A HIGH-TEMPERATURE DIFFRACTION STUDY OF REDUCTION AND REOXIDATION OF NICKEL OXIDE

MICHAEL D. DOLAN AND SCOTT T. MISTURE

NYS College of Ceramics at Alfred University, Alfred NY 14802

Nickel is widely employed as the anode material for solid oxide fuel cells, usually in the form of a cermet of NiO and YSZ. During cell operation, NiO is reduced to Ni, and conversely during shut down, the anodes are susceptible to oxidation to NiO. The rates at which these processes occur are of interest when modeling fuel cell operation. In-situ high-temperature X-ray diffraction has been used to evaluate the reaction kinetics associated with anode reduction/oxidation. Rate constants were evaluated between 500°C and 950°C. Both reduction and oxidation have been shown to obey first-order reaction kinetics. The activation energy for the anode reduction was 70±15 kJ mol⁻¹. The activation energy for the anode oxidation was 80±10 kJ mol⁻¹. Rate constants for oxidation were around an order of magnitude larger than those for reduction under 4% dry H₂ at the same temperature.

1. Introduction

The reducing conditions present on the fuel side of a solid oxide fuel cell (SOFC) allow the use of metal anodes. Since the fuel composition changes within the cell, the candidate material must maintain the reduced state at the strongly reducing fuel inlet and the weakly reducing fuel outlet. For this reason, the selection of anode materials is limited to nickel, cobalt and noble metals [1], however, economic considerations make Ni the most widely used material. Although novel anodes that allow electrochemical oxidation for hydrocarbon fuels without internal reforming are presently under development [2–4], the Ni/YSZ anode remains the current standard.

Anodes are formed from a cermet (ceramic–metal composite) of Ni and YSZ. Maximum electronic conduction is achieved when the Ni content exceeds 30% [5], as the conductivity mechanism transitions from ionic conduction through the YSZ to electronic conduction through the nickel. YSZ serves the dual roles of inhibiting coarsening of Ni particles at the fuel cell operating temperature [1], and minimizing thermal expansion mismatch between the anode and electrolyte.

The most straightforward manufacturing process for the Ni/YSZ anode is to begin with NiO and YSZ, and then reduce the NiO to Ni metal in-situ, during startup of the fuel cell. In-situ reduction of NiO to Ni introduces porosity to the anode, providing a diffusion path for fuel to reach the YSZ electrolyte. Naturally, thermal cycling of the fuel cell, or occasional shut-downs, might introduce oxygen into the system, and it is therefore important to understand not only the in-situ reduction of NiO but also the reoxidation of Ni to NiO.

High-temperature X-ray diffraction, combined with quantitative Rietveld analysis, was used to measure reaction rates associated with i) reduction of oxidized anodes, and ii) oxidation of reduced anodes. A brief overview of the experimental approach is provided.

2. Experimental Methods

Both powder and pre-sintered monolithic parts were tested. The composition of the composites was 50% YSZ–50% NiO. The anode surface was measured directly by X-ray diffraction in a custom high-temperature X-ray diffractometer [7], shown in Fig. 1. An mBraun linear position-sensitive detector allowed rapid data collection. The furnace temperature was calibrated using phase-transformation and melting-point standards. Samples were heated at 200°C/min from room temperature to the temperature of interest; at which point a series of consecutive isothermal measurements were made. Scan rate (10 to 30°2θ/min) and range (between 20 to 60°2θ) were varied at each temperature to give the highest data quality data while providing a sufficient number of XRD patterns to track the phase evolution and therefore to extract the reaction rates.

Reduction measurements involved evacuating the furnace chamber and back-filling with
4% H₂ in He prior to heating to the target temperatures. The 4% H₂ in He gas was maintained at a pressure of 3 psig during the experiments. Oxidation experiments were slightly more complicated, and required heating the sample in the 4% H₂ in He gas mixture to the target temperature, then immediately switching to flowing air when the sample reached the target temperature. Heating under a reducing atmosphere was highly effective in preventing oxidation during heating, which provides excellent confidence in the time-zero variable that is required to determine the reaction rate.

X-ray diffraction measurements were quantified using the analytical software Topas v3 [8], based on the Rietveld method. Weight fractions of each of the three components were calculated to high accuracy (within 5% relative). From this data, rate constants and the activation energy were determined. The data can be treated using analytical functions to describe the reaction order, or, more elegantly, using the Johnson–Mehl–Avrami (JMA) approach [9].

3. Results

3.1. Anode Reduction

Figure 2 shows a select region from a series of isothermal high-temperature X-ray diffraction measurements for the anode reduction at 850°C. Measurements were made at 230 second intervals. The figure clearly shows a decrease in NiO peak intensity, and accompanying increase in Ni peak intensity.

Quantification using the Rietveld method was successful in all cases. Typical refinements of the HTXRD data resulted in weighted residuals less than 8% and goodness-of-fit values on the order of 1.5 or smaller. Figure 3 shows a typical refinement for a specimen that contains all three phases of interest.

Figure 4 shows calculated weight percentages of each component during reduction at 850°C, calculated using the Rietveld method. The weight percentage of nickel increases to around 35%, while the NiO weight percentage approaches zero. The YSZ weight percentage shows an initial increase, corresponding to the loss of oxygen from the system.

An Avrami analysis was used to determine the applicable rate equation for the formation of nickel, according to the method in Hancock and Sharp [9]. The amount of nickel formed as \( t \to 0 \) was calculated by fitting an exponential function to experimental data. From this value, a relative fraction transformed \( (a) \) was calculated. Figure 5 shows the JMA plot for the reduction of NiO to Ni at 850°C. The traditional approach to fit the data to a first-order rate constant is shown in Fig. 6, and demonstrates good agreement with the theory. The rate constant determined from Fig. 5 or 6 is \( (6.5 \pm 0.2) \times 10^{-4} \text{ s}^{-1} \) which can be directly compared to the re-oxidation rate discussed in Section 3.2.

3.2. Anode Oxidation

Figure 7 shows a select range from a series of isothermal high-temperature X-ray diffraction measurements for the anode oxidation at 850°C. Measurements were made at 140 second intervals. The figure clearly shows an increase in NiO peak intensity, and accompanying decrease in Ni peak intensity.

Figure 8 shows calculated weight percentages of each component, extracted using the Rietveld method. The weight percentage of NiO increases to around 50%, while the Ni weight percentage approaches zero. The YSZ weight percentage shows an initial decrease, corresponding to the gain of oxygen in the system.

Figure 9 shows the JMA plot for the oxidation of Ni to NiO at 850°C, in which the model indi-
cates first-order kinetics, like the result shown for the reduction reaction in Fig. 5. The traditional first-order kinetics plot is highly linear as shown in Fig. 10, confirming the result of Fig. 9. The rate constant extracted from the isothermal data at 850°C is $3.7 \times 10^{-3}$ s$^{-1}$.

Figure 10 shows the kinetics plot for the 850°C oxidation step. Table 2 shows calculated Avrami exponents and rate constants for temperatures between 650°C and 950°C. $(3.70 \pm 0.3) \times 10^{-3}$ s$^{-1}$, a value that is ~5.6 times smaller than the rate constant for reduction.

3.3. Activation Energy
Any series of isothermal measurements can be used to obtain the temperature dependence of the rate constant, from which an apparent ac-
Activation energy may be derived. Figure 11 shows the Arrhenius plot for the reduction processes from 750°C to 950°C. The activation energy of the reduction step was $111 \pm 15$ kJ mol$^{-1}$. The activation energy of the oxidation step was $120 \pm 10$ kJ mol$^{-1}$, or nearly equivalent to that for reduction. At all temperatures, the rate of oxidation was approximately 5 times greater than reduction.

4. Discussion
The results show clearly that oxidation occurs faster than reduction, with the rate constants for oxidation being approximately 5 times greater.
than for reduction at the same temperature. This suggests the anodes are particularly susceptible to oxidation during fuel cell shut-down and start-up.

During initial start-up, a fuel cell operating at 800°C will require around 25 min for the anode to fully reduce. During this time, anode conductivity and therefore cell efficiency will be impaired. Efficiency during subsequent start-ups will be dependent on the degree of anode oxidation suffered during shut-down.

Further examination is required to examine the influence on the fuel gas (higher H₂ content, carbon-based fuels) and moisture content. Initial experiments were restricted to the non-explosive 4% H₂ in He for safety reasons, and much additional work could be performed with XRD systems optimized to control the humidity and to allow a simulated fuel mixture to be introduced into the diffraction furnace.

5. Summary

In-situ X-ray diffraction, coupled with Rietveld analysis, offers an unparalleled tool for the rapid and accurate study of kinetic processes in ceramic fuel cells. Other aspects of fuel cell performance are currently under study using in-situ XRD, for example, thermal expansion, cathode phase stability and component interactions. Additional experiments might be devised by suitable modification to diffraction furnaces to operate at pressures of several atmospheres with controlled humidity.

References