ELECTROCHEMICAL OXIDATION OF CO IN A CO-CO2 SYSTEM AT THE INTERFACE OF Ni GRID ELECTRODE/YSZ ELECTROLYTE

F. Z. Boulenouar, K. Yashiro, M. Oishi, A. Kaimai, Y. Nigara, T. Kawada, J. Mizusaki
Research Institute for Scientific Measurements (RISM), Tohoku University
2-1-1 Katahira, Aoba-Ku, Sendai, 980.8577, Japan

ABSTRACT

The electrochemical oxidation of CO at a nickel grid electrode on YSZ single crystal electrolyte in a mixture of CO-CO2-Ar was studied by means of electrochemical impedance spectroscopy at 850°C. At open circuit potential, the shape of the impedance spectra was dependent on the ratio of partial pressure of CO2 to CO in the gas mixture. At high PCO2/PCO ratio (high PO2), the impedance diagram revealed at least two relaxation times whereas, it exhibited a simplest shape when the PCO2/PCO ratio was low (low PO2). Impedance spectra were modelled using an equivalent circuit describing the involvement of two adsorbed species during the oxidation of CO. The interface conductivity, \( \sigma_p \), value was dependent on both CO and CO2 partial pressures in the mixture. All these observations led us to suggest that CO, O, and CO2 participate in the reaction mechanism where CO and O are in adsorbed form.

INTRODUCTION

The use of methane as a fuel in SOFCs offers many advantages including lower cost and lower storage pressure. However, the thermal decomposition of methane at high temperatures causes deterioration of the anode by coking. In order to reduce the coking formation in SOFCs, methane is co-fed with water, forming CO and H2. Nevertheless, the electrocatalytic activity of the anode towards these species still needs to be improved in order to minimise the problem of further coke formation. For that reason, the electrochemical reaction mechanism involving CO and H2 requires separate studies. While hydrogen oxidation has been deeply investigated by several authors (1,2,3 and references therein), little attention has been given to CO oxidation. Most of the works on CO-CO2 system were done on noble metals (4,5,6,7,8).

Setoguchi et al. (9) found that the anodic polarisation conductivity of the Ni-YSZ cermet /YSZ electrolyte interface was strongly dependent on oxygen partial pressure, PO2, in the fuel, but was independent of the kind of the fuel (H2-H2O, CO-CO2, CH4-H2O). The authors therefore suggested that activation of oxygen ion appears to be the rate limiting step in the overall reaction. Lauvstad et al. (10) have investigated by means of impedance spectroscopy the electrochemical oxidation CO at a Ni point electrode. The authors concluded that the reaction mechanism involves at least two adsorbed species
namely oxygen and CO. Aaberg et al. (11) found that the variation of the interfacial conductivity exhibits a maximum at around 45% CO in CO₂ and proposed the same mechanism postulated by Etsell and Flengas (4) which suggests that both CO and CO₂ are directly involved in the electrochemical step.

All the works cited above have been conducted by varying simultaneously the partial pressures of CO and CO₂. In this study the influences of partial pressures of CO and CO₂ on the electrochemical oxidation of CO on the nickel grid /YSZ single crystal interface were evaluated under the condition of one of the partial pressures of the two gaseous reactant is kept constant. The study was carried out by impedance spectroscopy measurements at open circuit potential at 850°C.

EXPERIMENTAL

The electrochemical cell was set in three-electrode, four- wire system as shown in Fig. 1. The working electrode was a nickel grid (Nisshin EN.Co, Ltd Tokyo) of 400 mesh/inch, 3 mm in diameter x 15μm in thickness. It was prepared on a (110) surface of a single crystalline 8YSZ pellet (Crystec KRISTALLTECHNOLOGIE) (10 x 3 mm) by annealing at 1400°C for 1 hour in a reducing gas atmosphere of H₂-Ar. The adherence of the working electrode to the surface of the electrolyte was checked by optical microscope taken from the counter side. Two Pt wires (current supply and potential probe) were spot-welded to a nickel wire current collector attached to each electrode. A platinum wire wound laterally around the YSZ disk with Pt paste (Tanaka Kinkinzuko, TR 7905) served as the reference electrode. The counter electrode was painted on the electrolyte using the same platinum paste.

Air at 1 atm was supplied to the cathode compartment. In the anode compartment mixtures of CO-CO₂-Ar were used at 1 atm, in a total flow of 100ml/mn and at a temperature of 850°C. By considering the thermodynamical data, the CO/CO₂ ratio and the partial pressures of CO and CO₂ were carefully selected to avoid the electrode oxidation and the carbon deposition. In the first place, CO₂ partial pressure was kept constant at PCO₂=0.1 atm and the CO partial pressure was changed from 0.01 atm to 0.9 atm by mixing with Ar as a balancing gas. Then the CO partial pressure was kept constant at PCO=0.2 atm while PCO₂ was varied from 0.01 atm to PCO₂=0.8 atm.

Electrochemical impedance measurements were carried out with a frequency response analyser 5080 (NF electronic instruments) connected to a potentiostat/galvanostat 2000 (Toho Technical Research) both controlled by a personal computer NEC /PC - 9801 RA. The applied ac-voltage between the working and the reference electrode was 5 mV RMS in the frequency range from 1 MHz to 1 mHz and 11 points per decade were measured at decreasing frequency. Modelling of the experimental data was performed using the non-linear least squares minimisation program developed by B. A. Boukamp (12).
RESULTS AND DISCUSSION

In general all spectra obtained at open circuit potential resembled more or less to the one shown in Fig. 2. This impedance diagram recorded for the CO-CO₂ system at PCO₂=0.06 atm and PCO=0.2 atm, consists of at least two time constants that are overlapped. At low frequencies, the data are scattered, this is because the system is unstable in this frequency domain. A small inductive effect was observed in the very high frequency region, this phenomenon is due to the contribution of the leads.

In order to investigate the variation of the interfacial conductivity, σp with PCO and PCO₂, it is necessary to know the total polarisation resistance, Rp, which represents the interfacial response. The total electrode resistance can be determined accurately by modelling the experimental results to an electrical equivalent circuit, which represents the simpler mathematical approximation of the interface.

The equivalent circuit that was found to describe adequately and most closely, the impedance diagrams is reported in Fig. 3. A similar equivalent circuit was used by Van Hassel et al. (13) and Lauvstad et al. (10) for the Au, O₂(gas)/YSZ and Ni, CO-CO₂(gases) /YSZ systems, respectively. It represents a reaction mechanism involving two adsorbed species. Rₜ is the resistance originating from the electrolyte and leads, and Rₜₑ is the charge transfer resistance. The two parallel C₁R₁ and C₂R₂ are resistance and capacitance that represent concentration impedance. These elements include the interaction between all processes involving two adsorbed species i.e. adsorption, desorption, charge transfer reaction and possibly chemical reactions between the adsorbed species. Q is the constant phase element (CPE). The constant phase element is frequently observed in electrochemical systems. According to Brug et al. (14) the CPE is generally believed to originate from inhomogeneities of the interfacial capacitance. The dispersion relation for a constant phase element (CPE) is expressed by:

\[ Z(\text{CPE}) = \frac{1}{Q(j\omega)^n} \]  

where \( j \) is the imaginary number (\( j^2=-1 \)), \( Q \) is a constant, \( \omega \) is the angular frequency and the factor \( n \) is an adjustable parameter that usually lies between 0.5 and 1. The CPE describes an ideal capacitor when \( n=1 \).

A comparison of the simulated and the experimental Nyquist plots is shown in Fig. 4. The impedance spectra shown on this figure were corrected from the inductance, which is in the order of \( 10^{-6} \) H. As can be seen from this figure, the measured and simulated data are in good agreement.

In the first instance, let us consider the total polarisation resistance calculated using the fitting results. The interface conductivity, \( \sigma_p \), can thus be expressed using the following equation:

\[ \sigma_p = \frac{1}{SR_p} \]  

where \( S \) is the apparent electrode area, and \( R_p \) corresponds to the faradaic impedance.
when the frequency tends to 0, which gives:

\[ R_p = R_{ct} + R_i + R_2 \]  \[3\]

The dependence of \( \sigma_p \) with the partial pressures of CO and CO\(_2\) are shown in Fig. 5 and 6, respectively. It appears that the reaction order with respect to CO\(_2\) is nearly 1/2 over the whole range of partial pressure investigated. Whereas, the dependence of \( \sigma_p \) on CO exhibits a complicated behaviour, \( \sigma_p \) has a more or less a constant value in the PCO range from 0.04 to 0.3 atm. At PCO lower than 0.04 the dependency could not be determined accurately because of lack of measurement points. Whereas at PCO higher than 0.3 the dependency of \( \sigma_p \) is equal to 1/2. If considering the whole range of PCO, then the slope of the plot gives a reaction order in respect to PCO equal to approximately 1/4.

On the other hand, on Fig. 7 are plotted the variation of the interface conductivity as a function of the oxygen partial pressure PO\(_2\) in the CO-CO\(_2\)-Ar mixture. PO\(_2\) was calculated from the equilibrium:

\[ P_{o2} = K P_{CO2}^2 / P_{CO}^2 \]  \[4\]

where \( K \) is the equilibrium constant.

As plainly seen from Fig. 7, \( \sigma_p \) has a different dependency on PO\(_2\) depending on which gas is kept constant. At constant PCO the interfacial conductivity is dependent on PO\(_2\) to the power 1/4 in the whole range of PCO\(_2\) investigated. However, for PCO\(_2\) constant and PCO variable, the interfacial conductivity can be considered almost constant from PO\(_2\)=7 10\(^{-19}\) atm to PO\(_2\)=4 10\(^{-17}\) atm. At PO\(_2\) lower than this domain, \( \sigma_p \) depends on PO\(_2\) to power -1/4. The two plots intercept for a value of PO\(_2\) which corresponds to PCO=PCO\(_2\). It is difficult to conclude about the nature of the dependency of \( \sigma_p \) on PO\(_2\) since it is not possible to change one parameter and keep the two others constant.

The variation of the shape of the impedance spectra with the gas composition is also illustrated in Fig. 4. It can be seen that the spectrum looks like a depressed semicircle under low PCO when PCO\(_2\) is kept constant, and also at high PCO\(_2\) for constant PCO. Both conditions correspond to a high PO\(_2\). On the other hand, the diagram consists of at least two time constants when PCO is high under constant PCO\(_2\), and also for low PCO\(_2\) at constant PCO that is corresponding to low PO\(_2\). The above distinctive changes in the appearance of the impedance diagrams with PO\(_2\) suggest that oxygen species are involved in the rate determining step (and possibly steps).

Considering the variation of \( \sigma_p \) with PCO, PCO\(_2\) and PO\(_2\), and also the evolution of the shape of the impedance spectra with PO\(_2\), the two adsorbed species considered in the proposed equivalent circuit (Fig. 3) may be identified as atomic oxygen adsorbed on the electrode or the electrolyte surface near the three phase boundary (TPB) line where the electrochemical reaction is supposed to take place. The other adsorbed species to be considered is CO on nickel electrode near TPB. This would be logical since CO\(_2\) can not adsorb (4).
According to (13,15), among the elements describing the reaction at the electrode, the charge transfer resistance $R_{ct}$ is the only parameter that is well defined with respect to a single physical process. However, $C_1 R_1$ and $C_2 R_2$ represent the interaction between all processes involving the adsorbed species (in this case two adsorbed species), i.e. adsorption, desorption, charge transfer reaction and possibly chemical reactions between the adsorbed species. $R_e$ and $Q_{dl}$, as described above are not related to the faradaic process.

$R_e$ was found as expected independent of the partial pressure of the gases CO and CO$_2$. The constant phase element $Q_{dl}$ was interpreted as an apparent double layer capacitance since its exponent, $n$, was found equal to 0.90 ± 0.02.

The variations of $R_{ct}$ versus PCO and PCO$_2$, are illustrated in Fig. 8a and Fig. 8b, together with the total polarisation resistance. $R_{ct}$ represents a non-negligible part of the total resistance especially at low partial pressures of CO and CO$_2$. At higher partial pressures its influence becomes less apparent, notably for high PCO$_2$.

More investigations are needed in order to further improve our understanding of the reaction mechanism involved during the oxidation of CO. Studies such as steady state polarisation measurements and impedance spectroscopy measurements under polarisation for various gas composition and temperature would be very helpful for that purpose.

**CONCLUSIONS**

In this study the influences of partial pressures of CO and CO$_2$ on the electrochemical oxidation of CO on the nickel grid /YSZ single crystal interface were investigated under the condition of one of the partial pressures of the two gaseous reactant is kept constant. The study was carried out by impedance spectroscopy measurements at open circuit potential at 850°C. The shape of the impedance spectra was dependent on the ratio of partial pressure of CO$_2$ to CO in the gas mixture. At high PCO$_2$/PCO ratio, the impedance diagram demonstrated at least two relaxation times. When the PCO$_2$/PCO ratio was low, it exhibited a simplest shape. Impedance spectra were modelled using an equivalent circuit approach. The equivalent circuit was based on a reaction mechanism including two adsorbed species during the oxidation of CO. The interface conductivity, $\sigma_p$, value was dependent on both CO and CO$_2$ partial pressures in the mixture. All these observations led us to suggest that CO, O, and CO$_2$ participate in the reaction mechanism where CO and O are in adsorbed form.

**ACKNOWLEDGEMENTS**

This work was supported by the NEDO International Joint Research Grant Program, 'DH-Q-SOFC'.
REFERENCES

(1) J. Mizusaki, H. Tagawa, T. Saito, T. Yamamura, K. Kamitani, K. Hirano, S. Ehara, T. Takagi, T. Hikita, M. Ippommatu, S. Nakagawa and K. Hashimoto, J. Electrochem. Soc. 141, 2129 (1994).
(2) M. Brown, S. Primdhal and M. Mogensen, J. Electrochem. Soc. 147, 475 (2000).
(3) P. Holtappels, I. C. Vinke, L. G. J. de Haart and U. Stimming, J. Electrochem. Soc. 146, 2976 (1999).
(4) T. H. Etsell and S. N. Flengas, J. Electrochem. Soc. 118, 1890 (1971).
(5) W. J. Fleming, J. Electrochem. Soc. 124, 21 (1977).
(6) B. C. Nguyen, T. A. Lin and D. M. Mason, J. Electrochem. Soc. 133, 1807 (1986).
(7) K. Saji, K. Haruyoshi, T. Takashi and I. Igarashi, J. Electrochem. Soc. 135, 1686 (1988).
(8) J. Mizusaki, H. Tagawa, Y. Miyaki, S. Yamauchi, K. Fueki, I. Koshiro and K. Hirano, Solid State Ionics 53-56, (1992) 126.
(9) T. Setoguchi, K. Okamoto, K. Eguchi and H. Arai, J. Electrochem. Soc. 139, 2875 (1992).
(10) G. O. Lauvstad, S. Sunde and R. Tunold, in High Temperature Electrochemistry: Ceramics and Metals, 17th Riso International Symposium on Materials Science, F. Poulsen, N. Bonanos, S. Linderoth, M. Mogensen and B. Zachau-Christiansen, Editors, p. 339, Riso National Laboratory, Roskilde, Denmark (1996).
(11) R. J. Aaberg, R. Tunold, S. Tjelle, R Odegard, High Temperature Electrochemistry: Ceramics and Metals, 17th Riso International Symposium on Materials Science, F. Poulsen, N. Bonanos, S. Linderoth, M. Mogensen and B. Zachau-Christiansen, Editors, p. 511, Riso National Laboratory, Roskilde, Denmark (1996).
(12) B. A. Boukamp, Solid State Ionics 20, 31 (1986).
(13) B. A. Van Hassel, B. A. Boukamp, A. J. Burgraff, Solid State Ionics 48, 139 (1991).
(14) G. J. Brug, A. L. G. Van Deen Eeden, M. Sluyters-Rehbach, and J. H. Sluyters, J. Electroanal. Chem. 176, (1984) 275.
(15) R. J. Aaberg, R. Tunold, R. Odegard Solid State Ionics 136-137, (2000) 707.
Fig. 1 Illustration of the electrochemical cell.

Fig. 2 Typical impedance diagram recorded for the CO-CO$_2$ system at the Ni/YSZ interface at 850°C.

Fig. 3 Equivalent circuit used to fit impedance spectra related to the CO-CO$_2$ on Ni/YSZ interface.

Re: electrolyte resistance
Qdl: constant phase element
Rct: charge transfer resistance
Zθ: concentration impedance
Fig. 4 Impedance spectra recorded under various CO and CO$_2$ partial pressures. (●) Experimental points, and (Full line) simulated according to the equivalent circuit shown in Fig. 3. (a) increasing PCO, and (b) increasing PCO$_2$.
Fig. 5
Variation of the interface conductivity vs. CO partial pressure at 850°C. PCO₂=0.1 atm.

Fig. 6
Variation of the interface conductivity against CO₂ partial pressure at 850°C. PCO=0.2 atm.

Fig. 7
Variation of the interface conductivity with partial pressure of oxygen at 850°C.
Fig. 8 Variation of $R_{ct}$ and $R_p$ with: (a) partial pressure of CO, and (b) partial pressure of CO$_2$. $R_p$ and $R_{ct}$ were determined using equivalent circuit shown in Fig. 3.