁹

A striking feature of Table 4 is that the exchange current density increases with the oxygen partial pressure when the NiO electrode is used as the anode in MCEC mode. The values are in the range $0.5\text{--}8.6$, $1.9\text{--}25.0$ and $3.8\text{--}41.4 \text{ A m}^{-2}$ at 600 , 625 and 650°C , respectively. However, concerning the carbon dioxide partial pressure, the exchange current density should be analyzed at low content and at higher concentration. For example, the exchange current density increases slightly from 5.0 to 5.7 A m^{-2} in the range $2.5\text{--}10\% \text{ CO}_2$ at 600°C . The value then shows a slow decrease to 4.1 A m^{-2} as the CO_2 concentration reaches 40% . The content of carbon dioxide affects the exchange current density differently for different operating temperatures, corresponding with the results of the polarization data discussed above. At 625°C , at CO_2 partial pressures of $2.5\text{--}15\%$, the exchange current density increases from 8.1 to 12.4 A m^{-2} ; quite a small decrease in the value, to $12.4\text{--}11.6 \text{ A m}^{-2}$, is then observed for $15\text{--}40\% \text{ CO}_2$ content. As the cell temperature goes to 650°C , the values of i_0 increase from 12.5 to 22.8 A m^{-2} with increasing CO_2 concentration from 2.5 to 20% , but then the data remain almost stable within the CO_2 range $20\text{--}40\%$. The exchange current density is not as strongly affected by the partial pressure of carbon dioxide as by that of oxygen. This indicates that carbon dioxide may have a smaller impact on the charge-transfer polarization of the electrode, since the exchange current density reflects the rate of the charge transfer.

Table 3 Parameter values used when solving eqn (3)

		600 °C	625 °C	650 °C
L	0.6 mm			
r	5 μm			
S	$3 \times 10^5 \text{ m}^{-1}$			
n	4			
k_1	1000 S m^{-1}			
k_2		1.7 S m^{-1}	1.8 S m^{-1}	2.0 S m^{-1}

Table 4 Experimentally obtained exchange current densities at different gas compositions and temperatures

Gas no.	$i_0/\text{A m}^{-2}$ 600 °C	$i_0/\text{A m}^{-2}$ 625 °C	$i_0/\text{A m}^{-2}$ 650 °C
(1) Changing O₂			
1.1	0.5	1.9	3.8
1.2	0.8	2.6	5.4
1.3	1.3	4.6	8.9
1.4	2.6	7.9	15.4
1.5*	4.0	12.0	21.6
1.6	5.9	16.5	29.2
1.7	7.3	20.8	35.2
1.8	8.6	25.0	41.4
(2) Changing CO₂			
2.1	5.0	8.1	12.5
2.2	5.4	9.7	15.0
2.3	5.7	11.8	19.7
2.4	5.5	12.4	21.4
2.5	5.1	12.4	22.8
2.6	4.6	12.2	22.6
2.7*	4.2	11.9	22.7
2.8	4.2	11.9	23.2
2.9	4.1	11.6	22.7

The reaction orders of oxygen and carbon dioxide at 600–650 °C are determined in Fig. 4 and 5. The linear regression results show that the oxygen partial pressure dependency decreases from 0.97 to 0.80 in the temperature range 600–650 °C. However, the dependency of the exchange current density on the carbon dioxide partial pressure shows two cases, as in Fig. 5. At lower CO₂ concentration, the reaction order of carbon dioxide gives positive values at all measured temperatures, and this then changes to negative values when increasing the CO₂

Fig. 4 Effect of oxygen partial pressure on the exchange current density, from 600 to 650 °C.

content. Specifically, at 600 °C the reaction order of carbon dioxide is 0.09 within the CO₂ content range 2.5–10%, and it becomes negative, −0.26, for 10–40% CO₂ content. In contrast to oxygen, the carbon dioxide partial pressure dependency increases with temperature. For 2.5–15% CO₂ content at 625 °C, the value of the reaction order is 0.25, and this becomes −0.07 within the concentration range 15–40% CO₂. When reaching 650 °C, the reaction order increases to 0.30 for 2.5–20% CO₂ content. The value then changes to 0.01 when increasing the CO₂ concentration to 40%. Thus, for all the measured temperatures from 600 to 650 °C, for a low concentration of CO₂, eqn (5) can be expressed as

$$i_0 = i_0^0(p_{\text{O}_2})^{0.97-0.80}(p_{\text{CO}_2})^{0.09-0.30} \quad (6)$$

and for high CO₂ content it could be expressed as

$$i_0 = i_0^0(p_{\text{O}_2})^{0.97-0.80}(p_{\text{CO}_2})^{-0.26-0.01} \quad (7)$$

As discussed above, the partial pressure dependencies obtained in this study are remarkably higher for oxygen than for carbon dioxide. The following reaction paths could probably be the mechanism for the oxygen production reaction in a molten carbonate electrolysis cell, on the basis of the reversed process of oxygen reduction in fuel cell operation (oxygen mechanism I) proposed by Kunz *et al.*¹¹

Fig. 5 Effect of carbon dioxide partial pressure on the exchange current density, from 600 to 650 °C.

It is assumed that (i) oxygen evolution reaction (12) is the rate-determining step and (ii) there is a low coverage of oxide ion. Assuming the symmetry factor $\beta = 0.5$ for the rate-determining step, the theoretical dependency of i_0 on the gas partial pressure is calculated in detail in the Appendix and is shown as

$$i_0 = i_0^0 (p_{\text{O}_2})^{0.875} (p_{\text{CO}_2})^{-0.25} \quad (13)$$

The theoretical reaction order is 0.875 for oxygen, satisfying the oxygen partial pressure dependency (0.97–0.80) determined from the experimental data. The theoretical value of -0.25 for carbon dioxide could reasonably fit the reaction order at high CO_2 concentration, as shown in eqn (7). However, it does not show agreement with the positive dependency at low CO_2 content. If assuming that the oxygen production is the reversed process of oxygen reduction in molten carbonate salts, the theoretical partial pressure dependencies for oxygen and carbon dioxide would be the same in both fuel cell and electrolyzer operations. Makkus¹³ reported the values of the reaction orders for all of the reaction mechanisms for oxygen reduction mentioned in Table 1. According to Makkus, the exchange current density with a high coverage of O^{2-} can be expressed as

$$i_0 = i_0^0 (p_{\text{O}_2})^{0.875} (p_{\text{CO}_2})^{0.75} \quad (14)$$

The partial pressure dependency of carbon dioxide, y , could be affected by the chemical decomposition of CO_3^{2-} , producing O^{2-} and CO_2 . For example, the reaction order is stable at 0.875 for oxygen and the value changes from negative (-0.25) to positive (0.75) for carbon dioxide when containing a high coverage of O^{2-} , see eqn (14). Upon lowering the carbon dioxide partial pressure, it makes sense from the perspective of chemical kinetics that the homogeneous reaction ($\text{CO}_3^{2-} \rightleftharpoons \text{O}^{2-} + \text{CO}_2$) will progress to produce the oxide ion. However, the theoretical value of 0.75 is still much higher than the experimental result (0.09–0.30), which indicates that reaction steps (8)–(12) with an intermediate coverage of O^{2-} could constitute a possible mechanism for oxygen production on the NiO porous electrode at a low CO_2 concentration.

The activation energy for the NiO electrode could be calculated by the Arrhenius equation, see Table 5.

$$E_a = -2.303R \frac{d(\log i_0)}{d(1/T)} \quad (15)$$

For oxygen production at the NiO electrode in MCEC mode with the standard gas, 15/30/55% $\text{O}_2/\text{CO}_2/\text{N}_2$, the value of the activation energy is $226 \pm 1 \text{ kJ mol}^{-1}$, which is in the same range as for oxygen reduction in fuel cell operation.²⁴ The calculated activation energy lies between 278 and 211 kJ mol^{-1} when increasing the O_2 concentration from 1.5 to 30%, but it increases from 124 to 229 kJ mol^{-1} when varying the CO_2 content from 2.5 to 40%. Gas compositions of low O_2 partial pressure, e.g. 1.5–10% O_2 , exhibit much larger activation energies than those with low CO_2 partial pressure, which means that oxygen appears to have a stronger effect on charge-transfer limitation. This is also evidenced by the higher reaction order values obtained for oxygen compared to carbon dioxide. As the activation energy is a clue in determining the rate-determining process,²⁵ it is probable that

Table 5 Calculation of the activation energy for the NiO electrode at different gas compositions

Gas no.	O ₂ /%	CO ₂ /%	N ₂ /%	E _a /kJ mol ⁻¹
(1) Changing O₂				
1.1	1.5	30	68.5	278.3
1.2	2.5	30	67.5	258.5
1.3	5	30	65	254.3
1.4	10	30	60	238.7
1.5*	15	30	55	225.1
1.6	20	30	50	214.7
1.7	25	30	45	211.1
1.8	30	30	40	211.2
(2) Changing CO₂				
2.1	15	2.5	82.5	123.6
2.2	15	5	80	138.3
2.3	15	10	75	167.6
2.4	15	15	70	183.5
2.5	15	20	65	202.6
2.6	15	25	60	214.4
2.7*	15	30	55	226.5
2.8	15	35	50	229.0
2.9	15	40	45	229.3

the NiO electrode is under mixed control at quite low CO₂ concentrations, and is then limited by charge-transfer at high CO₂ concentrations. This confirms that at low CO₂ partial pressure, the reaction $\text{CO}_3^{2-} \rightleftharpoons \text{O}^{2-} + \text{CO}_2$ plays an important role in oxygen production in MCEC mode.

Conclusions

Stationary polarization data have been studied for the NiO electrode, as the anode in an electrolyzer, under varying gas compositions and temperatures. The slopes of the polarization curves at a low overpotential range were analyzed, while assuming the electrode to be under kinetic control.

The partial pressure dependencies on the exchange current density lie between 0.97 and 0.80 for oxygen in the temperature range 600–650 °C. There are two cases for the reaction order of carbon dioxide, positive values of 0.09–0.30 at low CO₂ concentration and then negative dependency (–0.26–0.01) with high CO₂ content.

The reverse process of oxygen reduction in MCFC operation, based on oxygen mechanism I, was found to suitably describe oxygen production in the electrolyzer. The theoretical reaction orders were 0.875 for oxygen and –0.25 for carbon dioxide under the assumption of a low coverage of the oxide ion. Due to the reaction $\text{CO}_3^{2-} \rightleftharpoons \text{O}^{2-} + \text{CO}_2$, the coverage of O^{2–} is dependent on the carbon dioxide concentration. For a high coverage of O^{2–}, the theoretical dependency changed to 0.75 for CO₂. Thus, according to this study, an intermediate coverage of the oxide ion might be achieved at low CO₂ content.

The activation energy of the NiO porous electrode for oxygen production lies between 278 and 211 kJ mol⁻¹ for increasing O₂ content. In contrast, the values

increased in the range 124–229 kJ mol⁻¹ when increasing the CO₂ concentration. This indicates that the NiO electrode for oxygen production is generally under charge-transfer limitation, except at very low CO₂ partial pressure where it is under mixed control.

Appendix

Determination of reaction order

The reaction mechanism for oxygen production in a molten carbonate electrolysis cell follows

For this mechanism it is assumed that (i) reaction (A-5) is the rate-determining step and (ii) there is a low coverage of the oxide ion.

At equilibrium, reaction (A-1) can be written

$$k_{1a}(1 - \theta)C_{\text{CO}_3^{2-}} = k_{1c}\theta C_{\text{CO}_2} \quad (\text{A-6})$$

where θ is the coverage of the oxide ion (O²⁻).

Assuming a low coverage of O²⁻, $(1 - \theta) \sim 1$. From eqn (A-6) the fraction of θ is

$$\theta = \frac{k_{1a}}{k_{1c}} \frac{C_{\text{CO}_3^{2-}}}{C_{\text{CO}_2}} \quad (\text{A-7})$$

The net current from reaction (A-2) is

$$i_2 = F\{k_{2a}\theta e^{\beta_2 FE/RT} - k_{2c}(1 - \theta)C_{(\text{O}^-)}e^{-(1-\beta_2)FE/RT}\} \quad (\text{A-8})$$

E is the potential difference between the electrode and the electrolyte. At equilibrium, when $i_0 = 0$

$$C_{(\text{O}^-)} = \frac{k_{1a}}{k_{1c}} \frac{k_{2a}}{k_{2c}} \frac{C_{\text{CO}_3^{2-}}}{C_{\text{CO}_2}} e^{FE/RT} \quad (\text{A-9})$$

For reaction (A-3) the net current is

$$i_3 = F\{k_{3a}\theta C_{(\text{O}^-)}e^{\beta_3 FE/RT} - k_{3c}(1 - \theta)C_{\text{O}_2^{2-}}e^{-(1-\beta_3)FE/RT}\} \quad (\text{A-10})$$

When $i_3 = 0$ at equilibrium,

$$C_{O_2^{2-}} = \left(\frac{k_{1a}}{k_{1c}} \right)^2 \frac{k_{2a}}{k_{2c}} \frac{k_{3a}}{k_{3c}} \left(\frac{C_{CO_3^{2-}}}{C_{CO_2}} \right)^2 e^{2FE/RT} \quad (A-11)$$

The net current for reaction (A-4) is

$$i_4 = F \{ k_{4a} C_{O_2^{2-}} e^{\beta_4 FE/RT} - k_{4c} C_{O_2} e^{-(1-\beta_4) FE/RT} \} \quad (A-12)$$

At equilibrium, when $i_4 = 0$

$$C_{O_2^{2-}} = \left(\frac{k_{1a}}{k_{1c}} \right)^2 \frac{k_{2a}}{k_{2c}} \frac{k_{3a}}{k_{3c}} \frac{k_{4a}}{k_{4c}} \left(\frac{C_{CO_3^{2-}}}{C_{CO_2}} \right)^2 e^{3FE/RT} \quad (A-13)$$

For reaction (A-5) the net current is

$$i_5 = F \{ k_{5a} C_{O_2} e^{\beta_5 FE/RT} - k_{5c} C_{O_2} e^{-(1-\beta_5) FE/RT} \} \quad (A-14)$$

Reaction (A-5) is assumed to be the rate-determining step, the equilibrium expression of eqn (A-14) for the equilibrium potential E^0 upon substitution for $C_{O_2^{2-}}$ from eqn (A-13)

$$e^{FE^0/RT} = \left[\left(\frac{k_{1a}}{k_{1c}} \right)^2 \frac{k_{2a}}{k_{2c}} \frac{k_{3a}}{k_{3c}} \frac{k_{4a}}{k_{4c}} \frac{k_{5c}}{k_{5a}} \left(\frac{C_{CO_2}}{C_{CO_3^{2-}}} \right)^2 C_{O_2} \right]^{\frac{1}{4}} \quad (A-15)$$

Replacing $E = E^0 + \eta$, where η is the overpotential, in eqn (A-14), the following can be obtained

$$i_5 = F \left\{ k_{5a} \left[\left(\frac{k_{1a}}{k_{1c}} \right)^{\frac{1-\beta_5}{2}} \left(\frac{k_{2a}}{k_{2c}} \frac{k_{3a}}{k_{3c}} \frac{k_{4a}}{k_{4c}} \right)^{\frac{1-\beta_5}{4}} \left(\frac{k_{5a}}{k_{5c}} \right)^{-\frac{3+\beta_5}{4}} C_{CO_3^{2-}}^{\frac{1-\beta_5}{2}} C_{O_2}^{\frac{3+\beta_5}{4}} C_{CO_2}^{\frac{\beta_5-1}{2}} e^{(3+\beta_5)F\eta/RT} \right] \right. \\ \left. - k_{5c} \left[\left(\frac{k_{1a}}{k_{1c}} \right)^{\frac{1-\beta_5}{2}} \left(\frac{k_{2a}}{k_{2c}} \frac{k_{3a}}{k_{3c}} \frac{k_{4a}}{k_{4c}} \right)^{\frac{1-\beta_5}{4}} \left(\frac{k_{5a}}{k_{5c}} \right)^{\frac{1-\beta_5}{4}} C_{CO_3^{2-}}^{\frac{1-\beta_5}{2}} C_{O_2}^{\frac{3+\beta_5}{4}} C_{CO_2}^{\frac{\beta_5-1}{2}} e^{-(1-\beta_5)F\eta/RT} \right] \right\} \quad (A-16)$$

Eqn (A-16) may be compared with the general relationship for activation polarization according to the Butler-Volmer equation

$$i = i_0 [e^{\alpha_a \eta F/RT} - e^{-\alpha_c \eta F/RT}] \quad (A-17)$$

The exchange current density may be written as

$$i_0 = i_0^0 (C_{O_2})^{\frac{3+\beta_5}{4}} (C_{CO_2})^{\frac{\beta_5-1}{2}} \quad (A-18)$$

where

$$i_0^0 = \left(\frac{k_{1a}}{k_{1c}}\right)^{\frac{1-\beta_5}{2}} \left(\frac{k_{2a}}{k_{2c}} \frac{k_{3a}}{k_{3c}} \frac{k_{4a}}{k_{4c}}\right)^{\frac{1-\beta_5}{4}} \frac{(k_{5a})^{\frac{1-\beta_5}{4}}}{(k_{5c})^{\frac{3+\beta_5}{4}}} C_{\text{CO}_3^{2-}}^{\frac{1-\beta_5}{2}} \quad (\text{A-19})$$

We obtain $\alpha_A = 3 + \beta_5$, assuming the symmetry factor $\beta_5 = 0.5$, so $\alpha_A = 3.5$ and $\alpha_c = 1 - \beta_5 = 0.5$.

The dependency of i_0 on the gas partial pressure (for $\beta_5 = 0.5$) is

$$i_0 = i_0^0 (p_{\text{O}_2})^{0.875} (p_{\text{CO}_2})^{-0.25} \quad (\text{A-20})$$

List of symbols

F	Faraday's number, C mol^{-1}
i	Current density, A m^{-2}
i_0	Exchange current density, A m^{-2}
i_0^0	Standard exchange current density, A m^{-2}
L	Electrode thickness, m
n	Number of electrons
p	Partial pressure, atm
R	Gas constant, $\text{J mol}^{-1} \text{K}^{-1}$
S	Specific surface area, m^{-1}
T	Temperature, K
x	Partial pressure dependency of oxygen in MCEC mode
y	Partial pressure dependency of carbon dioxide in MCEC mode

Greek letters

α_A	Anodic transfer coefficient
α_c	Cathodic transfer coefficient
β	Symmetry factor
k_1	Effective conductivity of the electrode, S m^{-1}
k_2	Effective conductivity of the electrolyte, S m^{-1}
η	Overpotential, V

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