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CHARACTERIZATION OF MCFC CATHODE BY MEANS OF
### ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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ABSTRACT

By means of electrochemical impedance spectroscopy (EIS) the NiO cathode of a MCFC was characterized, as a function of the O_2 and CO_2 partial pressure. The electrode/electrolyte interface can be simulated with a R-C-O network, where the O element is concerning with a system in which is present a finite diffusion layer. As a consequence the concentration gradient of the reactive species is located in the film itself. Using a partial fitting tecnhiques at high frequencies, the charge transfer resistance (R_{ct}) for electroreduction of the reactive species was determined. A correlation between R_{ct} and pO_2, pCO_2 was found, making possible to determine the reaction orders. By these parameters was identified the peroxide as intermediate of reaction.

INTRODUCTION

The main problem for the commercialization of MCFCs is the lifetime of the cathodic structure; to achieve a long lifetime for electrode it is necessary to found the optimal operative conditions and for that it is essential to understand the kinetics of oxygen reduction in the carbonate melt. The general equation for the oxygen electroreduction is the follow:

$$1/2 \ O_2 + CO_2 + 2e^- \longrightarrow CO_3^{2-} \tag{1}$$
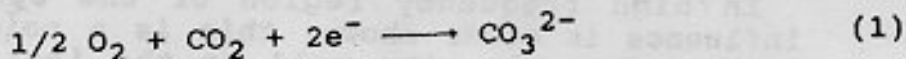
but the proposed mechanisms for this reaction consider the possibility to have intermediate species like superoxide (SOP), peroxide (POP) and peroxymonocarbonate (POMCP) [1,2,3].

Such a reaction take place on porous electrodes in which is present a triple contact (gas/solid/liquid), therefore it is very complicate to study systems like that. Such a complexity is due to the lack of knowledge about some properties of this system. For these reasons is very difficult to predict the validity of the proposed models for porous electrode [3,4].

The aim of the present paper is to investigate the porous electrode/molten carbonates interface, in the case of a in-situ lithiated nickel oxide electrode, by means of electrochemical impedance spectroscopy (EIS).

EXPERIMENTAL

The cell used in this work was the same described by Yuh [4], but in our case we used two identical Ni electrode with a

geometrical surface area of 3 cm^2, a porosity of 75±5% and a mean pore size of 9±1 μm. The tile was constituted by 48 %$_w$ τ-LiAlO$_2$ and 52 %$_w$ carbonate mixture; the carbonate salts were in the ratio Li/K=62/38 %$_{mol}$.

The instrumentation was a potentiostat-galvanostat Solartron mod.1286 and a frequency response analyzer Solartron mod. 1250. The measurements were made at 650 °C, with different gas compositions, by controlling the cell via galvanostatic polarization at i=0, with a superimposed sinusoidal signal of 236 μA/cm^2 (rms), in the frequency range from 0.1 Hz to 65 kHz.

RESULTS AND DISCUSSION

Analysis of EIS spectra

The EIS data point out that the spectra are depressed (fig. 1). This phenomena is correlated to the porous electrode structure and is a function of gas composition for pCO$_2$ > 0.1 atm. The global results show that at pressures less than 0.3 atm of CO$_2$, whatever is the pO$_2$, the depression angle value is so that the impedance phase angle is less than theoretical value of 22.5° for a porous electrode [5].

Such a condition is verified for d^{2}w/D < 10, where d is the electrolyte thickness, w the angular frequency and D the diffusion coefficient. This unequality is true when very thin electrolyte layer is present.

Starting from this point of view, the equivalent electrical circuit for the cathode/electrolyte interface can be simulated by a C(R-CPE) network [6], in which C is the elctrochemical double layer capacitance in parallel to the charge transfer resistance (R) and the constant phase element (CPE).

In high frequency region of the spectra, an inductive influence is clear shown; this is a noise introduced by the wires connecting the cell to the instrumentation. After a measurement of the inductance, this component was subtracted from the spectra.
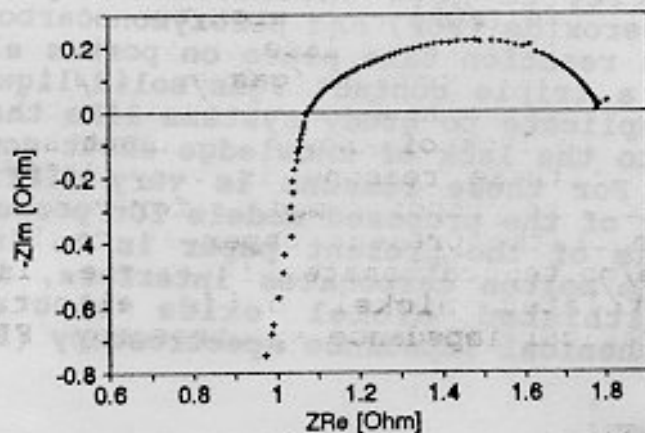

Fig.1 - Impedance spectra of NiO(Li) porous cathode at 655 °C in Li$_2$CO$_3$/K$_2$CO$_3$=62/38%$_{mol}$ (30% CO$_2$, 10% O$_2$, 60% N$_2$).

It is possible to eliminate the depression of the spectra by means of a mathematical correction. In this case the better simulation of the interface is given by network such as C(R-O), where the O element is characteristic of a system in which is present a finite diffusion layer, which impedance is an expression similar to

$$Z(w)=\tanh[B(jw)^{0.5}]/[Y^{*}(jw)^{0.5}] \tag{2}$$

where the B and Y^{*} parameters are a function of diffusion coefficient of reacting species and other coefficients depending by the system, like the thickness of electrolyte layer.

The fact that the electrode/melted carbonates interface can be simulated by means of a R-O elements, 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 located in the film itself.

These phenomena con be deduced from the slope of the EIS spectrum in the middle frequency region; such slope is not 45° as in the case of a pure Warburg diffusion, but is lower than 22.5°. If this angle is higher than 22.5°, it means the electrodes became to be flooded; therefore the measurement of this parameter can be used as a check for the operative conditions of a MCFC.

Determination of charge transfer resistance and rection orders

The spectra can be subdivided in two region: low frequencies in which the diffusion is predominant and high frequencies zone in which the kinetic aspect is prevalent.

The CPE element influences the shape of the EIS spetrum only at medium-low frequency, therefore it is possible to analyze the high frequency region without significant errors. Such a region of the spectrum is concerning with the kinetic of the interphase phenomena and it is possible to extract the value of charge transfer resistance (R_{ct}), which, in the case of a porous electrode, is inversely proportional to the partial pressures of O_2 and CO_2:

$$1/R_{ct}^{2} = k\ pO_2^{a}\ pCO_2^{b} \tag{3}$$

The theoretical reaction orders for the three proposed mechanisms are: a=0.375, b=-1.25 for POP; a=0.625, b=-0.75 for SOP; a=0.375, b=-0.25 for POMCP.

The easier way to determine the values of R_{ct}, is to extract the circle that fits the high frequency region of the spectrum and to calculate the diameter of this circle. But this methodology failed, because we did not find any correlation between the R_{ct} values and the gas composition. That is due to the very low numeric values of the R_{ct} compared to the total impedance; therefore the error in measuring R_{ct} is very high.

Then it was used a different methodology based on the global

fitting of the spectrum. The equivalent circuit deriving from the fitting is made up by two parallel RQ elements, in series among themselves. In this case it was possible to found a correlation, based on eq.3, between the R value of high frequency R-Q element and the gas composition.

To reduce the errors in calculating the high frequency resistance, a different approch was used to extract the R_{ct} values from the experimental spectra. This methodology was based on the consideration that the main depression influence on the spectra shape is concentrated at medium-low frequencies, whereas the kinetic contribution is located in high frequencies region. For this reason, the medium-low frequencies data points were subtracted from the spectra and a high frequencies region fitting was carried out. So the fitting errors were very low, and a very good correlation was obtained between log R_{ct} values and partial pressures of O_2 and CO_2 (fig. 2).
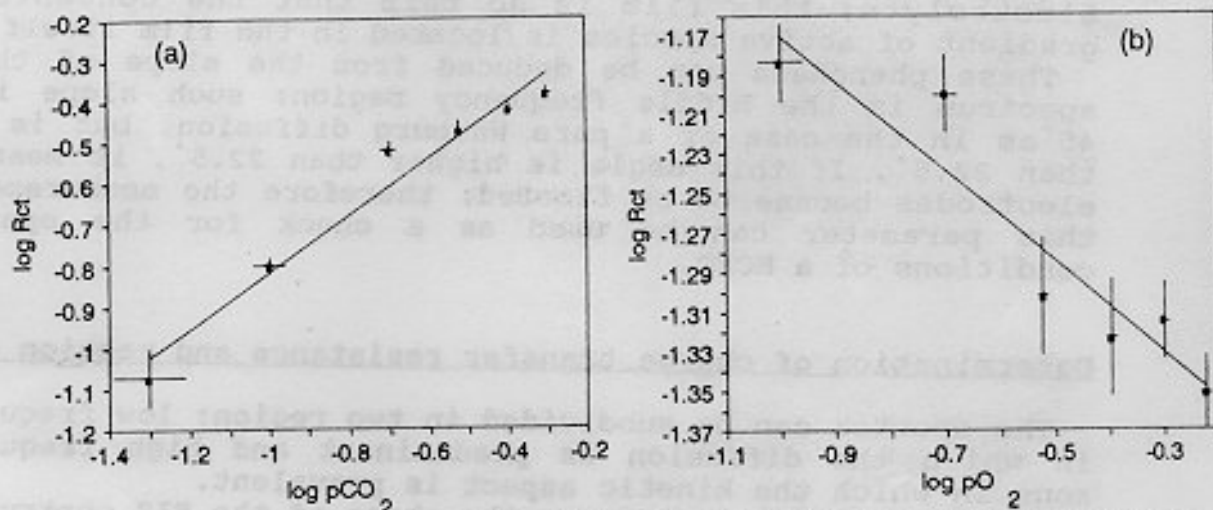

Fig.2 - The carbon dioxide (a) and oxygen (b) dependency of the charge transfer resistance for a NiO(Li) cathode at 655 °C.

From the dependency of charge transfer resistance from gas composition the reaction orders relative to O_2 and CO_2 were determinated by means of equation 1. The data obtained by different series of measurements, made on two different cells, are shown in Tab.I.

Tab.I- Calculated reaction orders

pO_2 (atm)	pCO_2 (atm)	a	b	r
0.10÷0.60	0.10	0.30±0.08		0.86
0.05÷0.65	0.30	0.4±0.1		0.91
0.10÷0.60	0.30	0.44±0.08		0.94
0.14	0.05÷0.65		−1.3±0.2	0.93
0.14	0.10÷0.60		−1.4±0.2	0.95
0.50	0.05÷0.50		−1.4±0.1	0.98

The mean calculated reaction orders are: $a=0.38\pm0.09$ and $b=-1.2\pm0.2$. They are in good agreement with the theoretical values for the peroxide mechanism. Therefore it is possible to estabilish that the predominant mechanism is the peroxide path.

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