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CHARACTERIZATION OF SOLID POLYMER ELECTROLYTE FUEL CELL CATHODES BY AC-IMPEDANCE SPECTROSCOPY

A. Pozio, L. Giorgi

ENEA, C.R. Casaccia, ERG-TEA-ECHI,
Via Anguillarese 301, 00060 S. Maria di Galeria (Roma), Italy
e-mail: giorgil@casaccia.enea.it

1. INTRODUCTION

Solid polymer electrolyte fuel cell (SPFC) utilizes porous gas-diffusion electrodes bonded to a Nafion membrane. Such electrodes are usually under mixed control of electrode kinetics, mass transfer, and ionic conduction [1]. The oxygen reduction occurring on the SPFC cathode is the kinetically slow reaction. It is well known that mainly oxygen reduction reaction determines the operation efficiency of SPFC. Platinum is commonly used as a catalyst for oxygen reduction in SPFC. Electrode structures in polymer electrolyte fuel cell (PEFC) have evolved from two layers to three layers structure. Dual-layer electrodes are constituted by a hydrophobic support layer and a porous electrocatalyst layer formed by Pt on carbon (Pt/C) as a catalyst agent, polytetrafluoroethylene (PTFE) and polyperfluorosulphonic acid (Nafion). Three-layer electrodes are made by a porous support layer, a diffusion layer consisting of carbon particles and PTFE and a catalyst layer formed by Pt/C and Nafion [5].

The performances of the electrodes depend on many parameters: type of support and its characteristics, type of catalyst (Pt or others, its amount and particles size), type of carbon, PTFE amount, Nafion amount, thermal treatment, thickness of diffusion and catalytic layers, fabrication process. Several studies have been conducted mainly on geometrically well-defined smooth noble-metal-ring and disk electrode, and smooth noble-metal electrode. Ac-impedance spectroscopy can provide a wealth of information on the reaction directly at the porous electrode/electrolyte interface. This technique supplies informations about the influence of morphology on the electrode performance [3,4].

In the present work the oxygen reduction on some different Pt/C porous electrode by analyzing ac-impedance spectra was investigated. EIS data were obtained on the Pt/C electrode in 1M H₂SO₄ at room temperature, with oxygen flowing at different concentrations. Some parameters were determined by complex non-linear least squares (CNLS) fitting method using the computer program EQUIVCRT [2].

2. EXPERIMENTAL

Different electrodes were prepared by spray or brushing technique [5] using platinum-on-carbon (20% Pt/C) catalyst (Electrochem. Inc.), grounded carbon powder (Vulcan XC-72, Cabot or Shawinigan), carbon paper (Toray TGPH-090) or carbon cloth (Electrochem. Inc.), polytetrafluoroethylene (PTFE) dispersion (35 wt % PTFE aqueous dispersion, Hostafion 5033, Hoechst), Nafion solution (5 wt% Nafion 1100 EW solution, Solution Technology Inc.) and glycerol. Tab. 1 gives information about the preparative techniques and compositions of different electrodes: the carbon loading in the diffusion layer was 2 mg cm⁻², the FEP (fluoroethylene propylene polymer, T120 Du Pont) was used to wet-proof the carbon paper only for dual layer electrodes.

A Pyrex cell with a platinum foil as counter electrode and a saturated calomel reference electrode was used for all electrochemical measurements. The working electrode (1 cm² of geometric area) was inserted in a PTFE specimen holder, which allowed to expose the electrode active reaction layer to the electrolyte (H₂SO₄ 1 M at 25 °C) and the backside to the flowing gas. The instrumentation for the electrochemical impedance spectroscopy (EIS) consisted in an electrochemical interface Solartron Instruments mod.1287 and an impedance

phase analyzer Solartron Instruments mod.1260, both interfaced via GPIB to a computer Hewlett-Packard Vectra 5/75. The EIS measurements were carried out at various cathode potentials in the range 500+900 mV vs. NHE, changing the N₂/O₂ ratio. An alternating sinusoidal signal of 10 mV peak-to-peak was superimposed on the dc-potential. The impedance spectra were collected in the frequencies range between 100 kHz and 50 mHz.

Tab 1 - Electrodes, preparative techniques and compositions.

Electrode	Component/Technique	Catalytic Layer			Diffusive Layer	Substrate
		Pt (mg cm ⁻²)	Nafion (mg cm ⁻²)	PTFE (wt %)		
EDG	<ul style="list-style-type: none"> • CP/Wet-proofed with FEP • Catalytic layer/ Screen Printing 	0.50		40		30
SPE	<ul style="list-style-type: none"> • CP/Wet-proofed with FEP • Catalytic layer/Screen Printing + Brushing with Nafion 	0.50	0.90	40		30
PLP	<ul style="list-style-type: none"> • CP • Diffusive layer/ Screen Printing • Catalytic layer/ Spraying 	0.15	0.15		10	
CLP	<ul style="list-style-type: none"> • CC • Diffusive layer/ Spraying • Catalytic layer/ Spraying 	0.14	0.22		50	

CP = Carbon Paper - CC = Carbon Cloth

3. RESULTS AND DISCUSSION

Impedance spectra were recorded at various potentials and gas composition to calculate the $D^{1/2}C$ product for dissolved oxygen in the catalytic layer, from the magnitude of Warburg impedance at open circuit voltage. In addition, the EIS data were used for the determination of Tafel slope [4] (without the need to correct for limiting current at high overpotentials) showing good agreement with steady state-techniques.

Fig. 1 shows the Nyquist plots obtained at 572 mV vs. NHE. They mainly consist of one semicircle characteristic of an electrochemical interface that can be simulated with an equivalent electrical circuit $R_0(R_pC)$, where R_0 is the sum of electrode and electrolyte resistance, R_p is the polarization resistance (charge and mass transfer) and C is a pseudocapacitance, taking in account also for the double layer capacity. The polarization resistance is the sum of two terms: charge transfer and diffusion resistance.

The highest impedance has been obtained for electrode with high Nafion loading (SPE). As the electrode overpotential increases, the charge transfer resistance and the relaxation time

of the charge transfer process decrease, whereas diffusion resistance increases or decreases as function of the type of electrode. Polarization resistance and double layer capacity are related to maximum frequency by the equation $\omega_{max}=1/(R_pC)$. From the ω_{max} value and assuming that the semicircle diameter like the polarization resistance, the pseudocapacitance was calculated. The value of this parameter was related to the ratio between effective electrode area and double layer thickness; so the change of C value was attributed to the modification of electrode morphology.

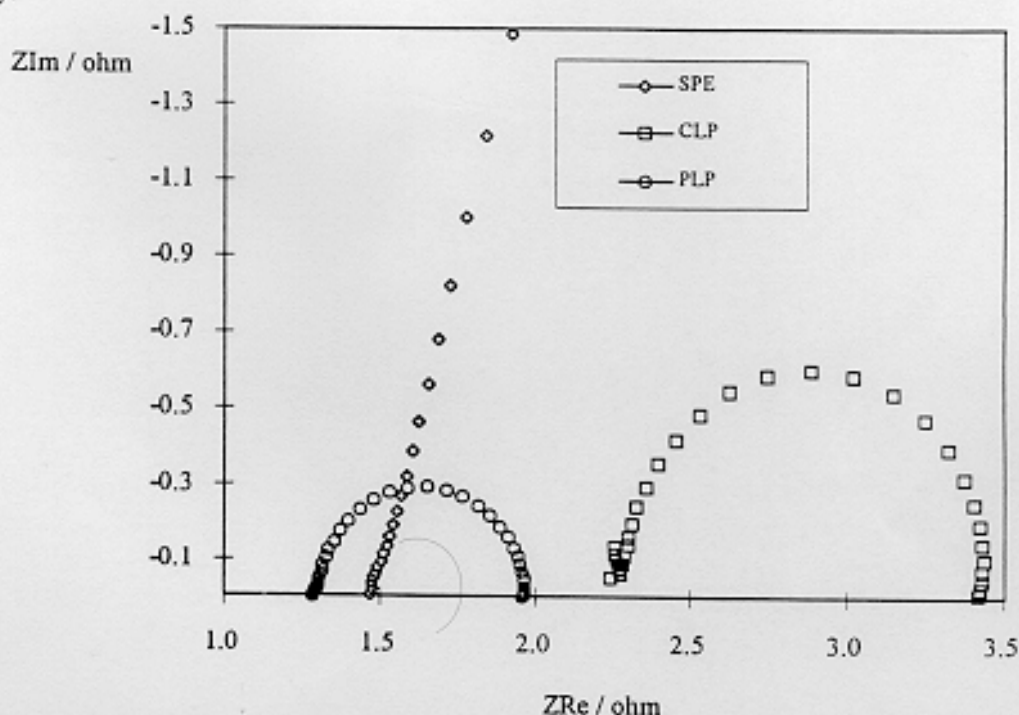


Fig.1 – Nyquist plots of different gas diffusion electrodes at 572 mV vs. NHE at 25°C in O₂.

4. CONCLUSIONS

A significant difference was found in the behavior of electrodes with and without Nafion in the catalytic layer. In absence of Nafion (EDG) the electrode showed, at high overpotentials, a consistent increase of impedance due to the existence of a finite-length in the diffusion layer. Electrodes with Nafion showed in all range of potentials the same behavior of smooth electrodes, with a decrease of impedance as the overpotential was increased.

Electrodes performance depends on Nafion loading; a too high polymer amount in the catalytic layer produces an increase of polarization resistance and a decrease of electrochemical active area.

The preparation technique of the gas-diffusion electrode influences the kinetic of oxygen reduction reaction (ORR), which is enhanced by the presence of liquid Nafion in the catalyst layer. To have the best performance the polymer must mixed directly to the Pt/C catalyst to increase the number of active site at the interface gas/Nafion/Pt. The spray deposition technique (CLP electrode) for preparation of gas diffusion electrode is the more effective method to improve the ORR performance.

5. REFERENCES

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