Short communication

Approach to equilibrium of the water-gas shift reaction on a Ni/zirconia anode under solid oxide fuel-cell conditions

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Abstract

The reverse water-gas shift reaction is carried out in a solid oxide fuel-cell at a range of fuel utilization levels and the approach of this reaction to thermodynamic equilibrium is calculated from the experimental data. It is found that the water-gas shift reaction is close to equilibrium only at high levels of fuel utilization. This is an important finding for modeling and simulation of fuel-cells. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: SOFC; Water-gas shift; Ni/zirconia anode; Fuel utilization

1. Introduction

Modeling is an important tool for the design and analysis of fuel-cell stacks. The reliability of any model depends, among other things, on the accuracy of kinetic data for the chemical and electrochemical reactions which occur during fuel-cell operation. For internal reforming stacks, considerable effort has been expended on generating kinetic expressions for steam-reforming of methane on solid oxide fuel-cell (SOFC) anodes [1–11]. Kinetic expressions for the accompanying water-gas shift reaction, however, have not been published so far for conditions of interest for intermediate- or high-temperature fuel-cells. One of the principal difficulties of generating accurate kinetic data for the shift reaction at the high-temperatures of fuel-cell operation is the possibility that the reaction may proceed thermally in the exit-line from the reactor, and thus, give rise to misleading results. To facilitate modeling, in the absence of reliable kinetic data for the shift reaction, it is generally assumed that this reaction is always at equilibrium.

One important observation to be made during the operation of fuel-cell stacks is that the methane steam-reforming reaction is completed (nearly 100% conversion) within a short distance along the anode. In most situations, this will occur before a fuel utilization level of 15% is reached, unless

the catalyst is poisoned which results in lower reforming activity. This means that beyond 15% fuel utilization, the chemical reaction which occurs on a fuel-cell anode is principally the water-gas shift reaction. Since fuel-cell stacks are intended to operate at high levels of fuel utilization, viz. 60–85%, any assumptions made for the water-gas shift reaction will have a significant impact on the accuracy of the modeling of the fuel-cell stacks. Information on the kinetics or approach to equilibrium of the water-gas shift reaction is therefore, an important and necessary ingredient for effective modeling.

We have undertaken a study of the reverse water-gas shift reaction at conditions of interest for intermediate- and high-temperature fuel-cells to determine the approach to equilibrium of this reaction.

2. Experimental

The experiments were carried out in a fuel-cell configuration which used a screen-printed Ni/zirconia-based SOFC anode. The temperatures of operation were 750, 800 and 850°C. The ratio of H_2/CO_2 was chosen to cover a wide range of fuel utilization, from 1 to 85%. The experiments were conducted at a constant space velocity of the reactant mixture. Piping materials were chosen to ensure that the reaction was not catalyzed in the fuel passages. The effluent from the reactor was brought to <100°C within a short distance from the reactor, and then cooled further to room temperature before analysis of a

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sample of the exit-stream by gas chromatography. This ensured minimal extent of the reaction proceeding thermally in the exit pipe. Even so, the experimental data have large error bars, which are contributions from $\pm 5\%$ accuracy of the calibration sample of the gas chromatograph, upto $\pm 3°C$ variability in temperature measurements, and $\pm 1\%$ error in mass-flow meter measurements.

3. Results

Approach to equilibrium of the water-gas shift reaction is normally ascertained by comparing the ratio

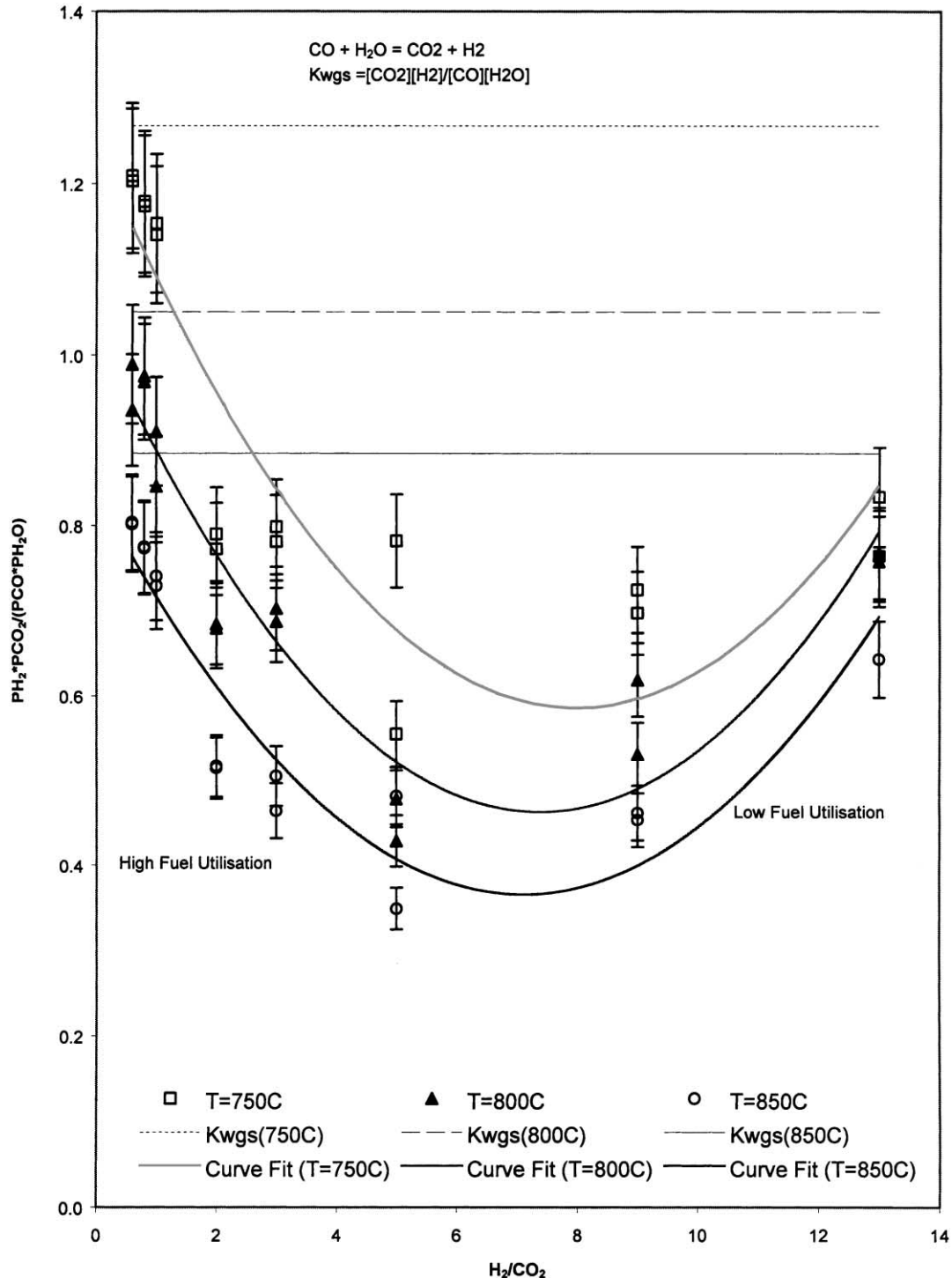$$\frac{P_{CO}P_{H_2O}}{P_{CO_2}P_{H_2}}$$

Fig. 1. Approach to equilibrium of water-gas shift reaction on a Ni/zirconia anode under SOFC conditions.

with the equilibrium constant for the reaction. This is done in Fig. 1, which shows that at all temperatures, the water-gas shift reaction is not at equilibrium under SOFC operating conditions. This is not unexpected since Ni-based SOFC anodes are not as effective as Cu- or Fe-based catalysts for

the shift reaction. The closest approach to equilibrium is at the high fuel utilization levels represented by $H_2/CO_2 < 2$. The reaction is furthest removed from equilibrium at medium levels of utilization which are represented by H_2/CO_2 ratios of 4:1 to 10:1. At low utilization ($H_2/CO_2 > 10$),
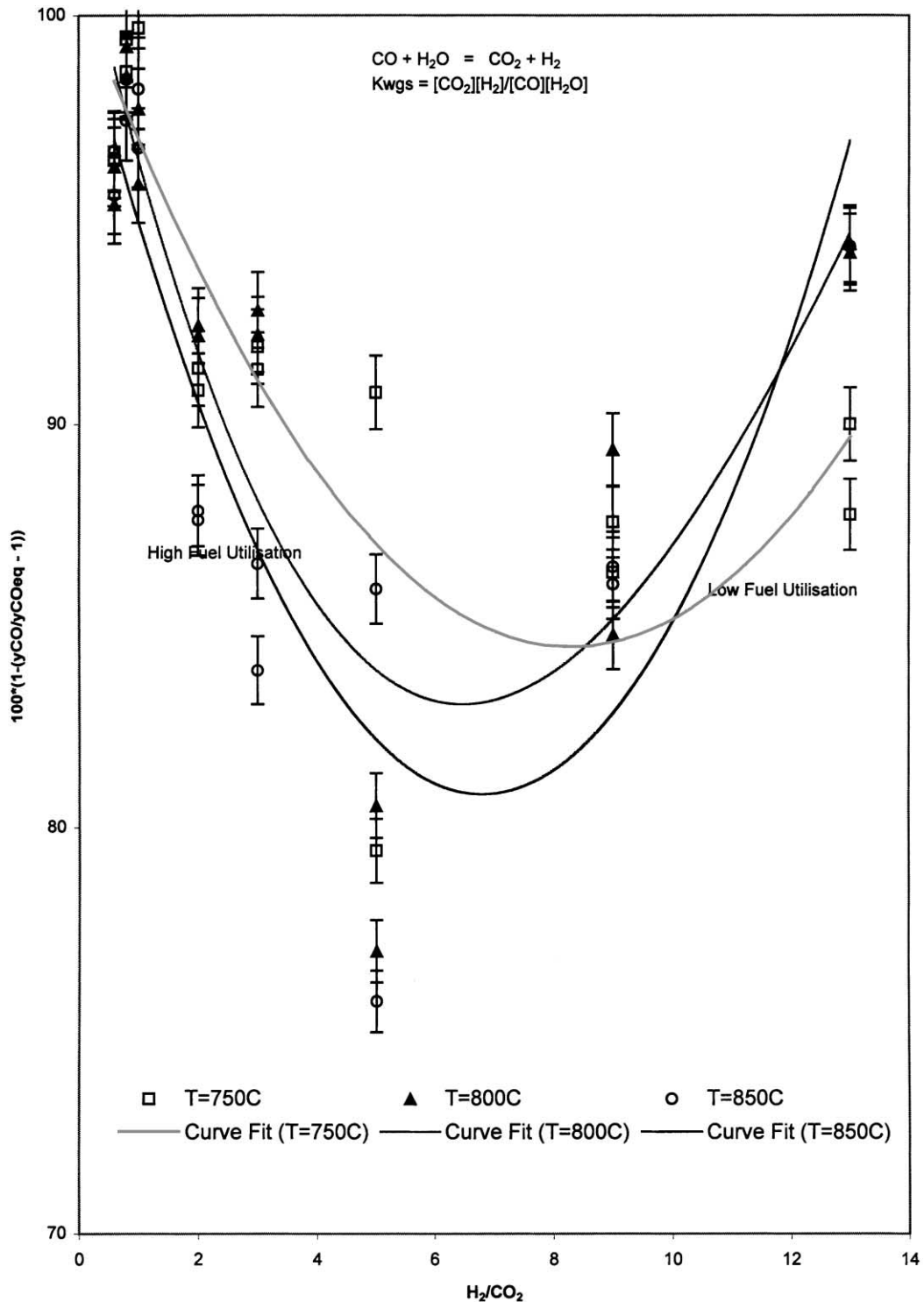

Fig. 2. Approach to equilibrium of water-gas shift reaction on a Ni/zirconia anode under SOFC conditions.

approach to equilibrium is somewhat higher than at medium levels, but still significantly away from equilibrium. The curve fit is a second degree polynomial.

Additionally, we have defined the percent approach to equilibrium by the following expression: $100 \times [1 - (y_{CO}/y_{CO,eq} - 1)]$. This is done in Fig. 2, which shows that the approach to equilibrium is greater at higher temperatures at low-to-medium levels of utilization. At high utilization, approach to equilibrium is greater at lower temperatures. The data in Fig. 2 further show that, for the most part, approach to equilibrium is only 80%. At very low utilization, this is 90%. At very high utilization, it is 95–100%. Although the two approaches give the same information, the latter approach in Fig. 2 gives a better graphical representation.

4. Conclusions

Based on the results of this study, the accuracy of fuel-cell modeling (intermediate- and high-temperature) can be improved by allowing the extent of the shift reaction to vary with the level of utilization. This work has shown that the nature of this dependence follows a second degree polynomial.

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