Kinetics of Solid Oxide Fuel Cells with Molten Tin Anodes

M. Colet Lagrille and G.H. Kelsall Department of Chemical Engineering Imperial College London, London SW7 2AZ, UK <u>g.kelsall@imperial.ac.uk</u>

Carbonaceous fuels including coal, lignite, biomass, waste materials such as paper and plastics, toxic wastes (cyanides, polychlorinated biphenyl, etc.), and refining by-products such as coke, are widely-dispersed regionally and easily accessible. In a carbon-air fuel cell (CFC), atmospheric oxygen is reduced at the cathode to oxide ions, $O^{2^{-}}$, which migrate through the electrolyte and react with the carbonaceous fuel housed in the anode to produce electrical energy. Alternatively, a metal oxide (e.g. SnO₂, Bi₂O₃ and Sb₂O₃) can be produced at the anode as an intermediate by-product to be reduced externally in a combustion reactor. This latter method avoids the accumulation of undesirable compounds such as ash, which could affect the stability and performance of the fuel cell materials (1, 2).

The kinetics and performance of a solid oxide fuel cell with a molten tin anode (Sn(l)-SOFC) at 900 °C were studied using electrochemical kinetic techniques. Reproducibility and stability were obtained with a cell consisting of a 2 mm thick yttrium-stabilized zirconia (YSZ) pellet as electrolyte, a double layered lanthanum strontium manganese (LSM) - YSZ/LSM cathode printed on the electrolyte using a doctor blade, and a pure molten tin anode directly in contact with the YSZ electrolyte. Platinum wires and mesh attached to the cathode with platinum paste, and a graphite rod immersed in the molten anode were used as current collectors.

Atmospheric oxygen is reduced at the cathode and the resulting oxide ions injected into the YSZ electrolyte:

$$O_2 + 4e^- \longrightarrow 2O^{2-}$$
 [1]

while at the anode | electrolyte interface, oxygen dissolves in the molten tin (Sn(l)) to its temperature-dependent solubility limit, above which tin dioxide forms locally:

$$2O^{2-} \longrightarrow 2[O]_{sn} + 4e^{-}$$
 [2]

$$Sn + 2[O]_{sn} \longrightarrow SnO_2$$
 [3]

The kinetic parameters α , $j_{0,a}$ and $j_{l,a}$ related to the anode activation polarization component of the cell voltage were obtained using the experimental polarization curves acquired using the Sn(l)-SOFC described above. Kinetic data for the cathode reaction [1] and diffusion of dissolved oxygen in molten tin was found in the literature (3, 4), while ohmic losses of 9.7 Ω cm² were determined from impedance spectroscopy measurements at an open circuit potential of 0.85 V. Using these data together, a MATLAB code was developed to estimate oxygen transport rates in molten tin and hence anode reaction kinetic parameters: transfer coefficient 0.6, exchange current density ca. 205 A m⁻² and limiting current density ca. 1980 A m⁻². The limiting rate process corresponds to the formation and deposition of SnO_2 at the electrolyte | anode interface by reaction [3], which inhibits reaction [2]. Based on these kinetic parameters, an optimized experimental reactor was modeled, excluding the undesirable ohmic losses components related to current collection and contact potential losses.

Results are presented in Figure 1 and Figure 2 for cell

potential difference (*U*), power density, and concentration and activation overpotentials as a function of operating current density. A maximum power density of ca. 470 W m⁻² was derived at a current density of ca. 1,130 A m⁻² and a cell potential difference of ca. 0.42 V for the quiescent molten Sn anode at 900 °C. These data are in accordance with a previous model developed for a micro-tubular Sn(*l*)-SOFC (5), and correspond to the minimum operating potential to avoid precipitation of SnO₂ by reaction [3]. Additional modeling predictions will be reported for a Sn(*l*)-SOFC in which a carbonaceous fuel is used to reduce *in-situ* the SnO₂ byproduct at: $SnO_2 + C \rightarrow Sn + CO_2$. The objective of this model was predicting its effect on the reactor kinetics.



Figure 1. Predicted effect of operating current density on the cell potential difference and power density for a Sn(l)-SOFC at 900 °C.



Figure 2. Predicted dependences of anode and cathode concentration and activation polarizations on operating current density in a Sn(l)-SOFC at 900 °C.

ACKNOWLEDGEMENTS

The authors thank the University of Chile and the Chilean Government for a CONICYT studentship for MCL.

REFERENCES

- 1. Jayakumar, A., J.M. Vohs, and R.J. Gorte, Ind. Eng. Chem. Res., 49(21): 10237-10241, 2010.
- Gur, T.M., J. Electrochem. Soc., 157(5): B751-B759, 2010.
- 3. Costamagna, P., et al., Chem. Eng. J., 102(1): 61-69, 2004.
- 4. Ramanarayanan T. A. and Rapp R. A., Mettal. Trans. A, 3(12): 3239-3246, 1972.
- 5. Colet Lagrille, M., U. Doraswami, and G.H. Kelsall, ECS Trans., 41(12): 137-148, 2012.