

# Electrocatalytic decomposition of hydrogen sulfide

Haytham Alqahtany, Po-Hung Chiang, Douglas Eng, Michael Stoukides \*

*Department of Chemical Engineering, Tufts University, Medford, MA 02155, U.S.A.*

and Albert Robbat, Jr.

*Department of Chemistry, Tufts University, Medford, MA 02155, U.S.A.*

Received 22 July 1991; accepted 4 February 1992

The recently discovered phenomenon of nonfaradaic electrochemical modification of catalytic activity (NEMCA) was explored for the electrocatalytic decomposition of  $\text{H}_2\text{S}$  to  $\text{H}_2$  and  $\text{S}_2$  over Pt electrodes at 600–750°C and 1 atm. It was found that upon applying a potential to Pt supported on a  $\text{O}^{2-}$  conducting yttria-stabilized zirconia disk, the decomposition of  $\text{H}_2\text{S}$  significantly increased up to a factor of 11 at 600°C. The results appear to verify several aspects of NEMCA including the phenomenon that the electrolyte needs not to conduct reaction-specific species and that the degree of rate enhancement is related to the working electrode polarization. In addition, results indicate that separate chambers are not always required for electrocatalysis.

**Keywords:**  $\text{H}_2\text{S}$  decomposition; electrocatalysis; solid oxide electrolyte; NEMCA

## 1. Introduction

In the past decade, studies involving applications of solid electrolytes in heterogeneous catalysis have steadily increased [1–3]. One such application is the recently explored phenomenon known as nonfaradaic electrochemical modification of catalytic activity (NEMCA) [1,4–7]. In NEMCA, the catalytic activity of the catalyst-electrode is modified when a polarizing potential is applied. It has been recently shown that the polarizing potential is related to changes in the catalyst work function [1,6,7]. Electrocatalytic rates and selectivities have been enhanced for reactions such as CO,  $\text{CH}_4$ , and  $\text{C}_2\text{H}_4$  oxidations over Pt and Ag electrodes supported on  $\text{O}^{2-}$  conducting yttria-stabilized zirconia [6–8]. Recently, it was found that NEMCA is not limited to  $\text{O}^{2-}$  conducting electrolytes

\* To whom correspondence should be addressed.

but includes other electrolytes (e.g.,  $\text{Na}^+$  conducting) in which the conducting species is not involved in the overall catalytic reaction [7].

In the present work, electrocatalytic rate enhancements during the decomposition of  $\text{H}_2\text{S}$  are reported. Hydrogen sulfide is a well-known environmental pollutant largely originating as a by-product from petroleum and coal industries. Recently, several investigators have studied  $\text{H}_2\text{S}$  reactions in high temperature electrochemical cells utilizing oxygen- or sulfur-ion conducting electrolytes [9–13]. The present communication investigates the possibility of electrochemically enhancing the rate of  $\text{H}_2\text{S}$  decomposition.

## 2. Experimental

The 8 mol% yttria-stabilized zirconia (YSZ), with a thickness = 1.8 mm, was purchased from Zircoa Products. Platinum paste (Engelhard EMS-SCA3786) was deposited on both sides of an electrolyte disk to form two or three electrodes. A 1-chamber cell with the configuration  $\text{Pt}|\text{YSZ}|\text{Pt}$  was prepared and placed inside a quartz tube with both electrodes exposed to the same  $\text{H}_2\text{S}$  feed as shown in fig. 1a. This 2-electrode cell was the first configuration explored. Fig. 1b shows a 3-electrode cell configuration which was used to investigate electrochemical voltage components. The working electrode had a superficial area of  $2.5\text{ cm}^2$  whereas the counter electrode was slightly smaller,  $2.0\text{ cm}^2$ . The reference electrode covered  $5\text{ mm}^2$ . The cell designs in figs. 1a and 1b were modifications of that by Otsuka et al. [14]. To investigate the effect of current direction on rate enhancement, a 2-chamber cell was utilized as shown in fig. 1c. In this 2-chamber cell,  $\text{H}_2\text{S}$  was present at one electrode and helium gas was present at the other electrode.

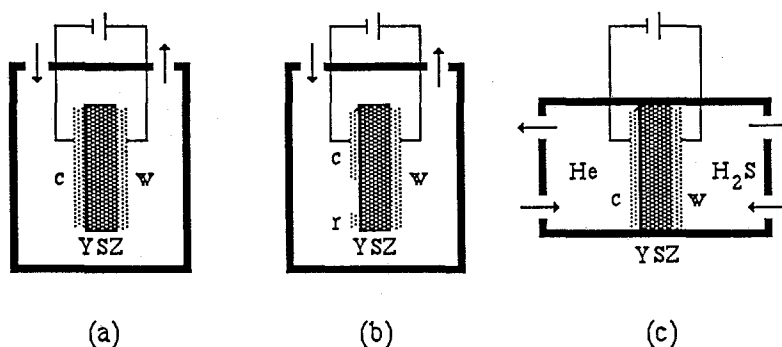


Fig. 1. Schematic diagram of reactor cell configurations. (a) Two electrode cell with both electrodes exposed to same  $\text{H}_2\text{S}$  feed. (b) Three electrode cell with all electrodes exposed to same  $\text{H}_2\text{S}$  feed. Cell was used for measurements of cell voltage components. (c) Two electrode cell with electrodes exposed to different gaseous mixtures. w = working electrode, c = counter electrode, r = reference electrode.

Thin-gauge wires from the electrodes connected the electrolyte cell to an EG & G Model 363 Galvanostat-Potentiostat (Princeton Applied Research). The effluent stream was analyzed by on-line gas chromatography (Perkin-Elmer) with thermal conductivity detection. A chromosorb 107 (Perkin-Elmer) column separated  $\text{H}_2$  and  $\text{H}_2\text{S}$  contents. A porapak N (Supelco) column separated  $\text{H}_2\text{O}$  contents. Oxygen and nitrogen were separated with a molecular sieve 5A (Perkin-Elmer) column. Supporting equipment included a Beckman Model 7C Thermal Conductivity Hydrogen Analyzer and a Beckman Trace Moisture Analyzer which continuously monitored  $\text{H}_2$  and  $\text{H}_2\text{O}$  content, respectively. For experiments in which the ohmic-free potential was measured (with the cell configuration shown in fig. 1b), an Explorer IIIA Digital Oscilloscope with storage capacity was used with a mercury switch to interrupt applied current.

### 3. Results and discussion

The reactor was isothermally operated in the temperature range 600–750°C and at 1 atm total pressure. The reaction rate was calculated from the  $\text{H}_2\text{S}$  balance; i.e.,  $r = G(Y_{\text{H}_2\text{S},\text{in}} - Y_{\text{H}_2\text{S},\text{out}})$  where  $G$  is the total inlet molar flowrate. The oxygen leak in the reactor system was  $< 0.04\%$  and remained unchanged during experiments. Oxygenated products including  $\text{H}_2\text{O}$  and  $\text{SO}_2$  were below detection limits in all the experiments.

Fig. 2 shows the transient effect of applying a constant current of 1 mA on the rate of decomposition at 600°C using the reactor cell depicted in fig. 1a. The inlet content of  $\text{H}_2\text{S}$  was 0.37% diluted in helium. Before time  $t = 0$ , the cell

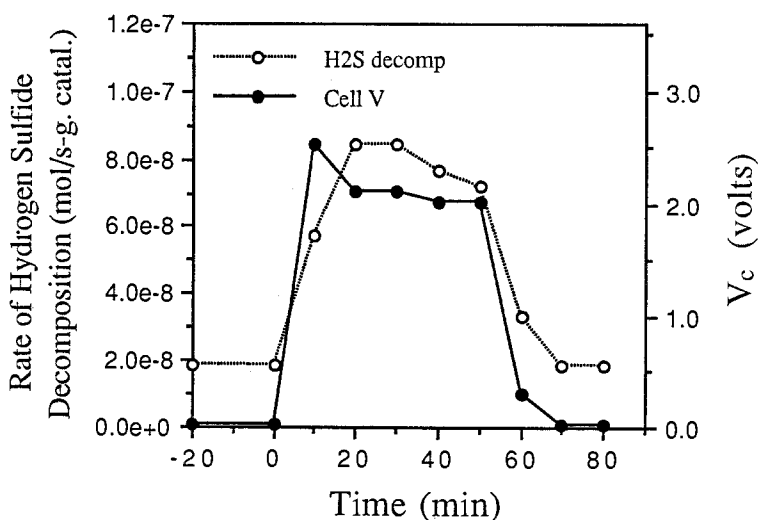


Fig. 2. Transient effect of imposing a current of 1 mA on the rate of  $\text{H}_2\text{S}$  decomposition and the corresponding cell potential,  $V_c$ , at 600°C for cell shown in fig. 1a.

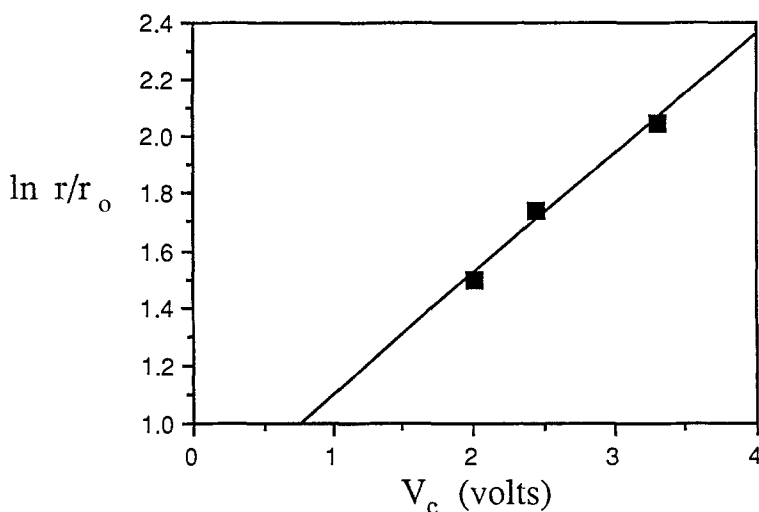


Fig. 3. Effect of cell potential  $V_c$  on  $\ln(r/r_o)$  at 600°C for cell shown in fig. 1a.

was at open-circuit operation ( $i = 0$ ) and a catalytic decomposition rate of  $1.89 \times 10^{-8}$  mol/s·g. catal. was attained. At time  $t = 0$ , a current of 1 mA was applied and sustained for about 50 min during which the rate of decomposition increased to a steady state rate of  $8 \times 10^{-8}$  mol/s. The increase in decomposition rate, therefore, was about 420% or  $r/r_o = 4.2$ , where  $r$  = rate of decomposition when the circuit was closed and  $r_o$  = rate of decomposition when the circuit was open. The cell potential,  $V_c$ , also increased from near zero to a steady state value of about 2.1 V. At time  $t = 50$  min, the circuit was interrupted and the current returned to zero. Upon interruption of the current, the decomposition rate and the cell potential gradually returned to the initial open-circuit values over several minutes as shown in fig. 2. The cycle was reproducible upon resumption of the imposed current and similar transient curves were obtained for other imposed currents.

Fig. 3 shows the effect of cell potential,  $V_c$ , on  $\ln(r/r_o)$  for the cell depicted in fig. 1a. The reactor temperature was constant at 600°C. The decomposition rate during the open circuit,  $r_o$ , was  $2.84 \times 10^{-8}$  mol/s. The ratio  $r/r_o$  increased to 7.72 for a cell potential of 3.30 V. The line drawn through the enhanced rates was fitted by the method of least squares with a correlation of 0.99. The ordinate-intercept was at 0.675 V. It has been shown that, during NEMCA effects on the catalytic work function, the rate enhancement is related to the ohmic-free catalyst potential [1] by the expression

$$\ln(r/r_o) = \alpha e(V_{wr} - V_{wr}^*)/k_b T \quad (1)$$

where  $V_{wr}$  is the ohmic-free catalyst potential from the working electrode (catalyst) to the reference electrode (fig. 1b). The terms  $\alpha$  and  $V_{wr}^*$  are described as “reaction and catalytic-specific constant” [1]. If in the regime of investigated

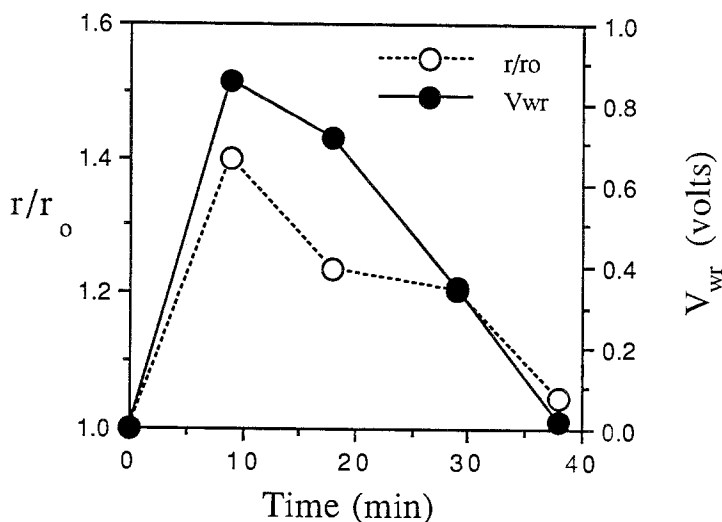


Fig. 4. Transient  $V_{wr}$  and  $r/r_0$  at 700°C. Results were obtained using cell shown in fig. 1b.

potentials,  $V_c$  and  $V_{wr}$  are approximately linearly related, then the voltage-rate enhancement relationship presented in fig. 3 is consistent with eq. (1).

To further investigate the relationship between  $r/r_0$  and  $V_{wr}$ , experiments were conducted to isolate the ohmic-free potential at the working electrode. For this purpose, a current interruption procedure using the 3-electrode reactor in fig. 1b was adopted. With a 3-electrode system, measurement of the ohmic-free potentials at the working and the counter electrodes could be determined. Fig. 4 shows transient  $V_{wr}$  and  $r/r_0$  values obtained at 700°C where 1%  $H_2S$  diluted in helium was fed at a flow rate of 168 cc/min. The direction of constant current was from the counter to the working electrode. Before time  $t = 0$ , the cell was at open-circuit. At  $t = 0$ , a constant current was applied. The ohmic-free potential  $V_{wr}$  initially increased to a maximum of 0.858 V before gradually dropping to 0.020 V. It can be seen that  $r/r_0$  changed similarly to  $V_{wr}$ .

The observed rate enhancements could not be attributed to thermal effects. For most experiments, the power output was normally in the range of 0.02–0.50 W. Actual surface temperature increases were less than 4°C even though the rate enhancements reached as high as 1100%.

NEMCA investigations have also found that as temperature increases, the rate enhancement become less pronounced [1]. In general, the electrode polarization becomes less significant at higher temperatures resulting in a weaker change in catalyst work function [1]. Fig. 5 shows the effect of temperature on the decomposition rates when a constant current of 10 mA was applied. At 600°C, the rate of decomposition increased 11 times (or 1100%) whereas at 750°C, the rate increased only by 10% ( $r/r_0 = 1.10$ ). Hence, the above results

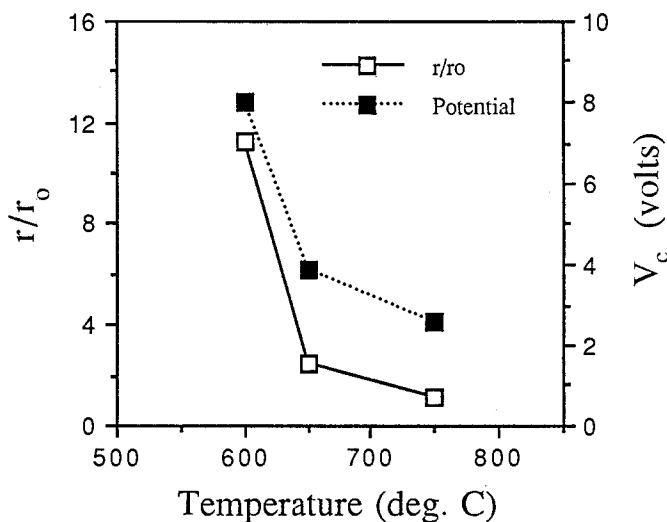


Fig. 5. Temperature dependence of  $r/r_0$  and  $V_c$  for cell shown in fig. 1a. Current was constant at 10 mA.

are in agreement with the temperature effect on reaction rate enhancement observed in previous NEMCA studies.

In the results thus far presented, it was not possible to determine if both the working and the counter electrodes were responsible for rate enhancements, or whether either electrode solely accounted for rate enhancements. Hence, further experiments were performed using the cell configuration is shown in fig. 1c. At 700°C, a 1%  $H_2S$  in helium feed was passed through the chamber exposed to the working electrode. Pure helium was fed to the chamber exposed to the counter electrode. Upon pumping current from the working to the counter electrode, no rate enhancements were observed. Upon pumping current towards the working electrode, however, a clear increase in  $H_2S$  decomposition was observed. Hence, in the 1-chamber cell of fig. 1a, only the properties of one electrode can be altered to induce an increase in decomposition rate. This phenomenon can be explained by what is specifically known as electrophobic and electrophilic effects on rate enhancements during NEMCA [1]. An electrophobic reaction, for example, is ethylene oxidation on Pt or Ag where the rate is enhanced upon pumping current or  $O^{2-}$  ions towards the catalyst. If the reaction rate increases upon pumping current away from the catalyst, the reaction is called electrophilic. The studied reaction therefore can best be described as electrophobic.

In summary, NEMCA presently appears to best explain the rate increases observed. The decomposition of  $H_2S$  over Pt can be classified as a reaction with NEMCA behavior. In this study, it was shown that electrocatalysis can occur in a 1-chamber cell and that separation of gases is not necessary as is common with electrolyte cells.

## Acknowledgements

We gratefully acknowledge the Center for Environmental Management at Tufts University for the support of this research. Partial support by the National Science Foundation (Grant #CBT 8815927) and the Department of Energy (Grant #FGO2/89CE90048) is also kindly acknowledged.

## References

- [1] C.G. Vayenas, S. Bebelis, I.V. Yentekakis and H.-G. Lintz, *Catal. Today* 11 (1992) 303.
- [2] P.J. Gellings, H.J.A. Koopmans and A.J. Burggraaf, *Appl. Catal.* 39 (1988) 1.
- [3] M. Stoukides, *Ind. Eng. Chem. Res.* 27 (1988) 1745.
- [4] C.G. Vayenas, S. Bebelis, I.V. Yentekakis, P. Tsiakaras and H. Karasali, *Platinum Metals Rev.* 34(3) (1990) 122.
- [5] C.G. Vayenas, *J. Phys. Chem.* 92 (1988) 5083.
- [6] C.G. Vayenas, S. Bebelis and S. Ladas, *Nature* 343 (1990) 625.
- [7] C.G. Vayenas, S. Bebelis and M. Despotopoulou, *J. Catal.* 128 (1991) 415.
- [8] S. Bebelis, C. Karavasilis, H. Karasali, P. Tsiakaras, I.V. Yentekakis and C.G. Vayenas, *Proc. 2nd Intl. Symp. Solid Oxide Fuel Cells* (1991) 353.
- [9] I.V. Yentekakis and C.G. Vayenas, *J. Electrochem. Soc.* 136 (1989) 996.
- [10] N.U. Pujare, K.W. Semkow and A.J. Sammells, *J. Electrochem. Soc.* 134 (1987) 2639.
- [11] H.S. Lim and J. Winnick, *J. Electrochem. Soc.* 131 (1984) 562.
- [12] I.V. Yentekakis, P.G. Debenedetti and C.G. Vayenas, *Proc. 2nd Intl. Symp. Solid Oxide Fuel Cells* (1991) 361.
- [13] F.M. Sutherland, C.D. Eastman and T.H. Etsell, *Solid State Ionics-8*, Lake Louise, Alberta, Canada, October 1991, paper W10.
- [14] K. Otsuka, K. Suga and I. Yamanaka, *Catal. Lett.* 1 (1988) 423.