Polarization Phenomena at the Metal/Proton Conducting Electrolyte Interphase

S. Zisekas, G. Karagiannakis, M. Ouzounidou, A. Skodra and M. Stoukides*
Chemical Engineering Department, Aristotle University and Chemical Process Engineering Research Institute, U.Box 1517, Thessaloniki 54124, Greece

Abstract. The electrokinetics at the H2 - Pd/SrCe0.95Yb0.05O3-α interphase are presented. Current-overpotential (I-η) curves were obtained at 400-700 °C and at hydrogen partial pressures from 1 kPa to 100 kPa, using a three electrode single chamber cell. The present data were assumed to be free of mass transfer effects. The anodic and cathodic charge transfer coefficients as well as the exchange current density were calculated from the experimental results by using the Butler-Volmer equation. The high and low field approximations were used to simplify the analysis.

1. Introduction
Materials that exhibit high protonic conductivity in the solid state and at elevated temperatures (T > 500 °C) are very useful in heterogeneous catalysis because they can operate at temperatures in which industrially important hydro- and dehydrogenation reactions take place [1,2]. Such proton conducting solid electrolytes are rare earth oxides or perovskites (SrZrO3 and SrCeO3) doped by a B-side acceptor, such as Yb3+ or Y3+. Although the bulk properties of these materials have been studied by a large number of investigators [3-7], much less information exists on the electrode kinetics at the electrolyte-electrode interphase [8-12].

Uchida et al. [8], used the Pt-SCY-Pt cell as a high temperature hydrogen pump. The solid state proton conductor denoted as SCY was a strontium cerate of the form: SrCe0.95Yb0.05O3-α. Experiments were conducted at temperatures between 650 and 800 °C and the limiting current was measured as a function of the partial pressure of hydrogen at the anode. Their results indicated that the limiting current density was controlled by diffusion of molecular hydrogen rather than by hydrogen atoms.

Chiang et al. [9], studied the polarization characteristics of the H2-Ag-SCY system. Experiments were conducted at temperatures between 600 and 700 °C and for 100% H2. Limiting currents were observed in most of the experiments and the dependence of exchange and limiting currents on temperature was measured. The temperature dependence of the limiting current density indicated that the surface diffusion of hydrogen atoms on Ag was rate controlling.

Bonanos and Mogensen, studied the polarization at the Ni-Sr0.995Ce0.95Y0.05O2.975 interphase at temperatures between 600 and 800 °C in various hydrogen-water vapor mixtures [10]. The limiting current density was found to depend on the partial pressure of hydrogen and to be essentially independent of the water partial pressure.

Mamellos et al. [11], studied the polarization characteristics of the H2-Pd-SCY interphase at 400 - 550 °C. A comparison of their results to those used by Chiang et al. [9] for the H2-Ag-SCY system, showed that for the limiting currents, the activation energy was substantially higher for the Ag-SCY interphase. This suggested that at low temperatures (< 500 °C) Pd would be a better choice for electrode material.

Kek et al. [12], studied the effect of electrode material on the electrode kinetics at the metal-proton conductor interphase. The solid electrolyte used was a perovskite of the form: Sr0.995Ce0.95Y0.05O2.975 and Ni, Ag, Au and Pt were
tested as electrode materials. It was found that the electrode kinetics were affected by both, the electrode material and the partial pressure of hydrogen. In all cases, limiting currents were observed in the anodic part of the polarization curve. The highest limiting current density was detected for Ni followed by Pt, Au and Ag.

In the present study, the Pd-SCY interphase is studied in a wide range of hydrogen partial pressures (1-100 kPa) and temperatures (400-700 °C). Results are compared to those obtained in previous studies.

2. Experimental Aspects
A schematic diagram of the experimental apparatus is shown in Fig. 1. The cell was placed in a 15 cm long quartz tube, closed at the bottom end. The proton conductor used was SrCe0.95Yb0.05O3-α prepared according to the procedure followed by Iwahara et al. [1]. Porous Pd films were used as electrodes. The Pd electrodes were prepared from a palladium paste (Engelhard A2985) followed by calcination at 800 °C for 2 hours. The superficial area of each electrode (cathodic or anodic) was about 7.2 cm² in both cases. The reference electrode was placed at least 0.5 cm far from the other electrodes and its area was kept as small as possible (<0.3 cm²). Details on the preparation and characterization of the Pd electrodes can be also found in a previous communication [11].

Hydrogen and the helium were of 99.999% purity. Analysis of the inlet gas was performed by on-line gas chromatography, using a 5890 Series II HP gas chromatograph equipped with a Molecular Sieve 5A column and a thermal conductivity detector (T.C.D.).

Constant voltages and currents across the cell were imposed using a 2053 AMEL Galvanostat-Potentiostat. Two differential multimeters were used in order to measure the potentials of the cell. To examine the overpotential characteristics at the electrodes, high frequency voltages were applied to the cell using a Programmable Function Generator (AMEL model 568), combined with the Galvanostat - Potentiostat and the oscilloscope (KENWOOD model DCS-8200) for measuring the high frequency current.

3. Results and Discussion
In order to calculate the ohmic-free overpotentials, an AC measurement of the resistance of the solid electrolyte was done. Figure 2 shows the dependence of the real part of impedance on the frequency of the alternating current at 700 °C and for 100% hydrogen (P_H2 = 100 kPa). The AC voltage varied between +500 mV and −500 mV. The shape of the curve is the expected one according to previous studies [12]. At high frequency, the overall resistance tends to become ohmic only (R_s). Thus, these AC data were used to calculate the IR_s contribution and consequently obtain