EXCESS ENTHALPY DURING ELECTROLYSIS OF D\textsubscript{2}O

K. S. V. SANTHANAM, J. RANGARAJAN, K. C. MANDAL and S. K. HARAM

Chemical Physics Group, Tata Institute of Fundamental Research, Bombay 400 005, India

RECENTLY several reports\textsuperscript{1-5} discussed the generation of excess enthalpy during the electrolysis of D\textsubscript{2}O and suggested the possibility of either nuclear fusion\textsuperscript{1,3,6} or chemical reaction\textsuperscript{2,7} as the cause of this excess enthalpy. We wish to consider here the enthalpy estimates arising from the adsorption of D\textsubscript{2} \((-\Delta H = 120 \text{ kJ mol}^{-1}\)) and the recombination of D\textsubscript{2} and O\textsubscript{2} in the electrolytic cell \((-\Delta H = 285 \text{ kJ mol}^{-1}\)).

D\textsubscript{2}O used in the experiments had a purity of 99.5% (as determined by NMR). The titanium cathode (4” x 4”) was cleaned and etched to remove oxide films and impurities on the surface of the metal. Platinum sputtered on glass and of the same area as the Ti cathode was used as the anode. Sodium chloride (BDH, Analar grade; 1.16 g) was dissolved in 20 ml of D\textsubscript{2}O and used for the electrolysis. The temperature of the electrolytic solution was measured continuously using either a Beckman or a Riege (DDR) thermometer. The cathode surface temperature was measured using a P 85 BIOA 202 N thermistor (Thermometrics, N. J., USA; \(R = 1.845\ \text{k}\Omega\)). The electrolytic cell was a 50 ml beaker to which a Perspex plate was fitted to hold the electrodes in parallel configuration. The cell was placed in a Dewar during the experiment. Cooling correction to be applied to the measured temperature was obtained independently running the electrolysis in the same cell to the steady state temperature and allowing it to cool to the initial temperature. The correction interval was kept the same as the temperature measuring interval, as Newton’s law of cooling is valid only for short temperature intervals.

Figure 1 shows the current–voltage curve of D\textsubscript{2}O at Ti working electrode. An interesting feature of this curve is the appearance of looping (hysteresis) during the anodic sweep following the cathodic potential sweep to \(-1.20\ \text{V vs SCE}\). Clearly there is no desorption peak observed during the anodic cycle, as is generally seen. The pronounced hysteresis resulting from adsorption sluggishness has been previously reported\textsuperscript{8} for some metals in the electrolysis of H\textsubscript{2}O. The features of figure 1 are attributed to specific adsorption of the product of electrolysis\textsuperscript{9,10}. Kolotyrkin and co-workers\textsuperscript{11-14} and Parsons\textsuperscript{15} have examined this behaviour in detail. A particular point to be noted here is that the hysteresis onset is not observed before the cathodic background limit of D\textsubscript{2}O is reached; it is likely to be caused by adsorption of D or D\textsubscript{2}. The current–voltage curve for H\textsubscript{2}O at Ti cathode has also been examined; here hysteresis is not observed (dotted line in figure 1). As predicted by the earlier theories\textsuperscript{15,16}, the desorption peak of H\textsubscript{2} is seen in the current–voltage curve. The peak shape is broad, indicating a slow desorption of the adsorbed species. This feature is interpreted on the basis of metal–gas physical adsorption based on the Lennard–Jones potential energy diagram\textsuperscript{17,18}. Physical adsorption is attributed to long-range forces and it does not involve dissociation of H\textsubscript{2}; the heat of adsorption \(-\Delta H_p\) is of the same order of
magnitude as the heat of liquefaction of gaseous H₂ (ref. 18). Chemisorption can also occur and this is discernible in the desorption peak as a shoulder (in the present case it is not observed). The distinction between weak and strong adsorption processes has been investigated previously, these results suggest that strong adsorption occurs only on permitted sites and the sites involve surface atoms. Each surface atom may act as one such site. One half of the available sites may be used for strong adsorption from structural considerations.

Galvanostatic electrolysis of D₂O in a partially closed container containing 1 M NaCl was conducted at 33.0 mA cm⁻² or 66.0 mA cm⁻². The temperature of the electrolytic solution was measured at regular times for a period of 8 h. Figure 2 summarizes the data obtained during the electrolysis. The experiment was repeated four times, using fresh D₂O and with newly prepared Ti cathode. The rise in temperature measured here is considered as the resultant temperature of heating and cooling of the electrolytic solution. At the current densities used for the electrolysis of D₂ and O₂ are produced [Cl₂ (g) + 2 e⁻ = 2 Cl⁻ (aq), E₀ = 1.358 V (ref. 19), and O₂ + 4 D⁺ + 4 e⁻ = 2 D₂O, E₀ = 0.815 V (ref. 19)].

We now analyse the rate of temperature increase, considering it as arising from Joule heating or from a chemical reaction (table 1). A combination of the

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Rationalization of power balance in the electrolysis of D₂O</th>
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<tr>
<td>E_app</td>
<td>2.58 V, iₙ 0.033 A cm⁻², cell current 0.50 A</td>
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**Case I:**

- Power consumed in the electrolysis of D₂O = 0.77 J s⁻¹ (W)
- Balance of power remaining = 0.52 J s⁻¹ (W)
- Expected rate of temperature change J s⁻¹/°C⁻¹ = 0.0004°C s⁻¹
- Experimentally measured rate of temperature change (after cooling correction) = 0.27°C min⁻¹

**Case II:**

a) Exothermic adsorption of D₂ on cathode

- Heat produced by exothermic reaction* = 120 kJ mol⁻¹
- Rate at which charge is passed (100% current efficiency for the electrolysis) = 0.50°C s⁻¹
- Moles of D₂ produced by electrode reaction = 2.59 × 10⁻⁶ mol s⁻¹
- Expected power from the exothermic reaction = 0.30 J s⁻¹ (W)
- Expected rate of temperature change = 0.15°C min⁻¹

b) Exothermic reaction due to 2D₂ + O₂ = 2D₂O

- Heat generated by recombination reaction = 285.83 kJ mol⁻¹
- Expected power for the number of moles of D₂ produced in 1 sec = 0.73 J s⁻¹ (W)
- Expected rate of temperature change = 0.38°C min⁻¹

These calculations were done by accurately measuring the potential difference across the cell and the current through the cell. Rate of cooling was measured by raising the electrolytic solution to the same steady state temperature as during electrolysis, turning off the electrolysis and monitoring the temperature over time. Mass of D₂O = 22.00 g, mass of Ti and Pt plates = 18.77 g, mass of glass beaker = 17.12 g. D₂ adsorption on Ti will increase the weight of the cathode very marginally (in mg) which is neglected in the calculation.

For a hypothetical situation in which all the input power is consumed for Joule heating, the expected rate of temperature change is 0.68°C min⁻¹ (no electrolysis occurring).

Experiments conducted with distilled water showed a rate of charge of temperature of 0.26°C min⁻¹, which is substantially less than the value obtained with D₂O.

two cases is also considered. For the Joule heating in
the electrolysis of D₂O, first the power required to
split D₂O into its constituents should be subtracted
from the total power that is fed into the electrolytic
cell. In other words, out of the total potential
difference applied to the cell, E_{app}, one part will go
to establish the thermoneutral potential of 1.54 V,
caused by the heat of reaction and the heat of
dissociation of deuterium and oxygen, i.e.:

\[
\begin{align*}
\text{D}_2 \text{O} + e & \rightleftharpoons \text{D}_{\text{ads}} + \text{OD}^- \quad (1) \\
\text{D}_{\text{ads}} + \text{D}_2 + e & \rightleftharpoons \text{D}_2 + \text{OD}^- \quad (2) \\
\text{D}_{\text{ads}} + \text{D}_{\text{ads}} & \rightleftharpoons \text{D}_2 \quad (2a)
\end{align*}
\]

and

\[4 \text{ OD}^- \rightleftharpoons \text{D}_2 \text{O} + \text{O}_2 + 4 \text{ e.} \quad (3)\]

The balance of power is considered as being
utilized for Joule heating, which produces the tempe-
rate change in the cell. This scheme is shown in
Table 1. For the second case, two possible
exothermic processes occurring in the cell are
considered: (i) adsorption of D₂ on Ti, which is
estimated to release 120 kJ mol⁻¹, and (ii) recombi-
nation of D₂ and O₂ in the electrolysis,
which releases 285.83 kJ mol⁻¹ (this calculation
assumes that D₂ is not adsorbed during electrolysis).

Pauling allocated the excess enthalpy in the
Fleischmann and Pons experiment¹ to the formation
of Pd deuteride and its subsequent decomposition.
The decomposition of deuteride is explosive. As Ti
has 0.72 orbital per atom of the orbitals vacant in the
outer shell⁵, this could be used for deuteride
formation. Our experiments do confirm, Ti lattice
expansion and generation of a cracking noise²
during the electrolysis due to adsorption of D₂.

The data presented in Table 1 allow an enthalpy
estimate to be made of the exothermic chemical
reaction. Subtraction of the expected excess tempe-
rature in case II from the measured excess tempe-
rature in case I yields 0.87°C min⁻¹ (a) or
0.65°C min⁻¹ (b). To obtain this temperature change
we should expect an exothermic reaction of
0.32 × 10⁶ J mol⁻¹ with D₂ adsorbed on the metal,
or 0.38 × 10⁶ J mol⁻¹ for the case when the diffe-
rence in temperature is solely due to the chemical
reaction with negligible adsorption of D₂ occurring.
Under the experimental conditions used here this is
inconceivable by ordinary processes.

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1. Fleischmann, M., Pons, S. and Hawkins, M.,
J. Electroanal. Chem., 1989, 261, 301; and
2. Santhanam, K. S. V., Rangarajan, J., O’Neil,
Braganza, Harn, S. K., Limaye, N. M. and
93, 4694.
6. Jones, S. E., Palmer, E. P., Czirr, J. B., Decker,
8. Frumkin, A. N., In: Advances in Electrochemistry
and Electrochemical Engineering, (ed.) P. Delahay,
455.
101, 709.
17. Hayward, D. O. and Trapnell, B. M. W.,
Chemisorption, 2nd edition, Butterworths, Lon-
don, 1964.
18. Bond, G. C., Catalysis by Metals, Academic
Potentials in Aqueous Solution, Dekker, New