

Zr/(Zr + Ti) = 0.5 concentration. The Pb content was strongly growth-temperature dependent, which decreased with an increase of temperature and was significantly deficient for depositions at temperatures above 600°C. The dielectric constant increased with an increase of growth temperature to a maximum of about 160, while the leakage current density decreased to about 2×10^{-8} A/cm² at 5×10^5 V/cm for growths at 550°C. At the optimum growth temperature (in this work 550°C) the remnant polarization was 5.1 μ C/cm² and the coercive field was 78 kV/cm.

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Interfacial Polarization Characteristics of Pt|BaCe_{0.8}Gd_{0.2}O₃|Pt Cells at Intermediate Temperatures

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ABSTRACT

Impedance spectroscopy of Pt|BaCe_{0.8}Gd_{0.2}O₃|Pt cells indicates that both mass and charge-transfer influence the electrode kinetics of the interfacial reactions. Charge-transfer appears to dominate the electrode kinetics when the partial pressure of oxygen is sufficiently high, whereas mass transfer seems to be rate limiting at low oxygen partial pressures. Under the influence of an applied dc bias, concentration polarization at the cathode is more severe than that at the anode. In a H₂-containing atmosphere, the electrode kinetics seem to be limited primarily by charge-transfer. Further, water vapor has a significant effect on the electrode kinetics. In an O₂-containing atmosphere, the introduction of 3 volume percent (v/o) H₂O dramatically increases the interfacial resistances. In contrast, in a H₂-containing atmosphere the presence of 3 v/o H₂O significantly reduces the interfacial resistances. Overall, the interfacial resistances are the factors limiting the performance of intermediate-temperature solid oxide fuel cells based on BaCe_{0.8}Gd_{0.2}O₃ electrolytes. Minimizing polarization resistance arising from both charge and mass transfer is the key to achieving high-performance solid oxide fuel cells.

Introduction

It is well recognized that the electrode-electrolyte interfaces become the factors limiting the performance of solid-state electrochemical devices as the thickness of the electrolyte or the operating temperature is reduced. BaCe_{0.8}Gd_{0.2}O₃ (BCG) has been studied as an alternative electrolyte for solid oxide fuel cells (SOFCs) to be operated at 600 to 800°C because of its high ionic conductivity at these temperatures.¹⁻⁵ However, preliminary studies of a fuel cell based on an 1 mm thick BCG electrolyte (H₂, Pt|BCG|Pt, air) indicate that the electrode resistance is comparable to the electrolyte resistance at 700°C and is about four times larger than the electrolyte resistance at 600°C.⁵ For thinner electrolytes, especially in the case of thin-film electrolytes, the interfacial resistances are likely to be the factors limiting cell performance at intermediate temperatures (600 to 800°C). In order to most effectively

improve the performance of SOFCs based on BCG electrolytes, it is necessary to gain a deeper understanding of the electrochemical behavior of the electrode-electrolyte interfaces.

Experimental

Pellets of BCG electrolyte (15 mm diam, 1.2 mm thick) were prepared using a conventional ceramic processing procedure described elsewhere.⁵ The pellets were ground flat before applying electrodes. Cells of Pt|BCG|Pt were prepared by screen printing Pt paste (Heraeus OS2) onto both faces of each BCG electrolyte pellet and subsequent firing at 1300°C for 10 min. This firing temperature appears to be the minimum necessary to achieve sufficient binding between the electrode and the electrolyte.

Both three-electrode and four-electrode configurations were used for electrochemical measurements as described elsewhere.⁵ Electrochemical measurements of the cells, including impedance spectroscopy and dc polarization

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measurements, were conducted in different atmospheres (including fuel cell conditions) and at temperatures varied from 600 to 800°C, which is the preferred operating temperature range of BCG-based solid oxide fuel cells (SOFCs). Electrochemical measurements in a uniform atmosphere containing different partial pressures of oxygen, hydrogen, and water vapor were performed by placing the cell in a tube furnace flowing with the gas of interest. The partial pressures of O₂ and H₂ were controlled by diluting O₂ (or air) and H₂, respectively, with argon. An oxygen sensor based on yttria-stabilized zirconia (YSZ) was used to monitor the actual partial pressure of oxygen in the gas mixtures. The partial pressure of water vapor was controlled by adjusting the temperature of a water bubbler through which a carrier gas was passed to pick up water vapor. Electrochemical measurements under fuel cell conditions were performed on cells sealed on a support alumina tube with glasses such that the cell is exposed to air on one side and to a fuel gas on the other side, as depicted in a previous paper.⁵ Based on these measurements, the dependence of interfacial resistances on temperature and atmosphere was determined to characterize the polarization behavior of each interface under various conditions.

Impedance spectroscopy.—A computerized impedance analysis system, consisting of an electrochemical interface (Solartron 1286) and a frequency response analyzer (Solartron 1255), was used for impedance measurements. In a Nyquist presentation of impedance spectra measured from the solid electrolyte cells in this study, the intercept of the impedance loop with the real-axis at high frequencies corresponds to the resistance of the bulk electrolyte, R_b (since the lead resistance is much smaller than R_b), whereas the intercept of the impedance loop with the real-axis at low frequencies corresponds to the total resistance of the cell, R_T .⁷ If the electrolyte is an ionic conductor with an ionic transference number of one, the polarization resistance of the interface, R_p , is simply the difference between R_T and R_b (i.e., $R_p = R_T - R_b$). However, BCG electrolytes exhibit mixed electronic-ionic conduction in oxygen-rich atmospheres.¹⁻⁵ In this case, R_p can be determined as follows⁷

$$R_p = \frac{R_b(R_T - R_b)}{t_i[t_i R_T - (R_T - R_b)]} \quad [1]$$

where t_i is the ionic transference number, which can be determined from impedance and open-circuit voltage (OCV) measurements under similar conditions⁷

$$t_i = 1 - \frac{R_b}{R_T} \left(1 - \frac{V_{oc}}{E_N} \right) \quad [2]$$

For a symmetrical cell immersed in a uniform atmosphere, it is reasonable to assume that the two electrodes contribute equally to the total impedance and, thus, the polarization resistance of each interface can be determined from impedance spectra of the full cell measured in a two-probe configuration. For an asymmetrical cell exposed to one gas on one side and to another gas on the other side, however, either three- or four-probe configurations must be used in impedance measurements in order to separate the two interfaces and to characterize the resistance of each interface.

The amplitude of the ac perturbation used in impedance measurements was usually quite small (e.g., 10 mV). In the absence of an applied dc bias, the obtained R_p value is directly related to the exchange current density i_0 . The dependence of the R_p or i_0 on partial pressure of oxygen can be used to identify the rate-limiting step of an interfacial process.⁷⁻⁹

On the other hand, under the influence of an applied dc bias, the determined R_p can be used to construct polarization curves from which the anodic and cathodic transference numbers (α_a and α_c) can be determined. Therefore,

impedance spectra measured under the influence of an applied dc bias can offer useful information on the effect of an applied voltage on electrode kinetics under conditions closer to practical.

DC measurements.—Both potentiostatic and galvanostatic modes were used for dc polarization measurements. The connections for measurements in both cases were essentially the same. In a potentiostatic (galvanostatic) mode, the voltages across (currents passing through) the cell were applied through the two principal electrodes while the currents passing through (voltages across) the cell were measured using the same electrodes. In the meantime, the voltages across the two half-cells were acquired, i.e., the voltages between either of the principal electrodes and a reference electrode, V_{ca-re} and V_{an-re} , where the subscripts ca, an, and re denote cathode, anode, and reference electrode, respectively. Whereas both the three-electrode and the four-electrode configurations could be used for measurements in a uniform atmosphere, the four-electrode configuration must be used for measurements of cells under a gradient in chemical potential, as in the case of fuel cell conditions.

The measured half-cell voltage, V_{ca-re} (or V_{an-re}), contains two terms: the interfacial overpotential, η_c (or η_a), and the ohmic drop across the electrolyte of the corresponding half-cell. The ohmic drop of the electrolyte can be determined from the measured current, ionic transference number of the electrolyte, and the parameters obtained from impedance spectra. Thus, the overpotentials of the cathode-electrolyte and the anode-electrolyte interfaces can be separated, as discussed in detail elsewhere.⁶

Results and Discussion

Measurements in oxygen and oxygen-containing atmosphere.—In an oxygen-containing atmosphere, the ionic transference number of a BCG electrolyte depends strongly on partial pressure of oxygen. At 722°C, for instance, t_i varies from 0.53 in oxygen to 0.90 in argon with $p_{O_2} = 5 \times 10^{-5}$ atm. For a given atmosphere, t_i changes slightly with temperature, as described in detail elsewhere.⁵ From the t_i values reported earlier⁵ and the R_T and R_b values determined from impedance spectra, the interfacial resistance of a cell may be calculated using Eq. 1. Shown in Fig. 1 are the interfacial resistances of a Pt|BCG|Pt cell as a function of temperature in oxygen-argon mixtures of different partial pressures of oxygen. The slopes of the plots of $\log(1/R_p)$ vs. $1000/T$, which are directly proportional to the activation energies for the interfacial processes, changes with partial pressure of oxygen. Higher activation energies (larger slopes) were observed in atmospheres containing higher partial pressure of oxygen, indicating a stronger dependence of the interfacial processes on temperature. These data are replotted in Fig. 2 to show the dependence of interfacial resistance on partial pressure of oxygen at each constant temperature. The slope of the $\log(1/R_p) - \log(p_{O_2})$ plots varies from about 0.30 at high oxygen partial pressures to about 0.45 at low oxygen partial pressures. This behavior suggests that, in the p_{O_2} range studied, both charge-transfer and mass transfer influence the electrode kinetics. However, at high oxygen partial pressures, the overall electrode kinetics were primarily controlled by charge-transfer, since the slopes of the $\log(1/R_p) - \log(p_{O_2})$ plots are close to 1/4. As p_{O_2} decreases, the effect of mass transfer became stronger. At very low oxygen partial pressures, the overall kinetics were primarily controlled by mass transfer, since the slopes are close to 1/2.⁷⁻⁹

The impedance spectra measured under the influence of an applied dc bias provides further information about the rate-limiting processes at interfaces. In general, an applied dc bias enhances the charge-transfer and hence reduces the charge-transfer resistance. However, it may increase the mass-transfer resistance due to the induced concentration polarization.^{5,9-11} Therefore, an increase in R_p with dc bias implies considerable concentration polarization near the interfaces (either in the gas phase or in the solid phase, or both), suggesting that mass transfer is rate

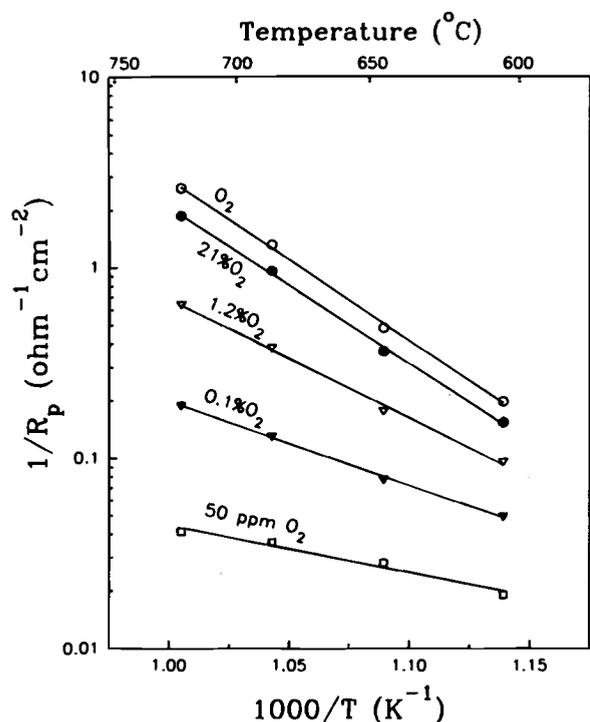


Fig. 1. Temperature dependence of the interfacial polarization resistance of a Pt|BCG|Pt cell immersed in oxygen-argon mixtures of different partial pressures of oxygen, as determined from impedance spectra.

limiting.^{5,9} In contrast, a decrease in R_p as dc bias increases is usually evidence of field enhancement of charge-transfer processes and thus implies that charge-transfer is rate limiting.^{10,11} Figure 3 shows a series of impedance spectra of a Pt|BCG|Pt cell measured at 722°C in O_2 under different dc biases. Note that the spectra of the anodic side half-cell and the cathodic side half-cell were actually taken from the same half-cell (by reversing the polarity of the two major electrodes) in order to avoid geometrical asymmetry of the two half-cells. In the anodic direction, interfacial resistances decreased as bias increased due to enhanced charge-transfer. In the cathodic direction, the

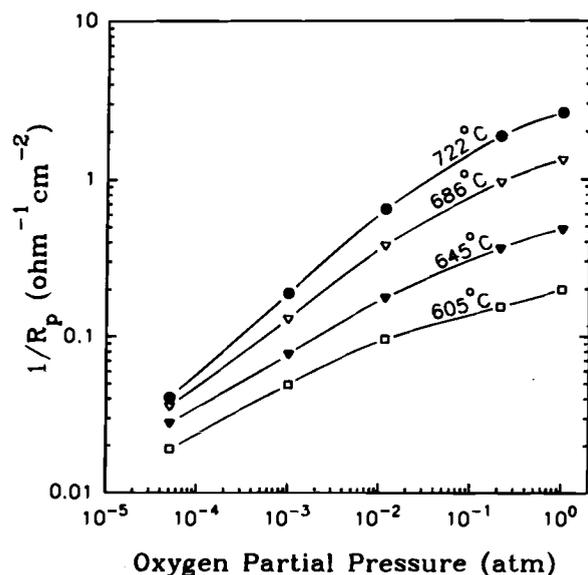


Fig. 2. Dependence of interfacial polarization resistance of a Pt|BCG|Pt cell on partial pressure of oxygen at different temperatures.

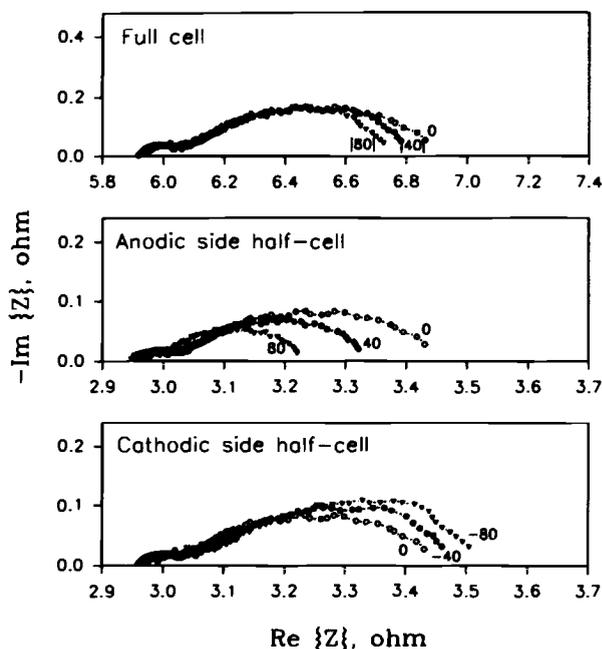


Fig. 3. Impedance spectra of a Pt|BCG|Pt cell measured in O_2 at 722°C under the influence of an applied dc bias. The numbers by the spectra represent the applied dc bias in mV (the electrolyte thickness was 0.11 cm and the electrode area was 0.385 cm^2).

total resistance of the half-cell appeared to increase as bias increased. However, the interfacial resistance of the cathode remained almost unchanged if the slight increase in the electrolyte resistance of the half-cell was taken into account. The shifts in the electrolyte resistance of the half-cell under the influence of an applied dc bias was explained in terms of the presence of a gradient in the electronic conductivity across the electrolyte induced by the gradient in oxygen partial pressure, noting that BCG is a mixed ionic-electronic conductor in an oxygen-rich atmosphere.⁵ The sum of the spectra of the two half-cells at each applied dc bias represents the impedance spectrum of the full cell. Figure 3 shows that the total resistance of the full cell decreases slightly as the amplitude of the dc bias increases. Since the electrolyte resistance of the full cell remains nearly unchanged, the decrease in total resistance results from a decrease in the interfacial resistance. This result suggests that the effect of the applied bias on charge-transfer enhancement is stronger than that on concentration polarization, thus confirming that at high oxygen partial pressures, the interfacial processes are limited more by charge-transfer.

At low oxygen partial pressures, the electrode processes are limited more by mass transfer, since a small dc bias may cause significant concentration polarization. Shown in Fig. 4 are impedance spectra of a Pt|BCG|Pt cell measured at 722°C in argon ($p_{O_2} = 5 \times 10^{-5}$ atm) under different dc biases. The resistance of the cathode-electrolyte interface increased dramatically with the amplitude of the dc bias. Consequently, the interfacial polarization resistance of the full cell still increased with dc bias, although the interfacial resistance of the anode decreased considerably due to enhanced charge-transfer. This behavior indicates that at low oxygen partial pressures, a small dc bias caused severe concentration polarization and hence increased the interfacial resistance.

The same conclusion can be reached by examining the shapes of the impedance spectra shown in Fig. 3 and 4. The impedance spectra of Pt|BCG|Pt cells measured in oxygen gas (Fig. 3) display two semicircles; the first semicircle at higher frequencies corresponds to charge-transfer whereas the second semicircle at lower frequencies is due to mass transfer near the electrolyte-electrode interfaces.

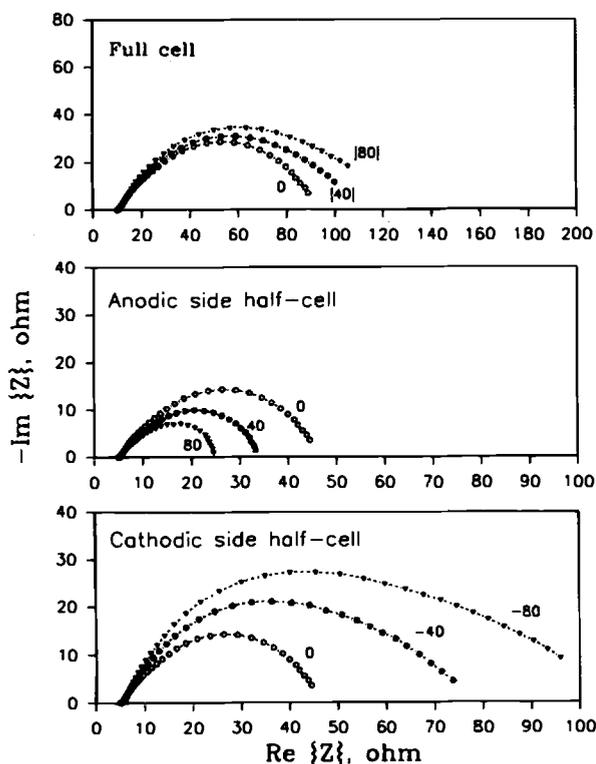


Fig. 4. Impedance spectra of a Pt|BCG|Pt cell measured in argon ($p_{O_2} = 5 \times 10^{-5}$ atm) at 722°C under the influence of an applied dc bias. The numbers by the spectra represent the applied dc bias in mV (the electrolyte thickness was 0.11 cm and the electrode area was 0.385 cm²).

Thus, the contributions from both mass and charge-transfer are observable in these spectra. In contrast, the impedance spectra of the same cell measured in argon (Fig. 4) apparently display only one semicircle at low frequencies, suggesting that mass transfer dominates the interfacial resistance of the cell. Careful analyses of each impedance spectrum shown in Fig. 4 indicate, in fact, that the semicircle due to charge-transfer at higher frequencies persists; it is almost invisible because the amplitude of the charge-transfer impedance is much smaller than that of the mass-transfer impedance.

Shown in Fig. 5 are several polarization curves of a cell in oxygen-argon mixtures of different oxygen partial pressures at 722°C determined using four-probe dc measurements. It can be seen from the figure that the cathodic overpotentials are larger than the anodic overpotentials at the same oxygen partial pressure and the same current density. This can be attributed to field-enhanced charge-transfer observed at the anode and concentration polarization induced by dc biases at the cathode. In addition, the figure shows that the cathodic overpotentials at low oxygen partial pressures are much more significant than at high oxygen partial pressures. This phenomenon can be associated with significant concentration polarization at the cathode at low oxygen partial pressures. These observations are consistent with conclusions drawn from impedance spectra measured under dc biases (Fig. 3 and 4), noting that the overpotential at an electrode-electrolyte interface is directly proportional to the R_p value under the voltage applied.

Tafel plots can be constructed by extending polarization measurements to high overpotentials. Shown in Fig. 6 are Tafel plots for the interfaces measured at 605°C in O₂ and in air. A Tafel slope is obtainable only at such high oxygen partial pressures as in O₂ and in air for the cathodic direction. It is not obtainable for the anodic direction due to deviations from Tafel behavior. At low oxygen partial pressures, mass transfer becomes rate limiting and con-

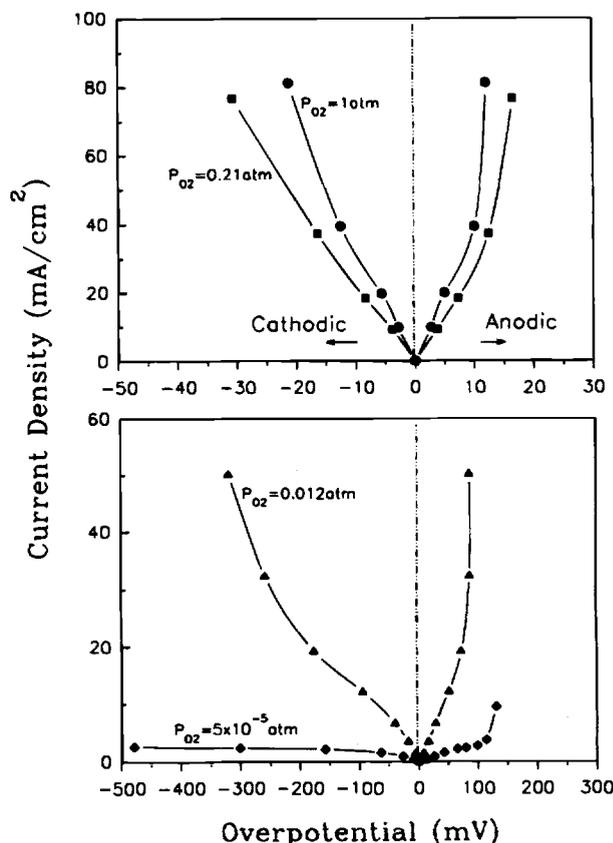


Fig. 5. Current-overpotential curves of a Pt|BCG|Pt cell measured in oxygen-argon mixtures of different oxygen partial pressures at 722°C.

centration polarization dominates so that the Tafel slope approaches zero. The exchange current densities read from the intercepts of the Tafel plots with the vertical axis at $\eta = 0$ (shown in Fig. 6) are about 10 mA/cm² in O₂ and about 8 mA/cm² in air, which are in rough agreement with the values calculated from R_p values determined from impedance measurements (8.7 mA/cm² in O₂ and 6.9 mA/cm² in air).

Measurements in hydrogen and hydrogen-argon mixtures.—The interfacial resistances of Pt|BCG|Pt cells in a H₂-containing atmosphere, like in an O₂-containing atmosphere, showed an appreciable dependence on partial pressures of hydrogen, as shown in Fig. 7. However, the dependence of R_p on p_{H_2} could not be investigated systematically due to difficulties associated with accurate meas-

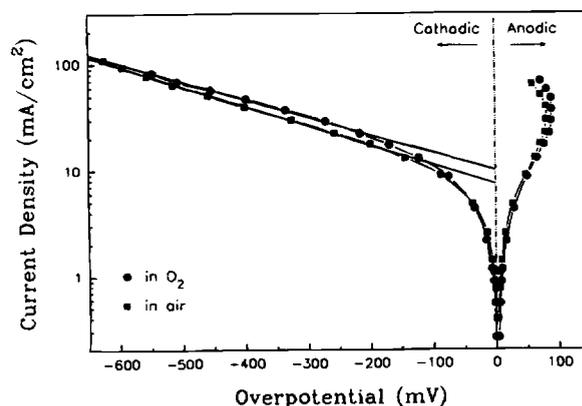


Fig. 6. Tafel plots of a Pt|BCG|Pt cell measured in O₂ and in air at 605°C.

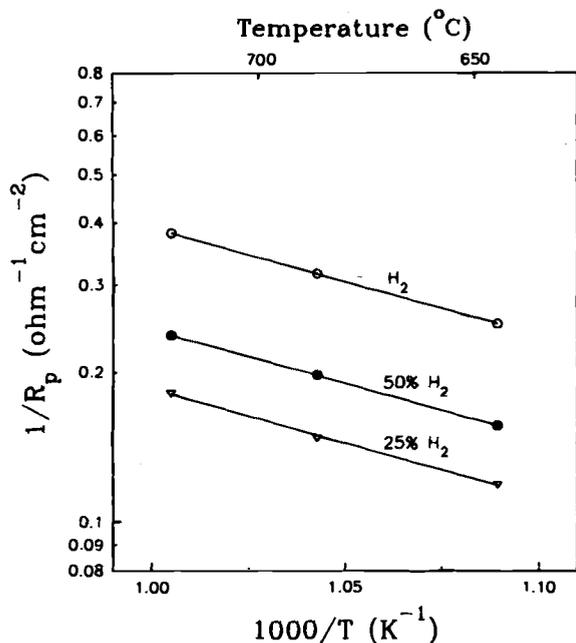


Fig. 7. Temperature dependence of interfacial polarization resistance of a Pt|BCG|Pt cell in hydrogen-argon mixtures of different partial pressure of hydrogen, as determined from impedance spectra.

urement of partial pressures of hydrogen. The observed interfacial resistances of the cell in H₂ (Fig. 7, without dc bias) are higher than those measured in O₂ or in air, and are comparable to those measured in oxygen-argon mixture of intermediate oxygen partial pressures (Fig. 2). This trend indicates that the same interfaces showed higher charge and mass-transfer resistance in a H₂-containing atmosphere than in an O₂-containing atmosphere.

Figure 8 shows a series of impedance spectra of a Pt|BCG|Pt cell measured at 722°C in H₂ under different amplitudes of dc biases. Similarly, the spectra in the anodic direction and in the cathodic direction were taken from the same half-cell in order to eliminate any possible difference due to geometric asymmetry of the cell. It is clear that, in H₂, the interfacial resistance decreased as the amplitude of the applied dc bias increased in both anodic and cathodic directions. The total polarization resistance of the full cell, of course, also decreased as the amplitude of the dc

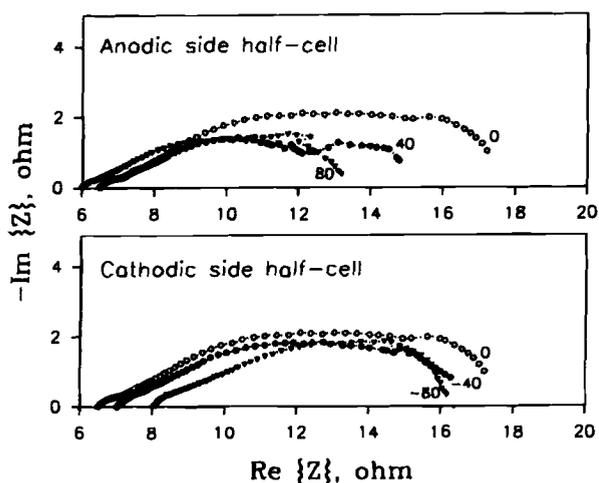


Fig. 8. Impedance spectra of a Pt|BCG|Pt cell measured in H₂ at 722°C under the influence of an applied dc bias. The numbers by the spectra represent the applied bias in mV (the electrolyte thickness was 0.11 cm and the electrode area was 0.385 cm²).

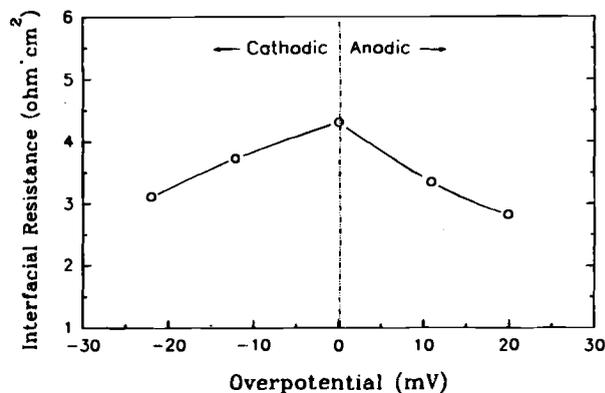


Fig. 9. Changes in interfacial polarization resistance with overpotential measured in H₂ at 722°C.

bias increased. This is evident of field enhancement of the charge-transfer process and thus indicates that charge-transfer is rate limiting in this case. The dependence of polarization resistance on dc bias is apparent from its dependence on the interfacial overpotential, as shown in Fig. 9, which clearly indicates that in both anodic and cathodic directions, the interfacial resistance decreased with the increase in interfacial overpotential.

Effect of water vapor.—Shown in Fig. 10 are impedance spectra of a Pt|BCG|Pt cell measured in different atmospheres containing 3 v/o of water vapor in comparison with those measured in dry atmospheres. The presence of water vapor not only causes changes in the electrolyte resistance⁵ but also results in dramatic changes in the interfacial resistance. The introduction of 3 v/o H₂O significantly increased the interfacial resistance in an O₂-containing atmosphere and reduced the interfacial resistance in a hydrogen-containing atmosphere.

The effect of water vapor on the interfacial resistance in O₂-containing atmospheres is further shown in Fig. 11 and 12. In the temperature range studied, the interfacial resistances in wet oxygen and wet air are typically 4 to 5 times higher than those in dry oxygen and dry air (Fig. 11). As a result, the cathodic overpotentials in wet oxygen and wet air are considerably higher than those in dry oxygen and dry air (Fig. 12). In a H₂ + 3% H₂O/air fuel cell, the resis-

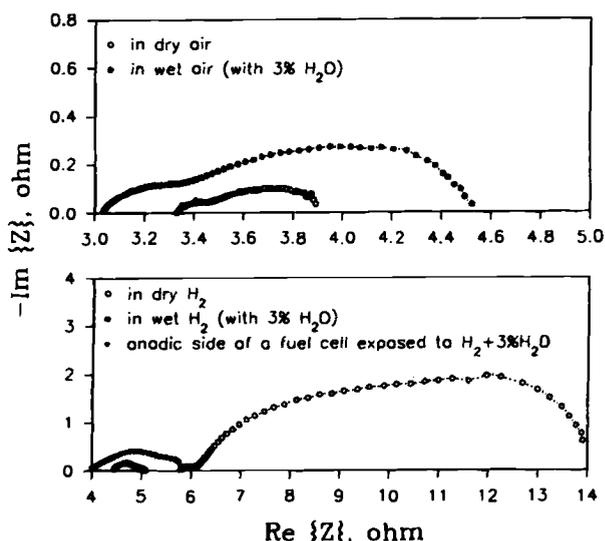


Fig. 10. Half-cell impedance spectra of a Pt|BCG|Pt cell measured in different atmospheres at 722°C (the electrolyte thickness was 0.11 cm and the electrode area was 0.385 cm²).

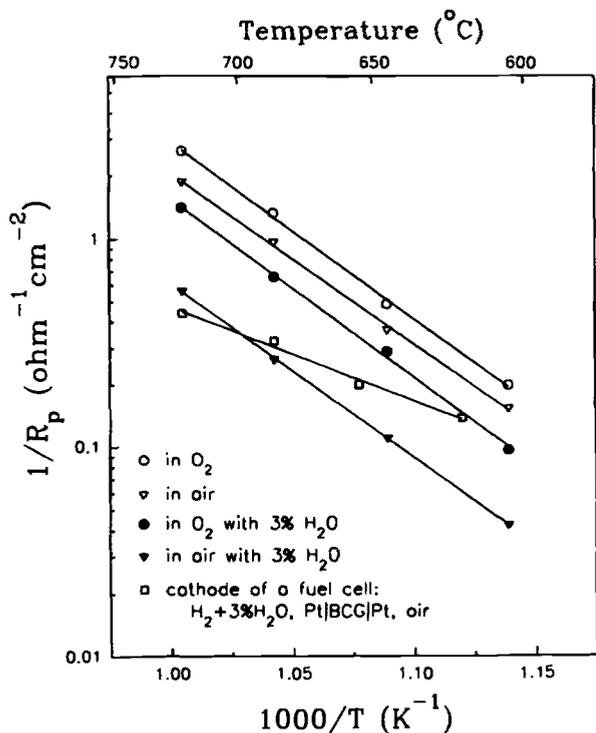


Fig. 11. Temperature dependence of interfacial polarization resistance of a Pt|BCG|Pt cell in different oxygen-containing atmospheres, as determined from impedance spectra.

tances and overpotentials of the cathode-electrolyte interface are even greater than those in wet air. This behavior can be attributed to the water formation on the cathode

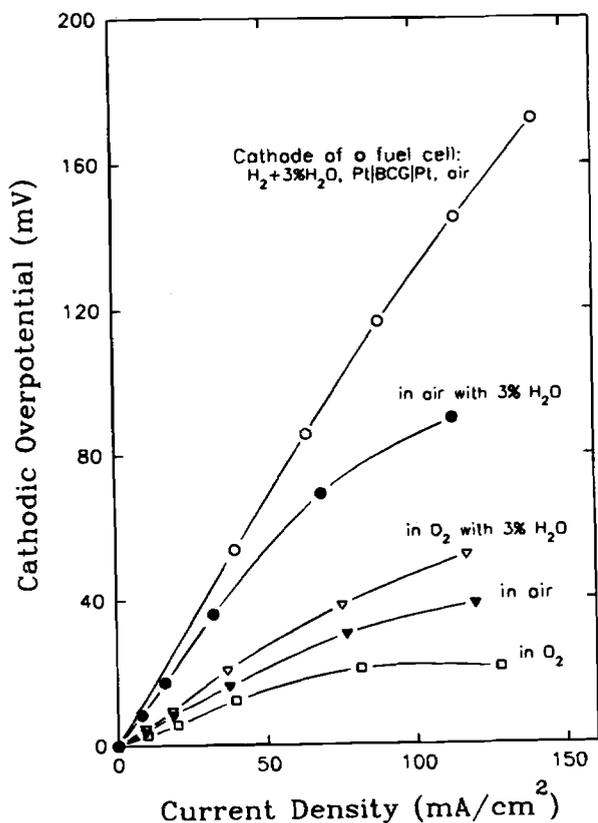


Fig. 12. Cathodic overpotentials of a Pt|BCG|Pt cell determined in atmospheres containing different partial pressure of oxygen at 722°C.

side of the fuel cell due to the conduction of proton through the electrolyte, noting that BCG conducts both oxygen anions and protons.¹⁻⁵ These results clearly indicate that the presence of water vapor hinders oxygen reduction and evolution.

Figure 13 compares Tafel plots for the electrode interface measured at 605°C in dry O₂ and in wet O₂ containing 3 v/o H₂O. The exchange current densities read from the intercepts of the Tafel slopes with the vertical axis of $\eta = 0$ are about 10 mA/cm² in dry O₂ and about 3 mA/cm² in wet O₂, consistent with the values calculated from R_p s determined from impedance measurements (8.7 mA/cm² in dry O₂ and 3.4 mA/cm² in wet O₂).

In contrast to the effect of water vapor on the interfacial resistance in O₂-containing atmospheres, the presence of 3% H₂O in H₂ significantly reduces the interfacial resistance as compared to that in dry H₂. Figure 14 shows that, in the temperature range from 650 to 750°C, the electrode resistances in H₂ with 7% H₂O are nearly one order of magnitude lower than those in dry H₂. In a H₂ + 3% H₂O/air fuel cell, the interfacial resistances of the anode-electrolyte interface are about five times lower than those in dry H₂. Similarly, the anodic overpotentials in wet H₂ or

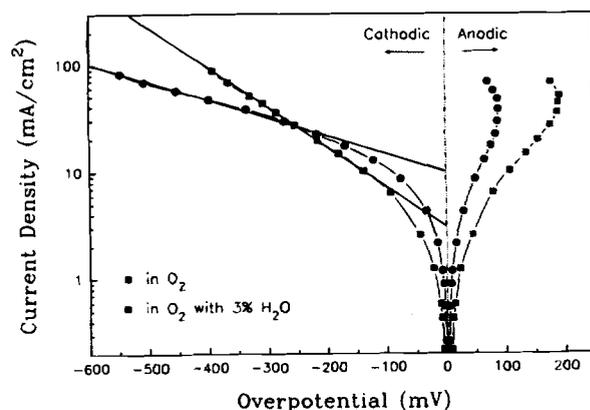


Fig. 13. Tafel plots for a Pt|BCG|Pt cell measured in dry and wet O₂ (with 3 v/o H₂O) at 605°C.

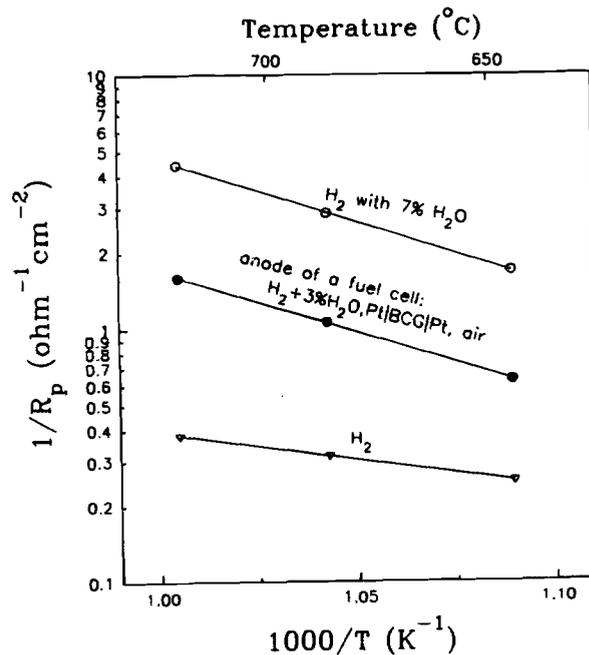


Fig. 14. Temperature dependence of interfacial polarization resistance of a Pt|BCG|Pt cell in different hydrogen-containing atmospheres, as determined from impedance spectra.

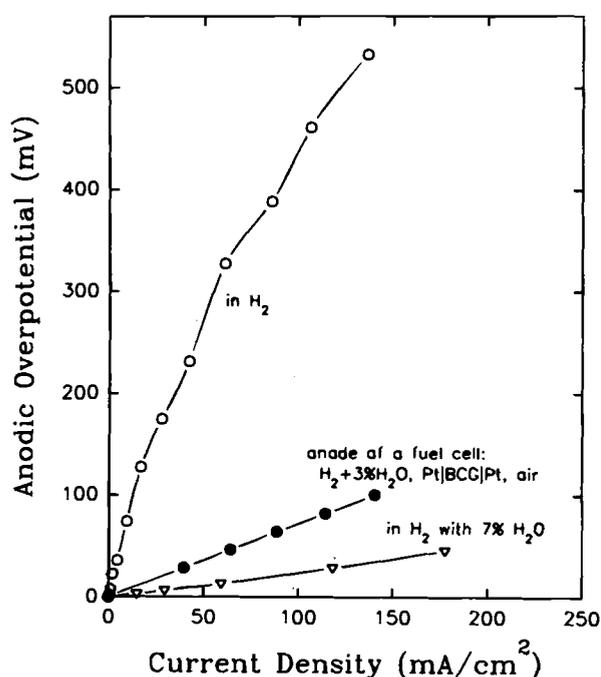


Fig. 15. Anodic overpotentials of a Pt|BCG|Pt cell determined in hydrogen containing different partial pressures of H₂O at 722°C.

under fuel cell conditions are much smaller than those in dry H₂ (Fig. 15).

Because water evolution takes place on both the cathode and anode of a BCG-based fuel cell, the opposing effects of water vapor on the cathode and anode reactions resulted in an interesting reversal: although the resistances or overpotentials of the electrode-electrolyte interfaces are much higher in dry H₂ than those in dry O₂ (or air), the anodic resistances or overpotentials become considerably lower than the cathodic resistances or overpotentials under fuel cell conditions (H₂ + 3% H₂O/air). For instance, for the H₂ + 3% H₂O/air fuel cell at 722°C at a cell current density of 150 mA/cm², the cathodic and anodic overpotentials were 180 and 105 mV, respectively.

Conclusions

In the temperature and p_{O_2} ranges studied, both charge and mass transfer influence the electrode kinetics of Pt|BCG|Pt cells. At high oxygen partial pressures, charge-transfer appears to be dominating the overall process and, as a result, a dc bias tends to reduce the interfacial resistances. This effect is more apparent in the anodic direction. As p_{O_2} decreases, limitations due to mass transfer become more severe and a dc bias results in a large increase in interfacial resistance due to concentration polarization. This effect is more pronounced in the cathodic direction.

In the H₂-containing atmosphere studied, the electrode kinetics seem to be limited by charge-transfer in both anodic and cathodic directions, since an applied dc bias always reduced the interfacial resistances due to the field-enhancement of charge-transfer.

Water vapor has a significant effect on the electrode kinetics. In an O₂-containing atmosphere, the introduction of 3 v/o H₂O significantly increased the interfacial resistances. As a result, the cathodic overpotentials in wet air (or O₂) were considerably larger than those in a dry air (or O₂) and increased with increasing water vapor content. In contrast, in the H₂-containing atmosphere studied the presence of 3 v/o of H₂O significantly reduced the interfacial resistances; the anodic overpotentials in wet H₂ or under a fuel cell conditions were much smaller than those in dry H₂.

Further, the interfacial resistances, especially the resistances of the cathode-electrolyte interface, are the limiting factor in the performance of intermediate-temperature SOFCs based on BCG. Minimizing both charge and mass-transfer resistances is the key to improving the performance of these fuel cells. Therefore, it is imperative to develop catalytically active and highly porous electrodes for the BCG electrolyte, such as silver-BCG¹² and Ag-Bi_{1.5}Y_{0.5}O₃¹³ composite electrodes.

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