

Importance of electrode/zirconia interface morphology in high-temperature solid electrolyte cells

TURGUT M. GÜR, ROBERT A. HUGGINS

Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, USA

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The role of electrode/electrolyte interface morphology in the overall polarization behaviour of high-temperature solid electrolyte cells has been studied. Carefully prepared and polished scandia-stabilized zirconia discs with sputtered platinum electrodes were examined using electron microscopy and electrical polarization techniques. Initially non-porous sputtered platinum electrodes were 'conditioned' by a progressive treatment to generate artificial porosity. This eliminated subsequent time-dependent changes in the interface-related impedance of such cells. After prolonged use, the anode and cathode morphologies were found to be distinctly different from each other.

1. Introduction

Solid solutions of alkaline or rare earth oxides in zirconium dioxide have the cubic fluorite structure where the oxygen anions occupy tetrahedral sites in a face-centred cubic array of cations. The presence of the aliovalent species leads to the formation of a large number of oxygen vacancies to preserve charge neutrality. Motion of these oxygen vacancies is responsible for the high ionic conductivity exhibited by these solids at elevated temperatures.

The first evidence of the importance of electrode morphology was reported by Karpachev and Filyaev [1], who found that increasing the length of the three-phase boundary between oxygen in the gas phase, platinum electrode material and a zirconia electrolyte by scratching the electrode with a sharp implement significantly reduced cathodic polarization effects. If oxygen incorporation into the electrolyte occurs predominantly at or near this three-phase boundary, increasing the boundary length should provide readier access. Similarly, Bauerle [2] suggested heavy current treatments for initially non-porous electrodes to induce artificial porosity. This may also increase the length of the three-phase boundary, leading to reduced interfacial impedance and polarization effects.

The effects of such current treatments, combined with heat treatment and annealing procedures, were studied by Pizzini *et al.* [3, 4] using electron microscopic techniques to observe various platinum electrode surfaces. It was found that changes in the electrode morphology affect the current–voltage characteristics of these high-temperature cells. More recently, Pizzini *et al.* [5] studied the effect of cell geometry on polarization behaviour of platinum electrodes on zirconia. Model electrochemical cells with various electrode configurations were investigated and it was shown that anodic impedances can be negligible at platinum electrodes, but only above 750°C. Similar observations have also been made in this laboratory [6, 7] where porous platinum electrodes on stabilized zirconia used in an O₂ environment showed characteristic changes in behaviour at about 700°C. This was believed to be related to the platinum electrode surface undergoing a reconstruction process.

The present paper relates some of the observed polarization characteristics of high temperature zirconia cells to the electrode–electrolyte interface morphology, as studied by electron microscopy. The effects of prolonged exposure to high temperatures and currents will also be discussed.

2. Experimental aspects

The zirconia high-temperature cell used in this work consisted of a calcia-stabilized zirconia hollow support tube with a 8 mol % $\text{Sc}_2\text{O}_3 \cdot \text{ZrO}_2$ disc, 1.3 cm in diameter, sealed onto one end by a suitable glass seal. The advantage of this disc-to-tube geometry is that it allows careful preparation of the electrode/electrolyte interface and study of its morphology at any desired stage by electron microscopy. The disc was thinned to about 0.6 mm and polished to a mirror shine using 1 μm diamond paste. It was ultrasonically cleaned in organic solvents and then heated for a few hours in air at 800°C to remove moisture and possible carbonaceous contaminants. An electron micrograph of the surface of such a zirconia disc carefully prepared under these conditions is shown in Fig. 1. With the exception of a few voids the microstructure looks very dense and the grain boundaries seem to be free of second-phase precipitates.

The polished faces of the scandia-stabilized zirconia disc were sputter etched initially for 5 min under 60 μm of argon pressure. It is found that this simple procedure significantly improves the bonding between sputtered platinum electrodes and the zirconia substrate. Further roughening of the surface either by mechanical means or by longer argon sputter etching does not seem to result in improved bonding. A layer of platinum about 1 μm thick and with a geometric area of 0.66 cm^2 was then sputtered onto each of the carefully polished faces of the zirconia disc, using a 99.99% platinum source and a potential of 2 kV under 30 μm of argon pressure.

The disc was then sealed onto the end of the calcia-stabilized zirconia support tube using a finely ground (< 270 mesh) powder of albite ($\text{NaAlSi}_3\text{O}_8$) glass, dispersed in a viscous organic vehicle. A single application of this mix, followed by firing at 1150°C in air, was sufficient to obtain a vacuum-tight seal between the disc and the tube which would endure prolonged use. In fact, such a seal was still found to be leak-tight after 11 months of continuous use under current-carrying conditions and frequent thermal cycling between 900 and 600°C, with occasional excursions down to room temperature.

Four spring-loaded platinum wire contacts

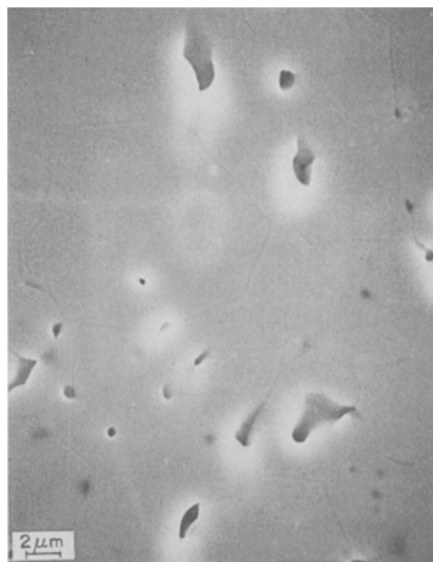


Fig. 1. Electron micrograph of surface of zirconia disc after diamond polishing and cleaning.

(two on each side) were used for the electrical connections. One pair of these leads was used for carrying the current, while the other pair was used to monitor the potential drop across the cell. Since the latter pair did not carry any current, no voltage drop due to contact resistance was present.

3. Results and discussion

The microstructure of the electrode/electrolyte interface plays an important role in influencing the rates of the various phenomena which cause the polarization behaviour of zirconia-based high temperature cells. Besides slow interfacial reaction kinetics and various mass transport limitations, an important and common source of potential drop in such cells is due to geometrically-related 'constriction' resistance. This arises when the bonding between the electrode and the electrolyte is incomplete and patchy, rather than uniform and complete across the interface. Under these circumstances the total current through the cell is 'constricted', and flows only through specific local spots at the interface. If the current is forced to flow through a small fraction of the total available interfacial area, the current density at these particular points can be very large. This may cause hot spots which

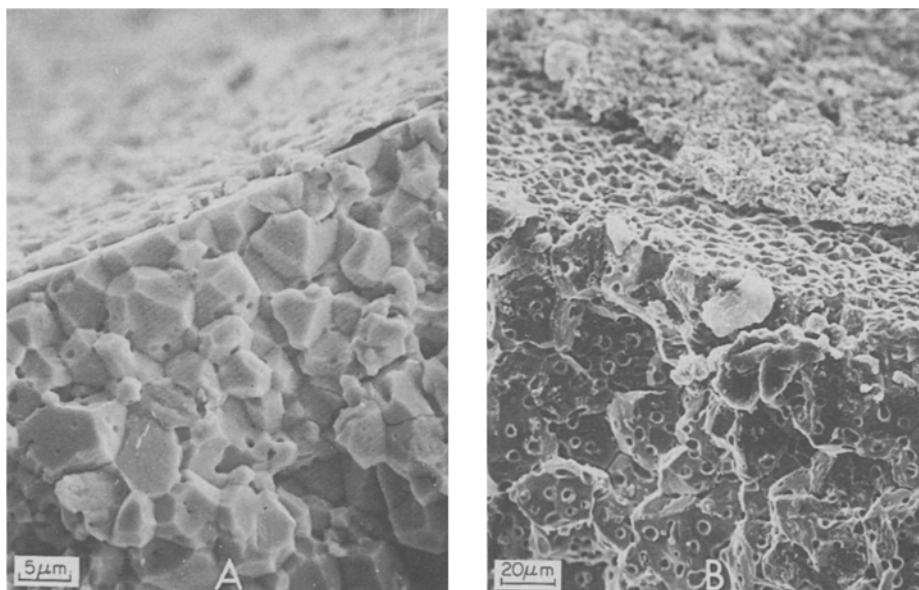


Fig. 2. Cross-sectional views obtained by electron microscopy: (A) sputtered platinum layer on top of polished zirconia; (B) platinum layer produced by paste technique on top of unpolished, but cleaned, commercial zirconia tube.

can lead to irreversible changes in the interface morphology and significant impedances. The undesirable effects of constriction resistance can be minimized by providing good, continuous and uniform bonding between the electrode and the zirconia. It was frequently observed in this study that carefully prepared, polished and argon-etched surfaces generally result in improved bonding.

The electron microscopy pictures of Fig. 2 provide cross-sectional views of two contrasting platinum/zirconia interfaces. Fig. 2A shows a carefully prepared interface between polished 8 mol % $\text{Sc}_2\text{O}_3 \cdot \text{ZrO}_2$, occupying the lower half of the picture, and a sputtered platinum electrode, 400 Å thick, at the upper left hand side. The zirconia microstructure is dense and there seem to be no second-phase particles at the grain boundaries. The platinum/zirconia interface is very sharp and planar, with almost no visible surface roughness. The platinum layer is bonded to the zirconia very uniformly throughout the interface, which minimizes the electronic constriction resistance. Note that the contact is virtually void-free, although the conditioned platinum electrode layer itself appears to be quite porous.

This interface differs appreciably from that

shown in Fig. 2B, in which platinum paste electrodes were deposited using Hanovia platinum paste # 6926. A sequence of two such coatings produces a porous and adherent layer a few micrometres thick. No special interface preparation procedures were applied to this interface except that the tube, as received from the vendor, was cleaned with an organic solvent and heated in air at 800°C prior to electroding. Both the roughness of the electrolyte surface and the non-planar nature of the overall interface are visible. The irregularities, voids and defects at the interface give rise to contact area much smaller than the macroscopic geometrical shape. This may result in appreciable interfacial impedance due to constriction resistance.

The microstructure of a freshly sputtered platinum electrode on a finely polished surface of a scandia-stabilized zirconia disc is shown in Fig. 3. The as-deposited platinum layer is dense and virtually non-porous. Hence, one expects to observe severe polarization effects associated with very slow diffusion of oxygen through the dense platinum layer before incorporation into the zirconia electrolyte. Indeed, the current-voltage characteristics of a zirconia cell operating in zero grade O_2 at 600°C with a freshly sputtered platinum electrode show such an

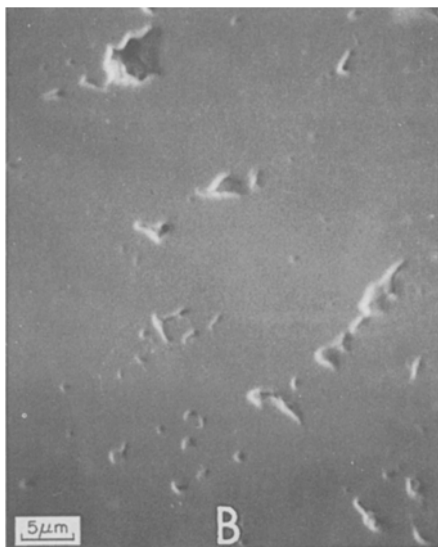


Fig. 3. Microstructure of freshly sputtered platinum electrode on polished zirconia surface.

effect. This is illustrated in Fig. 4 where the steady state current, I_{ss} , is plotted against the applied voltage, E_{appl} . More interesting, however, is the fact that large hysteresis is commonly observed with these fresh electrodes when the voltage is cycled up and down again. This large hysteresis effect indicates that significant morphological

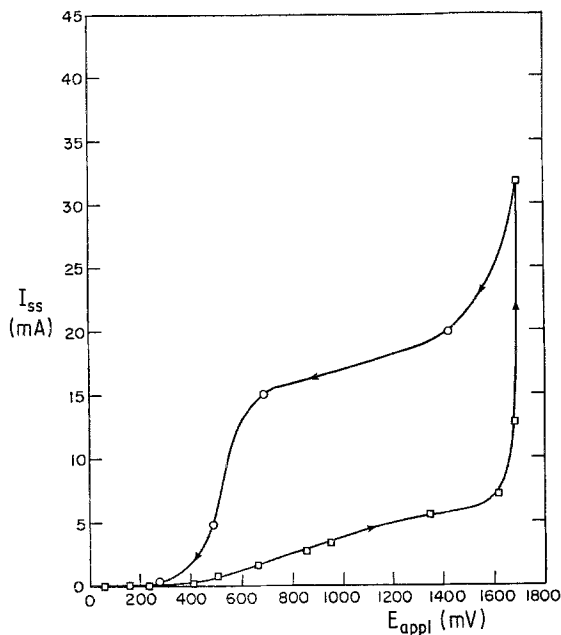


Fig. 4. Current-voltage characteristics of zirconia cell with freshly sputtered platinum electrode, $0.4\ \mu\text{m}$, at 600°C and with $P_{\text{O}_2} = 1.0\ \text{atm}$. \square , Ascending voltage; \circ , descending voltage.

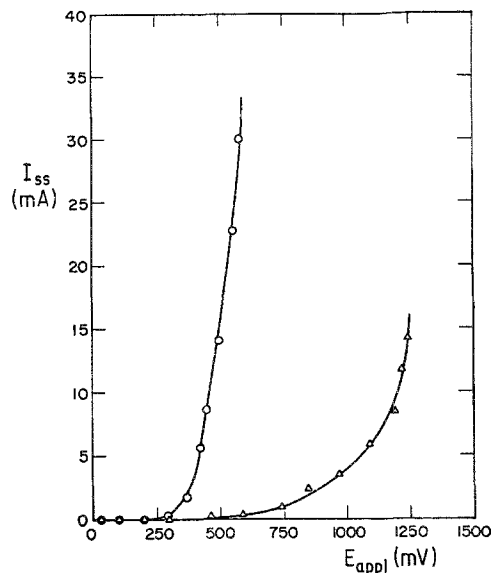


Fig. 5. Comparison of polarization behaviour of freshly sputtered electrode and electrode after prolonged use, at 600°C and with $P_{\text{O}_2} = 1\ \text{atm}$. Δ , Untreated, fresh platinum electrodes, $1\ \mu\text{m}$; \circ , heat and progressive current treated platinum electrodes, $1\ \mu\text{m}$.

changes take place during such voltage, and related current, cycling.

Similar results were obtained with thicker sputtered platinum electrodes. Fig. 5 compares the polarization behaviour of a fresh electrode, $1\ \mu\text{m}$ thick, with the same electrode after prolonged use which included exposure to high temperatures under current-carrying conditions. The dramatic decrease in the electrode impedance with use is obvious.

Sputtered platinum electrodes which are initially non-porous gradually become quite porous as more and more oxygen is forced through the platinum layer. Oxygen discharged at the anode side electrode/electrolyte interface forms small gas pockets under the dense platinum layer. These eventually burst and rupture the overlaying platinum layer, thus generating artificial porosity.

An 'electrode conditioning' technique was developed in the present study which involved a progressive treatment under potentiostatic conditions in air at a sufficiently high temperature. The objective was to generate the necessary porosity in a gradual and gentle manner. The external voltage applied to the cell was increased in small increments and the current was allowed to stabilize at each step. This treatment was also

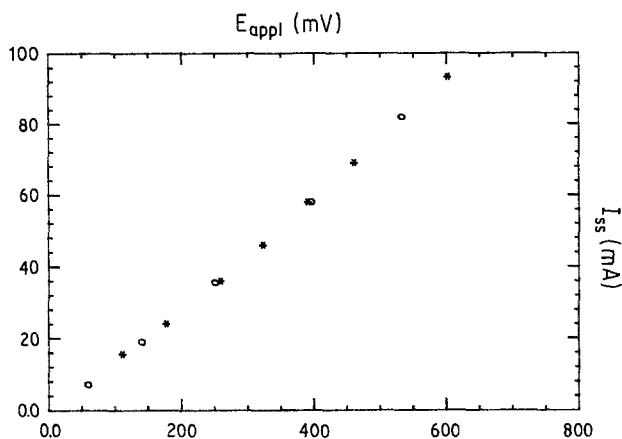


Fig. 6. Illustration of lack of hysteresis after conditioning treatment. *, Ascending voltage; O, descending voltage.

performed in the opposite current flow direction. It was repeated as many times as necessary until no hysteresis was observed between ascending and descending voltage measurements.

It was found that two complete cycles of gradual ascending and descending voltage between zero and 2 V at 900°C generally sufficed to obtain reproducible current-voltage characteristics, with virtually no remaining hysteresis. The lack of hysteresis after such a procedure is illustrated in Fig. 6. No further changes in current-voltage behaviour are observed upon additional cycling of an electrode that has undergone such a conditioning treatment.

We have found that this more gentle electrode conditioning technique is less apt to cause undesired mechanical failure of the electrolyte than the 'heavy current treatment' advocated by Bauerle [2], who suggested the use of current densities of about 1 A cm^{-2} . Although these two techniques are mechanistically the same, most of our attempts to induce artificial porosity by the 'heavy current treatment' of Bauerle, even under much less severe conditions than he suggested (e.g. with a current of 140 mA cm^{-2}), resulted in eventual mechanical failure. This technique imposes an oxygen pressure on the anode side so high that the force acting upon the platinum layer is too large to be accommodated by creep displacement or self-diffusion of platinum atoms, and either severe discharge blocking or mechanical rupturing of the platinum layer occurs. Oxygen depletion at the cathode electrode/electrolyte interface also occurs, since replenishment of oxygen at that interface to compen-

sate for the ionic flux in the electrolyte is limited by the slow transport of oxygen through the bulk platinum. The chemical potential of oxygen at the interface decreases to low values, and this causes the onset of electronic conduction in the zirconia. Prolonged treatment results in a visible blackening of the zirconia, starting at the cathode and progressing toward the anode.

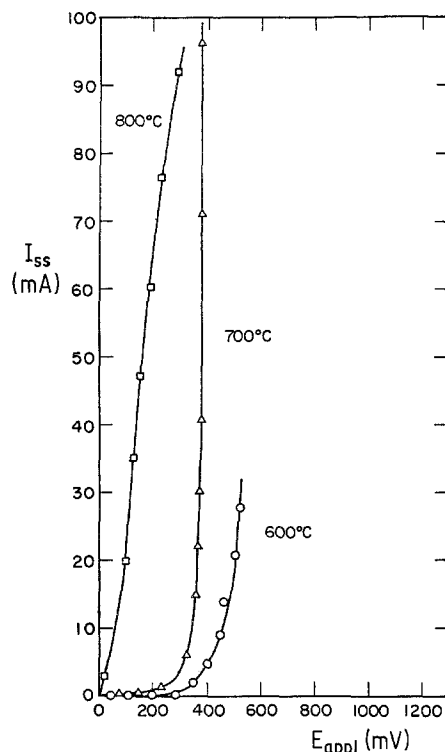


Fig. 7. Current-voltage behaviour of sputtered platinum electrodes conditioned by progressive method. $P_{\text{O}_2} = 1.6 \times 10^{-2} \text{ atm}$.

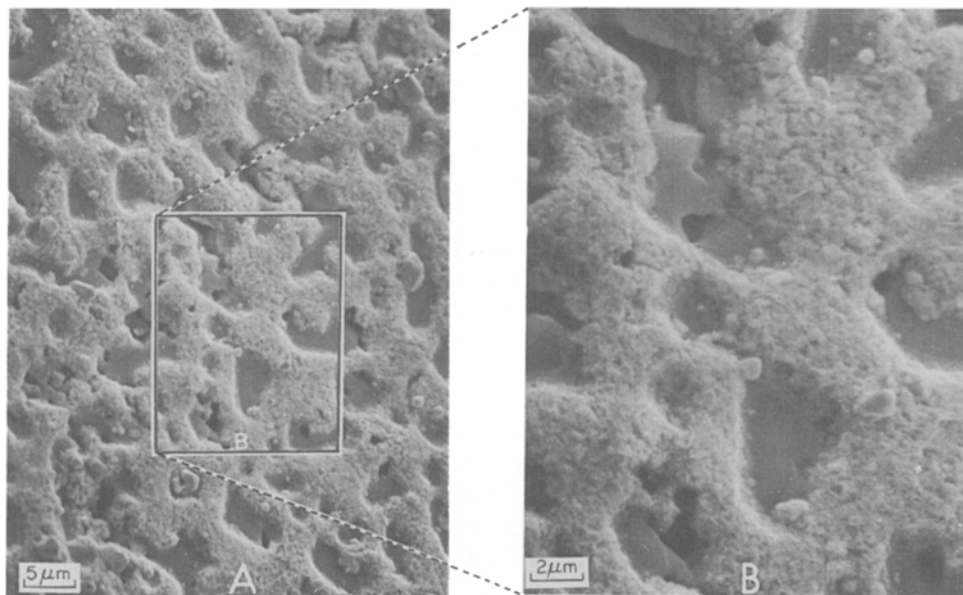


Fig. 8. Scanning electron microscope picture of cathode side of zirconia disc after 11 months of continuous use at 900°C.

Eventually, the bulk of the zirconia completely blackens and mechanical failure ensues.

The current–voltage behaviour of these sputtered platinum electrodes, conditioned by the progressive treatment described above, is illustrated in Fig. 7. At low temperatures and low voltages, the behaviour is characterized by a polarization effect which is probably related

to the slow diffusion of oxygen on platinum, as suggested earlier [6]. For voltages larger than 400 mV, the current–voltage characteristics become nearly reversible. At temperatures over 800°C, the behaviour is limited primarily by the ohmic resistance of the bulk electrolyte.

Electron microscopy was used to study the changes in morphology of these interfaces. After

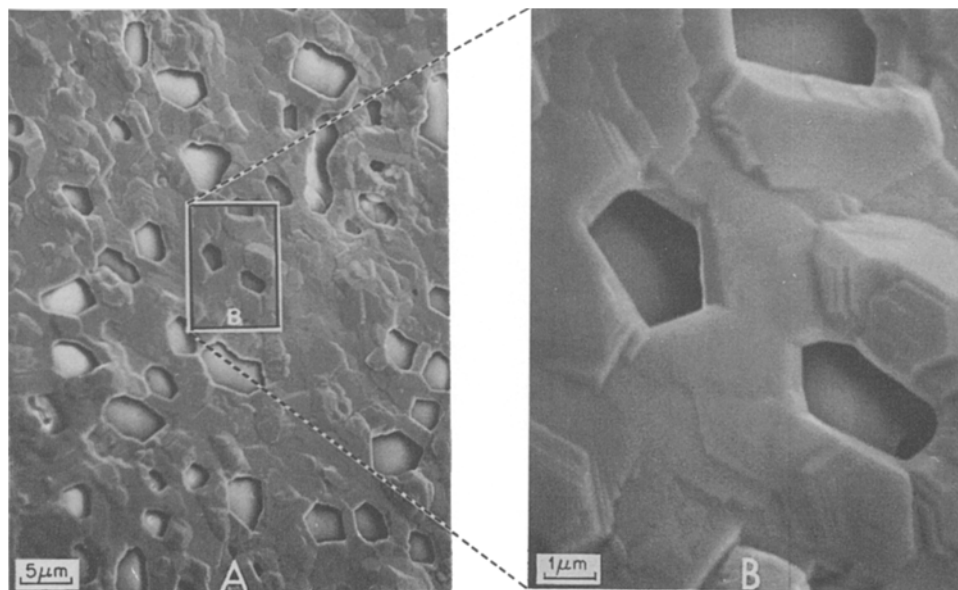


Fig. 9. Scanning electron microscope picture of anode side of zirconia disc after 11 months of continuous use at 900°C.

more than 11 months of continuous use under current-carrying conditions in various oxygen environments and after frequent thermal cycling up to 900°C, a zirconia disc was detached from its support tube. Scanning electron microscopic pictures of the cathode and anode side electrodes are shown in Figs 8 and 9, respectively. Despite the fact that these electrodes initially had the same microstructural morphology, they became quite different after prolonged use. Furthermore, these initially non-porous electrodes developed about 30% porosity.

The cathode side electrode of Fig. 8 has a very fine crystallite size, estimated to be about 1000 Å or less. Its visual appearance became black (i.e. platinum black). On the other hand, the anode electrode maintained the usual shiny metallic colour of platinum. The zirconia grains underlying the platinum electrodes show distortion and grain boundary separation at the cathode side, but seem to be smooth and planar at the anode side. The platinum on the anode side developed well-defined ledges and terraces, with a grain size much larger than that at the cathode side. X-ray diffraction analysis of the anode indicates a very strong preferred (1 1 1) orientation normal to the surface. The freshly sputtered platinum also shows a (1 1 1) preferred orientation, but the (1 1 1) and (2 2 2) intensities observed for fresh electrodes are not nearly so large as those observed for the used anode of Fig. 9.

There have been prior reports that platinum surfaces undergo faceting upon prolonged heating in oxygen. For example, the surface of platinum foil developed crystal planes with a (1 1 1) orientation after prolonged heating in O₂ during chemisorption studies [8]. Such changes have been interpreted as due to increased anisotropy of the surface energy and/or increased surface diffusion caused by the presence of adsorbed species [9]. Another possibility is facilitated transport through the formation of volatile oxides of platinum. These effects, coupled with the electrochemical dynamic influence of oxy-

gen pumping, may have combined to cause the changes in the morphology of the electrode/electrolyte interfaces observed in this work.

4. Conclusions

The electrode/electrolyte interfaces must be prepared with great care if reproducibility and reliability are desired in their use in high-temperature solid electrolyte cells. It has been found that sputtered platinum electrodes are virtually non-porous and are subject to drastic, time-dependent morphological changes under current-carrying conditions at high temperatures. After prolonged use under current-carrying conditions the anode and the cathode side electrodes show distinctly different microstructures. An electrode conditioning procedure has been developed to create artificial porosity and help minimize subsequent time-dependent morphological changes.

Acknowledgements

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