SECOND INTERNATIONAL SYMPOSIUM ON

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

UNIVERSITY OF CALIFORNIA, SANTA BARBARA

JULY 12-17, 1992

Schedule of Presentations

FINAL REMINDER

CALL FOR PAPERS

SECOND INTERNATIONAL SYMPOSIUM ON ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

University of California
Santa Barbara, California, USA

July 12-17, 1992

Electrochemical Impedance Spectroscopy (EIS) is now recognized as one of the most powerful techniques for studying charge transfer phenomena at electrified interfaces. The remarkable progress that has been made in developing EIS was reviewed and demonstrated at the First International Symposium on Electrochemical Impedance Spectroscopy, which was held in Bombannes, France in May 1989. As a natural and timely follow-on to the Bombannes meeting, the Second International Symposium on Electrochemical Impedance Spectroscopy will be held at the University of California, Santa Barbara during July 12-17, 1992. This circular calls for titles and short (75 word) abstracts for papers to be presented at the meeting. The full papers will be published in a special issue (Symposium Volume) of Electrochimica Acta. The deadlines for submission of papers are as follows.

Titles and Abstracts:	**November 20, 1991**
Full Papers:	**March 31, 1992**

The information requested above must be sent by mail or by FAX to:

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TOPICS

- Electrode kinetics
- Porous electrodes
- Corrosion
- Battery science and technology
- Mass transport
- Coatings
- Membranes
- Solid ionic conductors
- Molten salts
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ELECTRODE KINETICS OF OXYGEN REDUCTION ON POROUS NICKEL IN CARBONATE MELT

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The general equation for the oxygen electroreduction in molten carbonate fuel cell (MCFC) is the following:

$$1/2\ O_2 + CO_2 + 2e^- \longrightarrow CO_3^{2-},$$
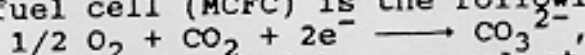
but the mechanism is complicated by several steps with the possibility to have intermediate species like superoxides, peroxides and peroxi-monocarbonates [1,2,3].

The aim of the present paper is to investigate the porous NiO(Li) electrode/molten carbonates interface by means of electrochemical impedance spectroscopy (EIS).

A symmetric cell made of recrystallized allumina was used. The electrodes were two identical porous (75±5 %) Ni electrodes, in situ oxidized and lithium doped, with a geometrical surface area of 3 cm^2 and a mean pore size of 9±1 μm. The electrolyte was constituted by 48 %$_w$ τ-LiAlO$_2$ and 52 %$_w$ lithium and potassium carbonate mixture (Li/K=62/38 %$_{mol}$).

The cell was operated at 650±2 °C and fed with a variable composition of CO$_2$/O$_2$ mixture.

The cell was controlled by a galvanostatic polarization at i=0, with a superimposed sinusoidal signal of 236 μA/cm^2, in the frequency range from 0.1 Hz to 65 kHz.

A typical EIS spectrum is shown in fig.1. At a first look the spectrum is evidently depressed (this phenomena is correlated to the porous electrode structure) and it is clear the presence of several processes.

The spectra can be subdivided in two region: low frequencies in which the diffusion is predominant and high frequencies in which the charge transfer aspect is predominant. The equivalent circuit for the interface is a R-C-O network, where the O element is characteristic of a system in which is present a finite diffusion layer [4]. This latter is a confirmation that the pores of the cathode are not completely flooded, but the walls of the pore are coated with a thin film of electrolyte; this film is so thin that the concentration gradient of active species is concentrated in the film itself.

Following Appleby [2] it is possible to derive the relationship between the exchange current density (i$_o$) and partial pressure:

$$i_o = k \, pO_2{}^a \, pCO_2{}^b$$

where a and b are, respectively, the reaction order relative to oxygen and carbon dioxide. In the following, the theoretical reaction orders for the different mechanism are: peroxide path (POP): a=0.375, b=-1.25; superoxide path (SOP): a=0.625, b=-0.75; peroximonocarbonate path (POMCP): a=0.375, b=-0.25.

The value of charge transfer resistance (R_{ct}) in the case of a porous electrode [5], is inversely proportional to the partial pressures of O_2 and CO_2:

$$1/R_{ct}{}^2 = k \, pO_2{}^a \, pCO_2{}^b$$

The problems arising from the depression of the spectra and the closed time constants were overcome by using a non linear last square fit (NLLSF) [6] made on the whole spetrum.

$$\log R_{hf} = -1/2 \log k' - a/2 \log pO_2$$

A similar relationship can be obtained in the case of constant pO_2:

$$\log R_{hf} = -1/2 \log k'' - b/2 \log pCO_2$$

Therefore from the slope of the previous equations it is possible to draw out the reaction orders.

In order to get a very reliable correlation the medium-low frequencies data points were subtracted from the spectra and a high frequencies region fitting was carried out [7,8].

The following procedure was adopted: subtraction of wires' inductance; simulation of RQ circuit at medium-low frequencies; medium-low frequencies fit with the RQ circuit; subtraction of RQ from the spectrum; simulation with a R(RQ) of the remaining data; final fit with R(RQ) circuit on the remaining data.

Adopting such a procedure the fitting errors were very low, and a very good correlation between log R_{ct} values and partial pressures of O_2 and CO_2 was obtained (fig.2).

The data obtained from several series of measurements, made on two different cells, gave the following mean calculated reaction orders: a=0.38±0.09 and b=-1.2±0.2.

These results are in good agreement with the theoretical values for the peroxide mechanism (a=0.375, b=-1.250), expecially in the case of oxygen reaction order. Therefore it was established that the predominant mechanism is the peroxide path.

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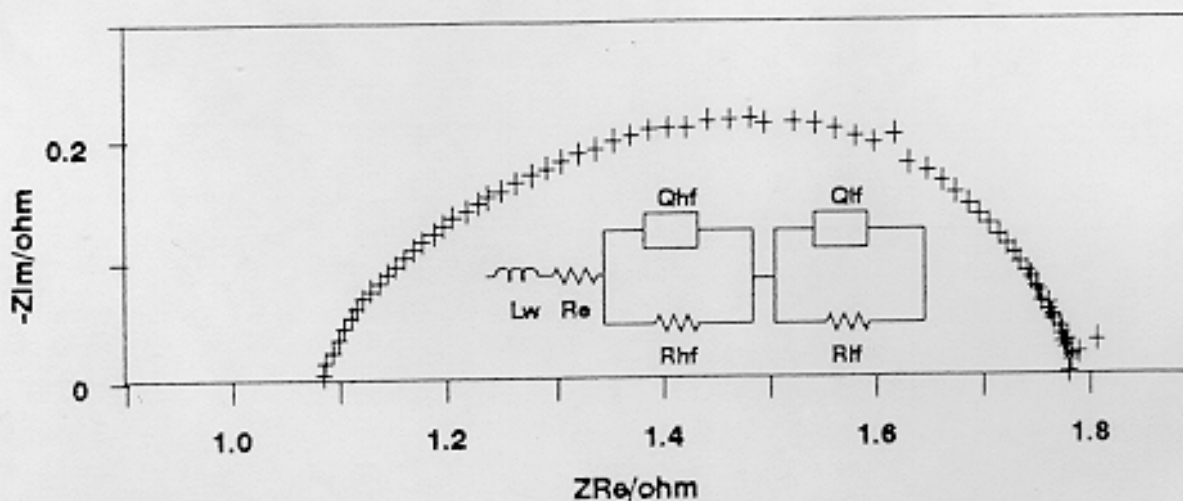
Fig. 1 - Example of experimental and simulated data by means of a total fitting. (pCO_2=0.30 atm, pO_2=0.15 atm, T=650 °C)
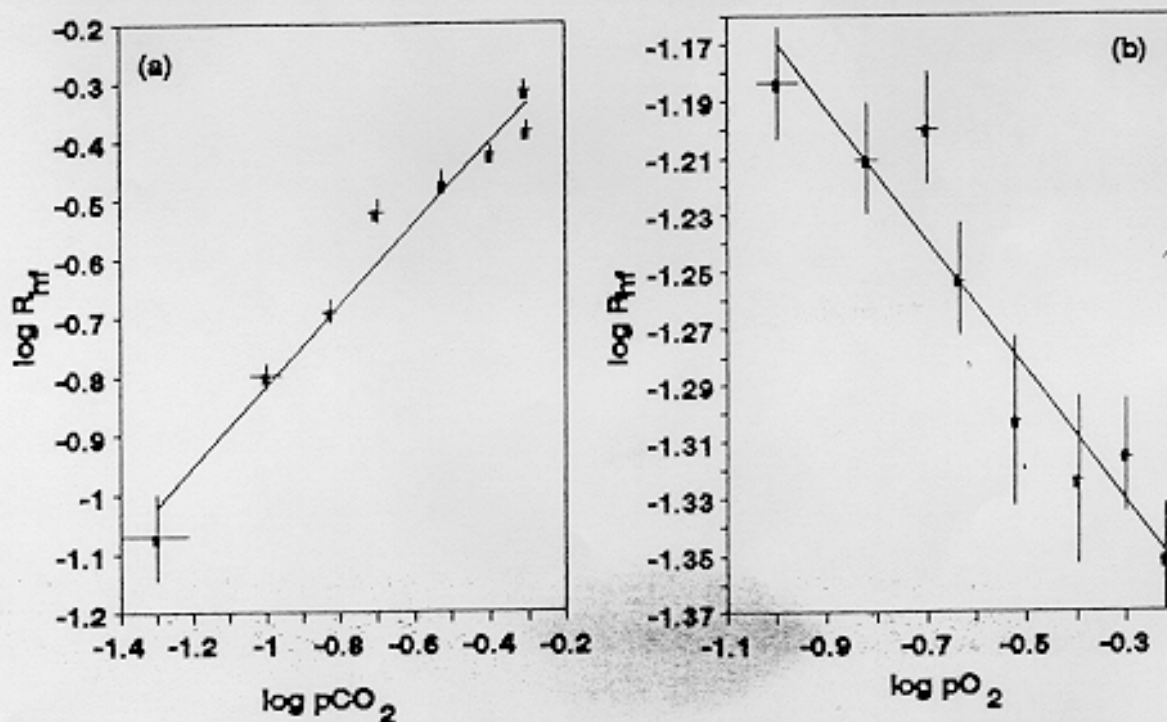

Fig. 2 - Log-log correlation between the high frequencies real impedance and the partial pressure of carbon dioxide (a) and oxygen (b).