Oxygen Reactions at Platinum/Yttria-Stabilized Zirconia Interfaces

Anne C. Co, Shen-Jiang Xia and Viola I. Birss

Department of Chemistry, University of Calgary
Calgary, AB, Canada T2N 1N4

Introduction

Knowledge of the oxygen reduction reaction (ORR), which occurs at the gas/electrode/solid electrolyte triple-phase boundary (TPB) in solid oxide fuel cells, is essential to optimization of fuel cell performance. Over the last few decades, the kinetics and mechanism of the ORR at Pt/yttria-stabilized zirconia (YSZ) interfaces have been widely investigated using electrochemical impedance spectroscopy and dc polarization techniques. In most of these studies, experiments have been carried out using Pt paste as the working electrode, in a half cell configuration. Inductive behavior was reported for the ORR at temperatures above 900 ^{o}C [1-3]. It has been suggested that this is due to either an increase in the activation of the Pt/YSZ interface [1] while others have suggested the formation of an electronically conductive YSZ subsurface region [2]. However, the nature and origin of the inductive effect is still under great debate.

Results

In the present work, both oxygen reduction and evolution were investigated at temperatures between 450 - 950 ^{o}C, using a half cell setup and current interruption methods for IR correction. Various electrode configurations were examined, with the optimum involving the reference electrode located on the same side as the working electrode, both on opposite sides of the YSZ disc from the counter electrode. Cyclic voltammetry, run between 0 V and –0.8 V vs. Pt, reveals predominantly capacitive behavior for both reaction directions at temperatures below 700 ^{o}C, an inductive response at above 780 ^{o}C, and a mixed behavior between 700 and 780 ^{o}C. These results show that the inductive behavior is very temperature dependent, perhaps arising only when high currents (> 10 mA/cm^2) are passed at higher temperatures. As well, the CV response at any temperature remains the same, even after excursions to higher or lower cell temperatures. This indicates that irreversible morphological/structural changes in the TPB, which may occur as a function of temperature or positive/negative polarization, cannot be related to the inductive response of this system.

At 800 ^{o}C, the effect of scan rate on the CV response was also examined. Surprisingly, it was found that the current increased with decreasing scan rates, i.e., at –0.8 V (vs. Pt pseudo-reference), a current density of 80 and 125 mA/cm^2 were observed for scan rates of 50 and 5 mV/s respectively. This unusual effect will be discussed in more detail.

Impedance data collected at the OCP yielded the charge transfer resistance, R_{ct}, and the double layer capacitance, C_{dl}, at the Pt/YSZ interface. R_{ct} was found to decrease, as expected, with increasing cell temperature and was used to calculate the reaction exchange current density. C_{dl} was used to determine the relative TBP interfacial areas of different Pt paste electrodes, by referencing to the measured capacitance of a press-contacted Pt grid electrode of known surface area.

At high temperatures and at applied potentials between 0 and –0.17 V, the ac impedance response is typical of an RC circuit, while at potentials less than -0.2 V, inductive behavior was observed during the ORR at low frequencies, in agreement with what is seen by CV and reported by others [1]. A more detailed discussion of these CV and ac impedance data, and in particular the inductive behavior, will be given in the presentation.

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References

1. T. Jacobsen, B. Zachau-Christiansen, L. Bay, M. Juhl Jorgensen, *Electrochim. Acta*, 46 (2000) 1019.
2. E.J.L. Schouler and M. Kleitz, *J. Electrochem. Soc.*, 134 (1987) 1045.
3. T.M. Gur, I.D. Raistrick, R.A. Huggins, *J. Electrochem. Soc.*, 127 (1980) 2620.