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TITLE RECENT ADVANCES IN SOLID POLYMER ELECTROLYTE FUEL CELL TECHNOLOGY

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MASTER

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RECENT ADVANCES IN SOLID POLYMER ELECTROLYTE FUEL CELL TECHNOLOGY

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RESUMO

As celulas a combustivel que utilizam eletrolito polimerico solido (SPE) e eletrodos contendo 4 mg/cm^2 de platina tem-se destacado dentre as demais tecnologias, pois fornecem um elevado nivel de densidade de potencia, funcionam em temperaturas relativamente baixas (80°C) e nao requerem sistemas perifericos de controle muito complicados. No presente trabalho sao resumidas as etapas principais de desenvolvimento das celulas SPE que utilizam eletrodos contendo apenas um decimo da quantidade de platina do sistema convencional (0.4 mg/cm^2), mas que apresentam o mesmo nivel de alta performance. Os aspectos considerados sao: (i) otimizacao da concentracao de polimero impregnado no eletrodo; (ii) otimizacao da etapa de prensagem-a-quente dos eletrodos na membrana; (iii) humidificacao dos gases reagentes; (iv) operacao em temperaturas e pressoes elevadas; e (v) localizacao da platina perto da fronteina eletrodo/membrana.

1. INTRODUCTION

Until the present time, the platinum electrocatalyst has been the most expensive material used in the fabrication of components for aqueous electrolyte fuel cells. With the current technologies, the total cost of materials for the electrochemical cell stack is about $200/kw for the phosphoric acid and alkaline fuel cell systems and about $600/kw for solid polymer electrolyte (SPE) fuel cell systems. Technoeconomic assessments reveal that the SPE fuel cell system is the most feasible power plant for electric vehicles.[1] With the "state-of-the art" technology, it requires 16 g of platinum per kilowatt.[2] Apart from cost considerations, even if 10% of the automobiles are to be manufactured in the future with fuel cell power plants, the platinum requirements will exceed the production rate of this metal. Thus, not only from a capital cost standpoint, but also from the availability standpoint of this noble metal resource, it will be necessary to minimize its use in fuel cell power plants.

and volume of fuel cell power plants. High power densities should be achieved without sacrifice of loss of efficiencies. Thus, if the efficiency of the electrochemical cell stack is to be greater than 40%, the cell potential under rated load should be greater than 0.6 V. In addition, high power densities are necessary for several applications; one good example is the transportation application where a high power density is necessary during cruising of the vehicle and two to three times the rated power is required for start-up and acceleration. A performance goal which appears particularly attractive for the transportation application is a rated power density corresponding to current density of 1 A/cm^2 at 0.7 V. Space and military applications also demand high power densities.

The "state-of-the-art" SPE fuel cell technology utilizes electrodes containing unsupported platinum black and hence, the noble metal loading is high (4 mg/cm^2 on cathode and 2 mg/cm^2 on anode) compared to that in the phosphoric acid fuel cell system containing electrodes made with supported platinum electrocatalysts (Pt loading 0.25 and 0.5 mg/cm^2 for the hydrogen anodes and oxygen cathodes, respectively). Even though current densities of 500 mA/cm^2 at 0.7 V (with H_2/air as reactants, temperature of 80°C and a pressure of 5 atm) have been reported,[2] the platinum requirements for such a SPE fuel cell system is about 16 g per kilowatt. In recent communications from our Laboratory,[3,4] it was demonstrated that by the use of porous gas diffusion electrodes containing supported electrocatalysts (0.4 mg Pt/cm^2) in SPE fuel cells, it is possible to achieve nearly the same level of performance as in fuel cells containing 10 times the platinum loading. This was done by impregnation of a proton conductor (Nafion) into the electrode structure to extend the three-dimensional reaction zone. Thus, the interfacial reaction zone is similar to that of a porous gas diffusion electrode/liquid electrolyte interface.

During the last 18 months, several methods have been developed at Los Alamos National Laboratory (LANL) to use low platinum loading electrodes in solid polymer electrolyte fuel cells (single cells) with the objective of approaching performances close to the fuel cells containing high platinum loadings.[4,5] The approaches taken to make these improvements is reviewed in this paper.

II. EXPERIMENTAL

Unless otherwise stated, experiments were carried out using the standard low platinum loading (0.35mg/cm^2) electrodes commercially available from

50 wt% each of high surface area carbon (Vulcan XC-72) and Teflon particles, and an electrocatalyst layer 100 μm thick and consisting of 40% PTFE and 60% catalyzed carbon (10 wt% Pt/Vulcan XC-72).

In order to increase the platinum concentration near the front surface of the electrode, two methods were used. In the first, a thin film of platinum was sputter-deposited on the catalyst layer of the standard Prototech electrodes. In the second, electrodes with thinner electrocatalyst layers (50 and 25 μm) were custom-made by Prototech, using 20 and 40 wt% Pt/C instead of the standard 10 wt% Pt/C, but maintaining the same platinum loading (0.4 mg Pt/cm^2).

Also, low catalyst loading gas diffusion electrodes were prepared by the filtration method. First, a mixture of 50 wt% carbon powder (Vulcan, XC-72) and floculated PTFE dispersion (Dupont, T-30,) were filtered through a carbon cloth (Stackpole, PWB-3) to form the diffusion layer on the electrode. Subsequently, platinum supported on high surface area carbon (Vulcan XC-72) was mixed with the floculated PTFE dispersion and deposited by filtration on the opposite side of the carbon cloth, thus forming the catalyst layer. Finally, the electrode was placed in an oven at 330°C for 15 minutes, in a low oxygen environment for sintering of the Teflon and bonding of the electrode.

The experiments were carried out in single cells made with carbon (Union Carbide nuclear grade graphite) end plates. The cell was equipped with a reversible hydrogen reference electrode. The graphite end plates contain gas feed inlets and outlets, ribbed channels for gas flow behind the porous gas diffusion electrodes, and holes for a cartridge heater and for a thermocouple. After positioning the membrane and electrode assembly (see Section 3.2 for its preparation by hot pressing) between two gaskets and the graphite end plates, the latter were clamped between stainless steel plates that were insulated from the cell body with PTFE sheets. The active electrode area (geometric) in this cell is 5 cm^2.

Cell potential/current density measurements were made galvanostatically with a programmable power supply (HP-6033A), a microcomputer (IBM-PC), and a data acquisition unit (HP-3421A) that were interfaced with the electrochemical cell.

III. RESULTS AND DISCUSSION

1. Optimization of Concentration of Proton Conductor Impregnated Into the Electrode. The proton conductor (Nafion) impregnated into the electrode

forms a film in the pores of the catalyst layer of the porous gas diffusion electrode. Varying quantities of Nafion solution (5% in lower alcohols) were impregnated into the low electrocatalyst loading electrodes (0.4 mg Pt/cm^2) by a brushing or spraying procedure to determine the optimum amount of Nafion necessary to maximize the cell performance. The solvent was allowed to evaporate first under ambient conditions and then in a vacuum oven at 70°C for one hour.

Figure 1 shows the effect of the Nafion loading on cell performance. Too thin a film causes increases in activation and ohmic overpotentials. On the other hand, a thick film introduces mass transport limitations in the high current density region. The optimum quantity of Nafion was determined to be 3.3 wt% of the weight of the electrode.

2. Optimization of Hot-Pressing Conditions of Electrodes to Membrane. To minimize the contact resistance between the Nafion membrane and Nafion impregnated electrodes, optimization of the hot pressing conditions is essential. The membrane was treated in a 5% H_2O_2 solution heated to the boiling point to oxidize organic impurities, secondly rinsed in deionized water, thirdly immersed in hot diluted sulfuric acid to get rid of metallic impurities and finally treated several times in boiling deionized water to remove traces of this acid. The ideal procedure for hot-pressing was found to be: two Nafion-impregnated electrodes were placed on both sides of the Nafion membrane. The assembly was then inserted within the two platens of the hot-press set at a temperature of 100°C. The temperature of the hot-press was raised to 130°C (the glass transition temperature of Nafion) and a pressure of 50 atm was applied for 90 seconds in order to obtain a good contact between the electrodes and the membrane.

3. The Vital Role of Water Management In The Cell.

3.1 Humidification of Reactant Gases. One of the most crucial factors in the operation of a solid polymer electrolyte fuel cell is water management (maintaining the SPE wet and removal of product water). The reactant gases can be humidified externally by passing these through water contained in stainless steel bottles maintained at the desired temperature or internally by passing the gases through humidification chambers built adjacent to the electrochemical cell. To obtain stable long-term performance, it was found to be desirable to humidify hydrogen at 10-15°C and air at 5°C above the cell temperature.

3.2 Optimization of Teflon Content in Electrode. The PTFE content in the electrode structure may play an important role in the water management in SPE fuel cells. Electrodes were fabricated in house with varying PTFE content in the catalyst layer and their performance evaluated as cathodes in single cell experiments. Figure 2 shows these results. The optimum PTFE content seems to be close to 40 wt% in the catalyst layer of electrodes for obtaining the best cell potential-current density characteristic. For the hydrogen electrode a higher Teflon content (60%) in the catalyst layer gave the best performance.

4. Advantages of Operation at Elevated Temperatures and Pressures. Operation at elevated temperatures and pressures is necessary to attain high power densities for at least three reasons: (1) better electrode kinetics of fuel cell reactions; (2) better mass transport and lower ohmic resistances; (3) less water loss from the membrane (because lower flow rates of reactant gases are sufficient for higher-pressure operation).

The effects of temperature and pressure on the cell operation are illustrated in Figure 3 for H_2/Air fuel cells at 50°C at 1/1 and 3/5 atm and at 80°C at 3/5 atm. The combined effects of ohmic and mass transport control are evident at 50°C. These effects are considerably diminished at the higher temperature and pressure (80°C, 3/5 atm). In this case mass transport limitations are visible only at 800 mA/cm^2. At 1A/cm^2 mass transport overpotential diminishes the cell potential by about 0.100V. Even if this is taken into consideration, the cell potential is only about 0.300 V at 1A/cm^2. To obtain a cell potential of 0.6 V at this current density, it is necessary to further reduce the differential resistance (mainly ohmic) in the cell.

5. Localization of Platinum Near the Front Surface of Electrodes. At high current densities (> 0.5 A/cm^2), most of the current tends to be generated near the front surface of the electrode because of the predominance of ohmic and mass transport overpotentials. Thus, use of electrodes with thin active layers and a higher platinum concentration near the front surface will be most beneficial.

Results in Figures 4-6 show that localization of platinum near front surface is very effective in the attainment of high power densities. Use of the sputtering technique for the standard electrode reveal enhancement in power densities by 100-150% at 1A/cm^2 (Figure 4). There was a significant improvement in performance of the cells in which electrodes with 20 and 40 wt% rather than when 10 wt% Pt/C were used (Figure 5). The sputtering of Pt on the 20 wt% Pt/C gave rise to the highest power density in the fuel cell. The improvement in performance by using thinner electrolytic layers and by sputtering a thin film of platinum near the front surface correlates well with the increase in the electrochemically active surface area, as ascertained by the charge necessary for hydrogen adsorption or desorption on Pt, using the cyclic voltammetric technique.

IV. CONCLUSIONS

With the above methods used to advance solid polymer electrolyte fuel cell technology, we are close to obtaining the goal of $1 A/cm^2$ at 0.7 (see Figure 6). Higher power densities have been reported ($2 A/cm^2$ at 0.5 V) but only with high catalyst loading electrodes ($2 mg/cm^2$ and $4 mg/cm^2$ at anode and cathode, respectively) and using a Dow membrane with a better conductivity and water retention characteristics. Work is in progress in our laboratories to ascertain performances of cells with Dow membrane impregnated electrodes and Dow membrane electrolytes.

V. ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Fig. 1. Effects of Nafion content of electrodes on cell potential vs current density plots, H_2/Air 3/5 atm, 50°C, 0.4 mg Pt/cm^2: (O) 5%; (O) 4%; (Δ) 3.3% and (□) 2wt% Nafion.

Fig. 2 Effect of PTFE content in the catalyst layer of electrodes (cathodes, 0.4 mg Pt/cm^2) on the fuel cell performance, H_2/Air 3/5 atm, 80°C.

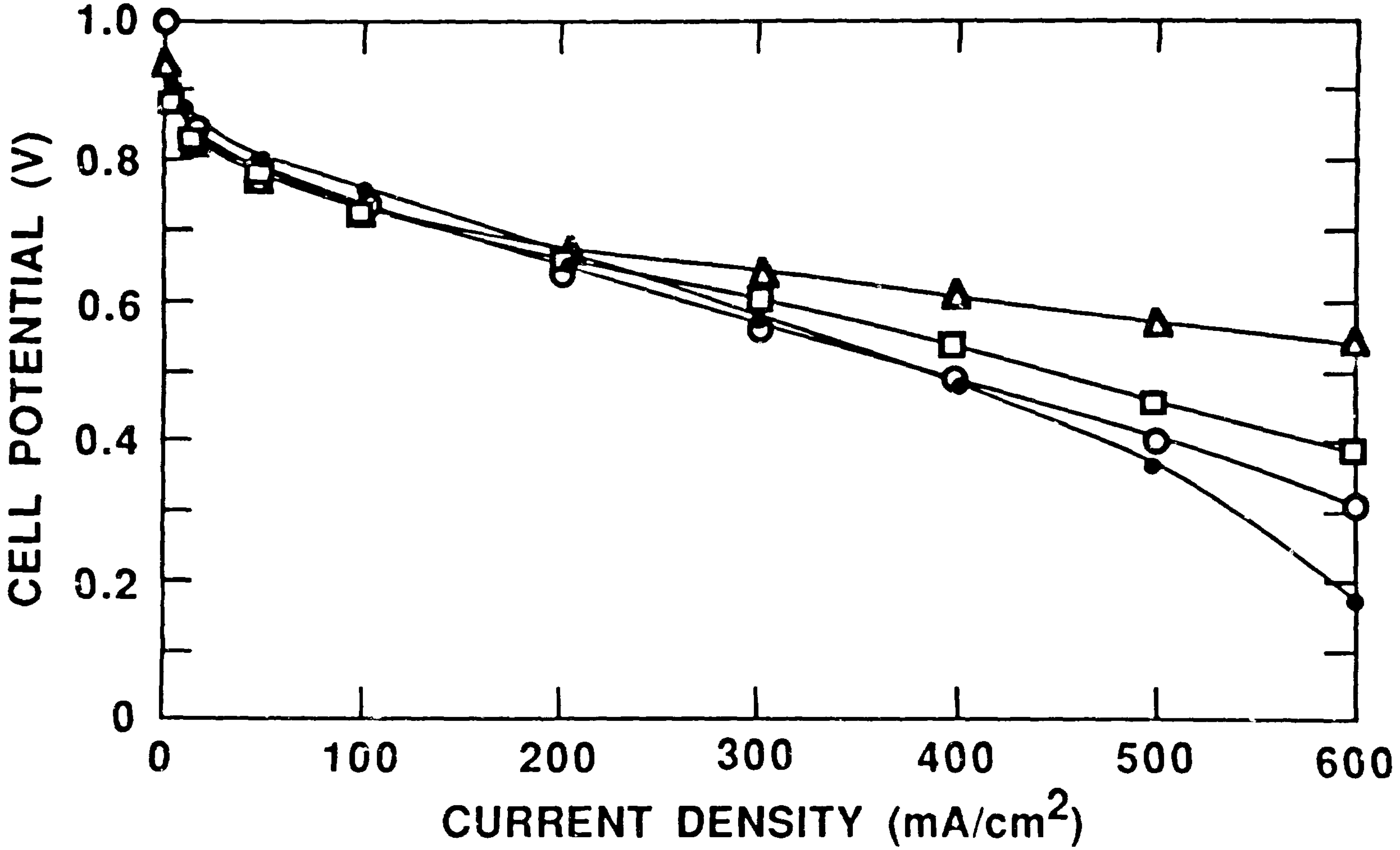
Fig. 3. Effects of pressure and temperature on cell potential vs current density plots for 4% Nafion-impregnated electrodes (0.4 mg Pt/cm^2): (a) H_2/Air 1/1 atm, 50°C; (b) H_2/Air 3/5 atm, 50°C; and (c) H_2/Air 3/5 atm, 80°C.

Fig. 4. Effect of increasing platinum loading near front surface of electrodes by sputtering Pt on standard electrodes, on H_2/Air 3/5 atm, 80°C single cell performance.

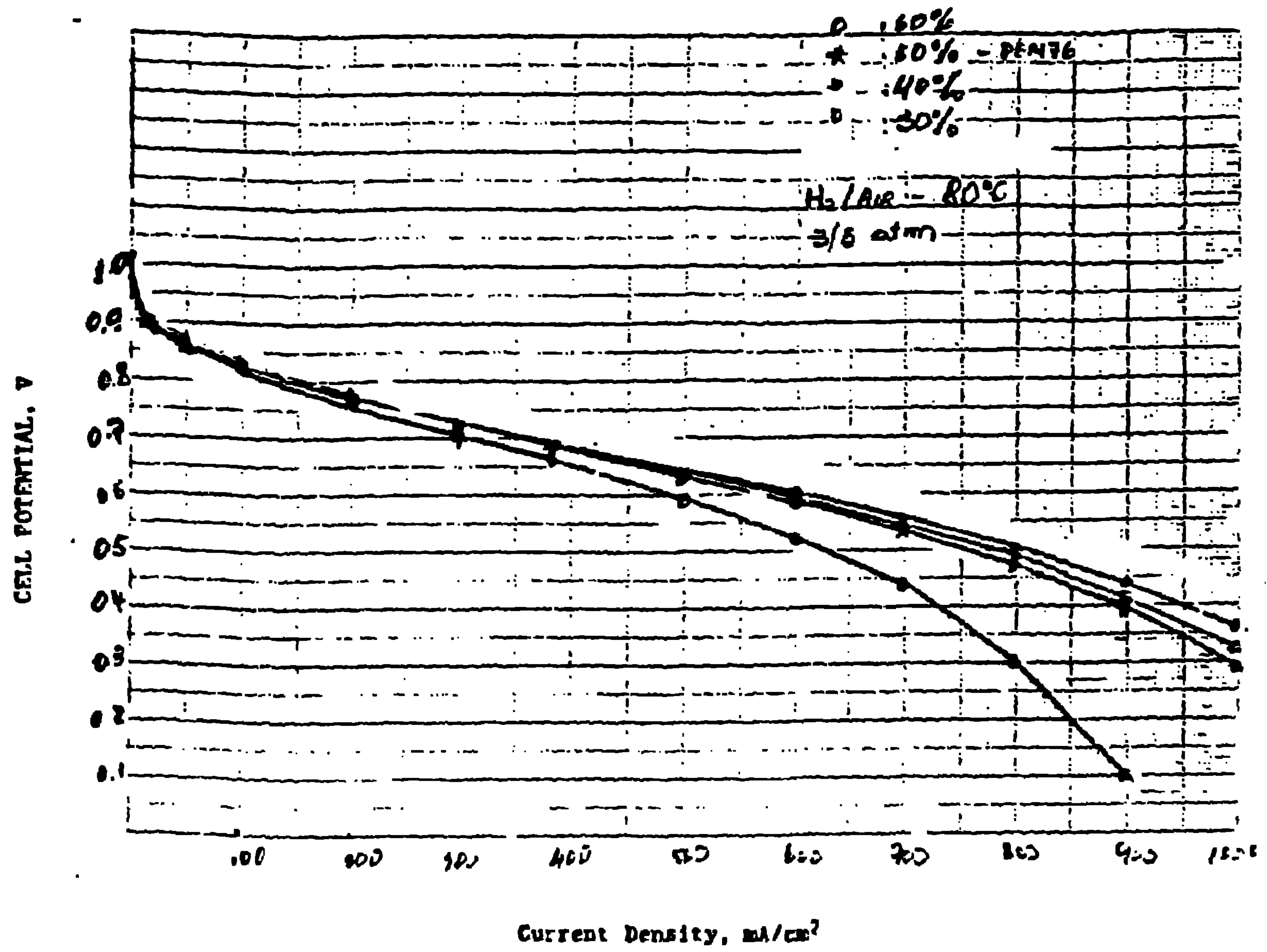
Fig. 5. Effect of increase Pt/C wt ratio in electrodes on H_2/Air 3/5 atm, 80°C single cell performance. (A) 10 wt% Pt/C; (B) 20 wt% Pt/C; and (C) 40 wt% Pt/C. All electrodes with 0.4 mg Pt/cm^2. Thickness of catalyst layers in electrodes are approximately 100 μm in cell A, 50 μm in cell B, and 25 μm in cell C.

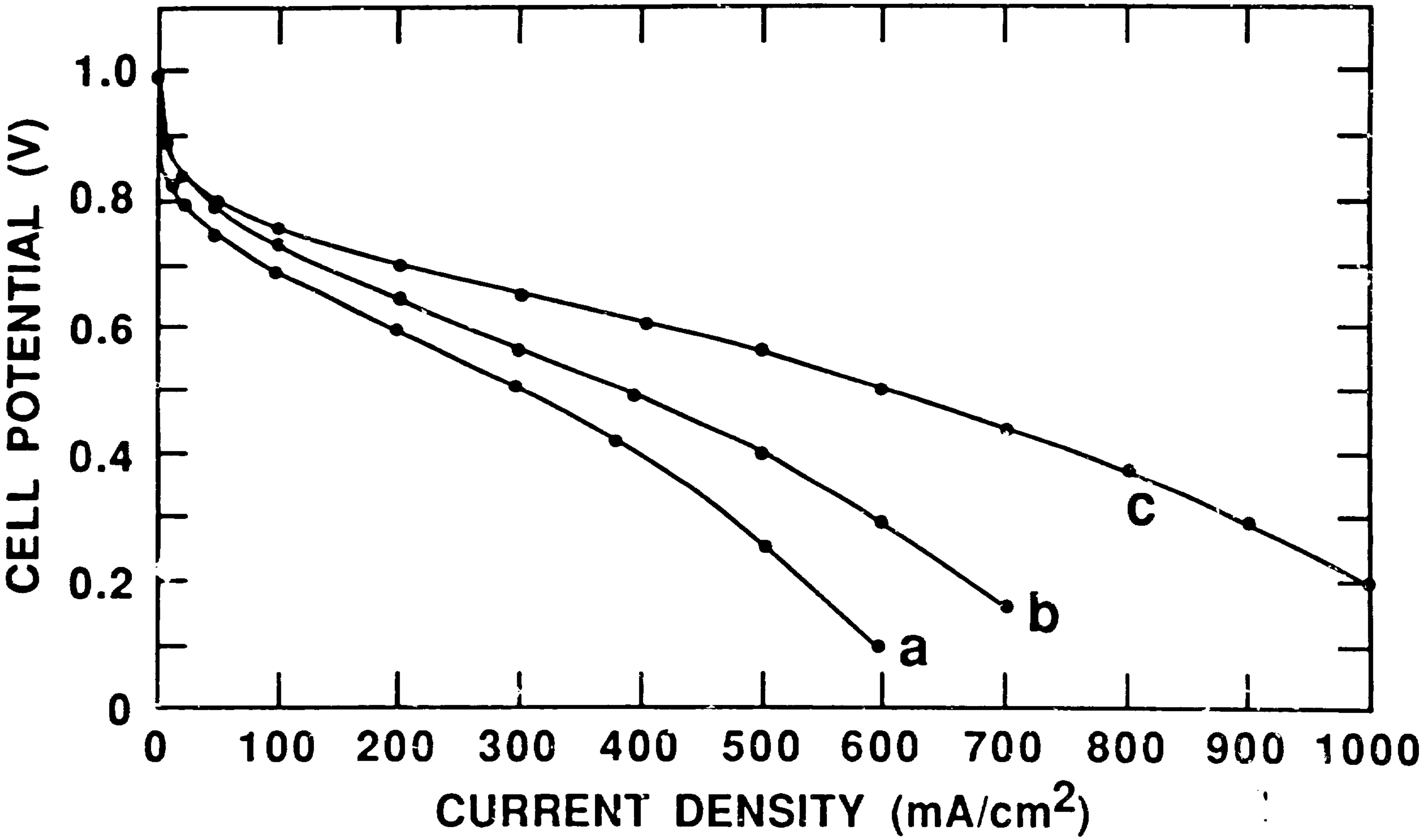
Fig. 6. Effect of increasing platinum loading near front surface of electrode by sputtering Pt on electrode with 20% Pt/C, on H_2/Air 3/5 atm, 80°C single cell performance.

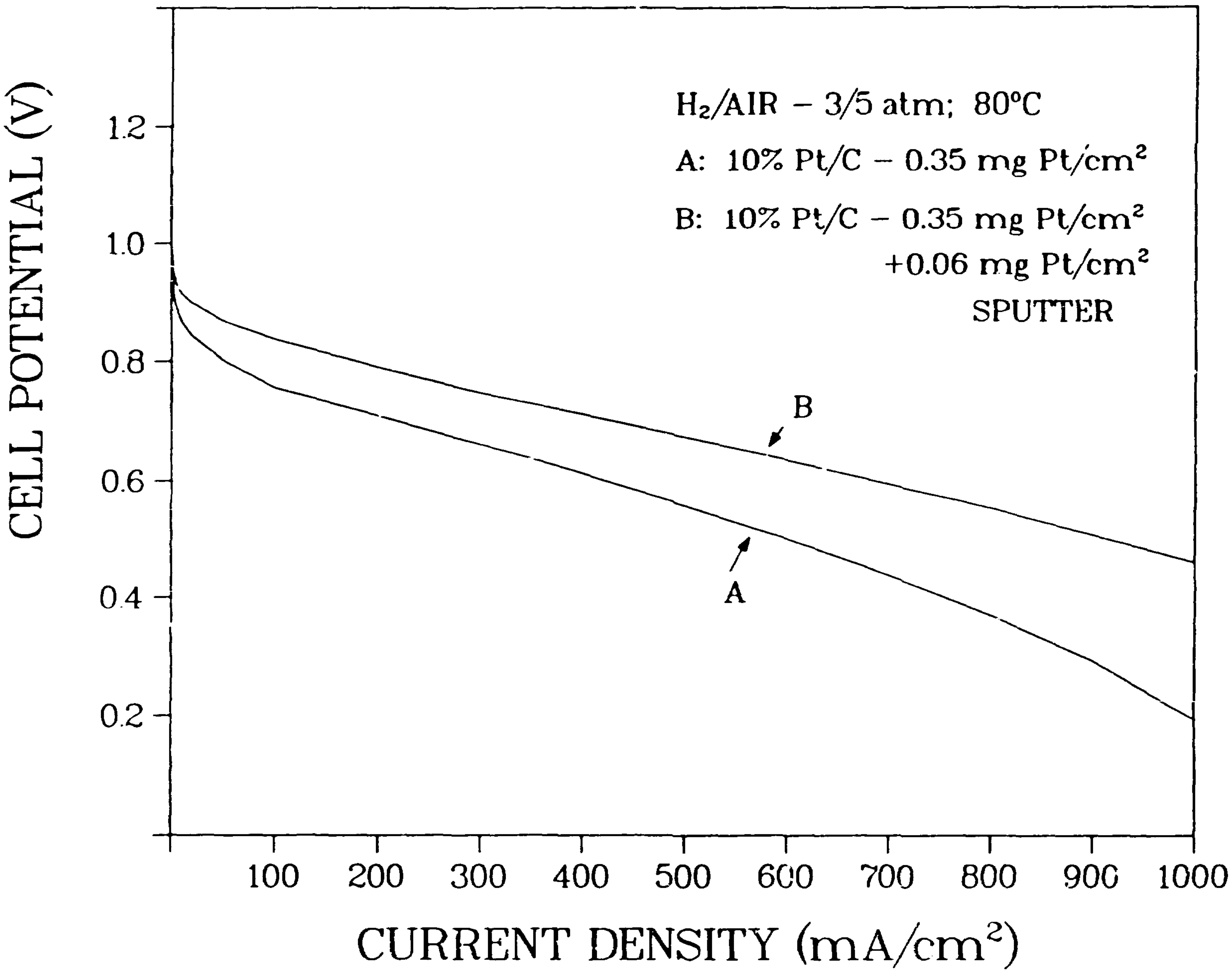
①

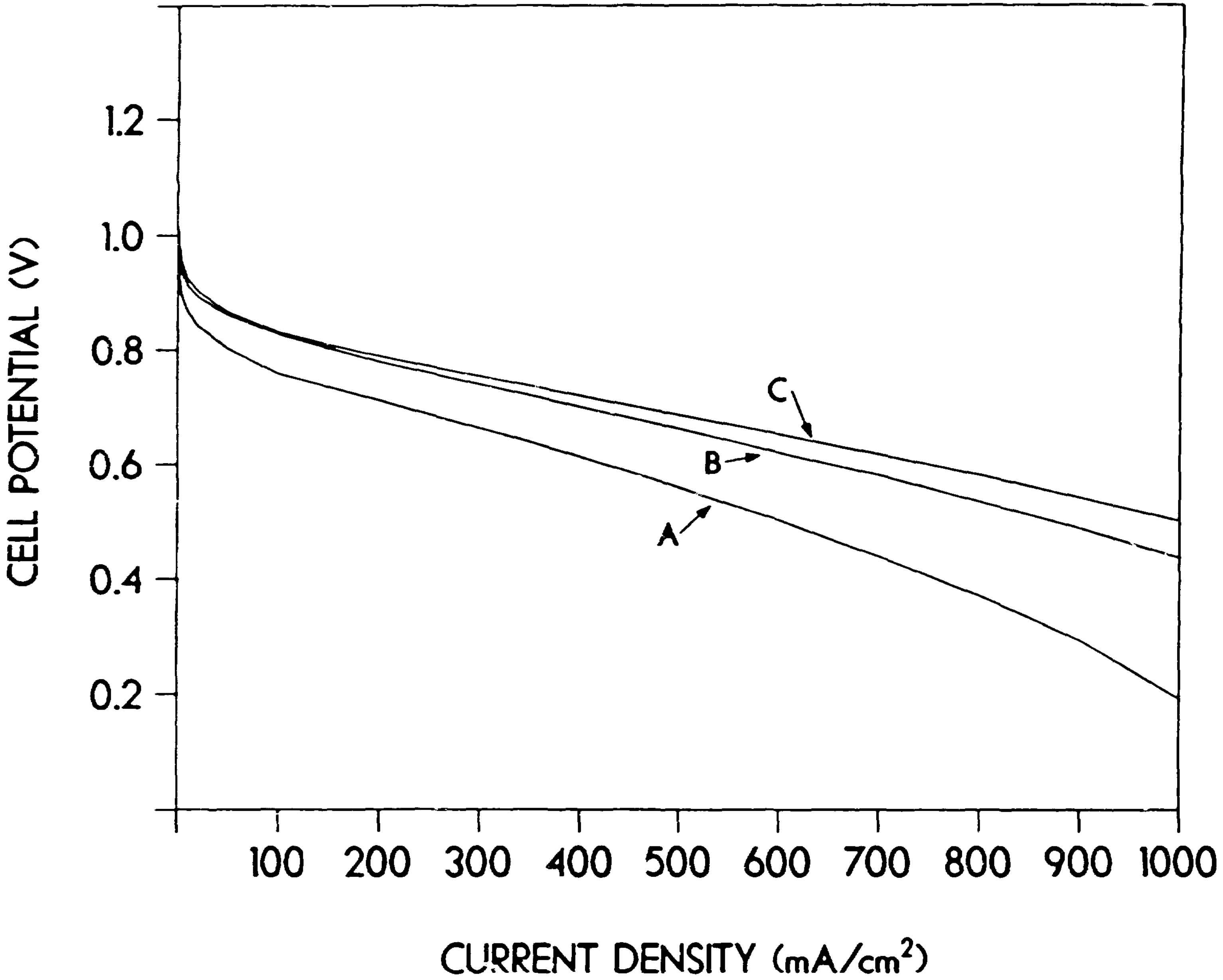

1.0
0.8
0.6
0.4
0.2
0
CELL POTENTIAL (V)
0
100
200
300
400
500
600
CURRENT DENSITY (mA/cm²)

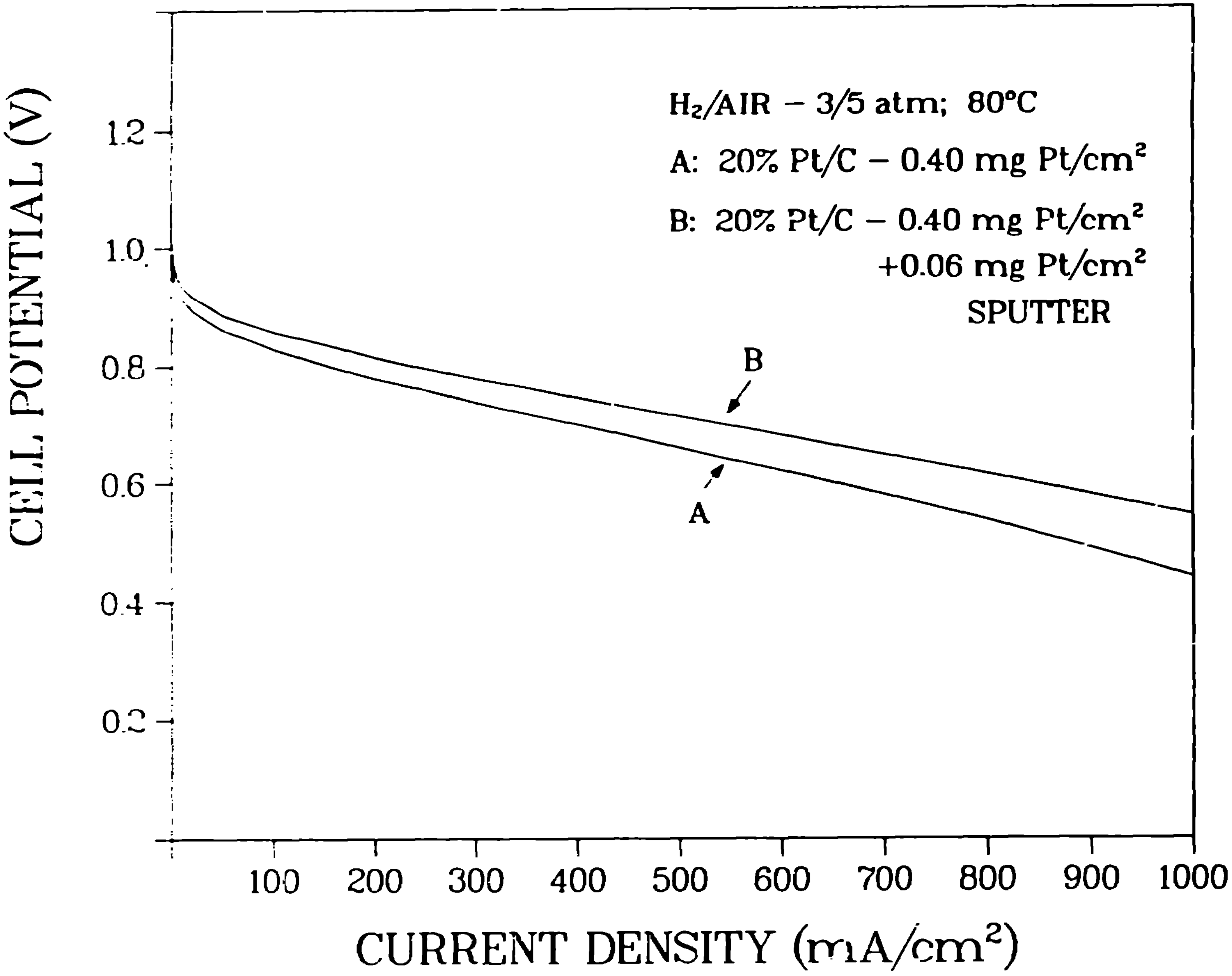
②


o :60%
* :50% - PEN76
• :40%
▫ :30%
H2/AIR - 80°C
3/5 atm
CELL POTENTIAL, V
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
100
200
300
400
500
600
700
800
900
1000
Current Density, mA/cm²


CELL POTENTIAL (V)
1.0
0.8
0.6
0.4
0.2
0
0
100
200
300
400
500
600
700
800
900
1000
CURRENT DENSITY (mA/cm^2)
a
b
c


H₂/AIR – 3/5 atm; 80°C
A: 10% Pt/C – 0.35 mg Pt/cm²
B: 10% Pt/C – 0.35 mg Pt/cm² +0.06 mg Pt/cm² SPUTTER
B
A
CELL POTENTIAL (V)
1.2
1.0
0.8
0.6
0.4
0.2
100
200
300
400
500
600
700
800
900
1000
CURRENT DENSITY (mA/cm²)


1.2
1.0
0.8
0.6
0.4
0.2
CELL POTENTIAL (V)
C
B
A
100
200
300
400
500
600
700
800
900
1000
CURRENT DENSITY (mA/cm²)


H₂/AIR – 3/5 atm; 80°C
A: 20% Pt/C – 0.40 mg Pt/cm²
B: 20% Pt/C – 0.40 mg Pt/cm²
+0.06 mg Pt/cm²
SPUTTER
B
A
CELL POTENTIAL (V)
1.2
1.0
0.8
0.6
0.4
0.2
100
200
300
400
500
600
700
800
900
1000
CURRENT DENSITY (mA/cm²)