CATHODE COOLING BY EXPANSION OF HYDROGEN IN CALORIMETRIC TESTS FOR COLD FUSION

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Expansion of hydrogen and its isotopes from hydrogen-absorbing cathodes can transfer significant amounts of energy to the surrounding aqueous media. In calorimetric efforts to confirm cold fusion, allowance must be made for thermal conduction along electrical leads. In conjunction with consideration of the extent of cathode cooling by expansion of hydrogen, the rupturing of the cavities within the cathodes and limitations to charging of the electrode by hydrogen flowing from fresh cracks are briefly addressed.

INTRODUCTION

In recent years, there have been reports of the production of excess power during the electrolysis of deuterium oxide[1] and light water[2,3] with hydrogen-absorbing cathodes. In these experiments, the isotopic forms of hydrogen, presumably, were charged into the cathodes to near the limiting values of hydrogen-to-metal atom ratios where the chemical potential of the hydrogen, and thus its equivalent gas pressure, was extremely high.[1] For a fuller account of related studies concerning "cold fusion" of the isotopes of hydrogen, the reader is referred to the recent review by Storms.[4]

In reports of excess power, adequate care has not been exercised in many of the calorimetric investigations to safeguard against thermal conduction from outside the cell along the electrolysis leads. In their original experiments, Fleischmann et al.[1] used calorimetric cells in which the electrical leads were brought from the active electrodes directly out of the solution and up through elastomer stoppers that were outside the active calorimetric region. Some subsequently reported calorimetric confirmations of excess power production employed a similar arrangement.

In unpublished results from this laboratory,[5] one of our earliest calorimetric experiments, though compromised by an electrical grounding fault, appeared to show excess power generation during electrolysis of LiOD + D$_2$O. This experiment did not provide for tempering of the electrical leads. In subsequent experiments, we exercised more careful calorimetric discipline in tempering the electrical leads by providing an electrically insulated, long-thermal-contact path through the solution to ensure that the leads were at the temperature of the electrolytic solution before exiting the calorimeter. None of these latter experiments showed excess power. However, this is not necessarily a cause-and-effect argument owing to difficulties in charging cathodes to the high hydrogen isotope loadings suggested as a requirement by Fleischmann et al.[1]

Contrary to common behavior with many fluids at ambient conditions, hydrogen warms when expanded. If the gas is released at high pressures as it loses thermal contact with the cathode, then it carries significant amounts of energy away from the cathode. As a result, the cathode temperature must decrease enough to develop the temperature differences necessary for the same amount of energy to be conducted back (from the solution and from outside the cell along the electrical lead) to the cathode at the same rate that it is being removed by the released hydrogen. The size and implications of this warming of the isotopes of hydrogen in cold fusion experiments are considered in this technical note.

HEATING AND COOLING BURSTS WITHIN CATHODES

Arata and Zhang[6] reported experimental measurements of heating and cooling bursts within palladium cathodes during the electrolysis of D$_2$O + LiOD solutions. Some of these may be related to the rupture of cavities discussed in the following. The bursts can give rise to conduction of energy along the electrical lead attached to the cathode and reinforce the need to temper electrode leads in calorimetric measurements. However, even in the absence of these bursts, expansion of the gas from the cathode must produce a temperature gradient between the cathode and the electrolyte.

CHARGING OF CATHODES AND CAVITY RUPTURES

Cracks and channels within the cathode may impede the charging of the hydrogen isotopes to high loadings. Formation of such fissures is a necessary consequence of charging hydrogen isotopes to high chemical potentials in cathodes that contain cavities and related imperfections.

With careful choice of electrolytes and electrode materials, a cathode can be charged with hydrogen or its isotopes to near its limiting value, where the hydrogen attains a high chemical potential. The choice of electrolytes, including isotopic species, and electrode materials is critical to this process. The electrode must be capable of accepting hydrogen under

practical electrolysis conditions, and the electrolyte must be capable of passivating the surface of the cathode so that the particular isotope of hydrogen can be charged to a very high chemical potential.

Any cavities within the cathode must have hydrogen at the same chemical potential as that within the cathode and thus must be at very high pressure for high hydrogen loading. The tensile strength of the cathode provides a limit for the pressure that can be reached within the cavities before they rupture. The hydrogen loading may be limited by gas issuing from new cracks within the electrode if the gas flux prevents the electrolyte from wetting new surfaces created by fracturing and thus prevents the electrolyte from forming the species that prevent the hydrogen from being released at a low chemical potential. This cannot always be a limitation because electrolytic charging of hydrogen to extents higher than those arising from this limitation has been repeatedly reported. Interruptions of the gas flow can allow the electrolyte to enter by capillary action and to thus permit surface reactions that impede the release of hydrogen at low chemical potentials from these surfaces of limited accessibility.

The tensile strength of palladium and other hydrogen-absorbing metals[7] is near 300 MPa (44 000 psi). During electrolysis, the metal is alloyed with hydrogen to produce much higher tensile strengths (not to be confused with brittleness). Tensile strengths are not available for the metal hydrides in question, but increased tensile strength is evidenced by the approximate doubling[8] of the Vickers hardness when palladium is fully charged with hydrogen. Arata and Zhang[6] report tripling of the Vickers hardness when palladium is fully charged with deuterium and suggest that the tensile strength of palladium deuteride may be three times that of annealed palladium. For comparison, values for some high-tensile-strength materials of construction are as much as 3500 MPa (520 000 psi).

GAS BUBBLE FORMATION

The dispersal of hydrogen from the cathode serves a key role in the transport of energy from the cathode to the solution and in the source of resupply of this transported energy. The constant flux of gas from the cathode reduces the thermal contact between the solution and the cathode. The size of the gas bubbles formed at the cathode and in the solution is indicative of the energy carried by the gas. Small bubbles can be formed only from a very high energy source owing to the relationship of internal bubble pressures to the radius of the bubbles and the surface tension of the fluid. The relationship of gas bubble size to the energy source can be found in discussions of foams and aerosols in basic engineering texts.

Green and Lewis[9] published photographs and a description of hydrogen bubbles formed on palladium cathodes during the electrolysis of aqueous solutions. They suggested that two types of bubbles were formed. One type formed slowly at particular sites on the cathode and was much larger than the second type. The second type was small bubbles that arose in continuous streams from other select sites on the cathode. The steady streams of bubbles are consistent with the gas issuing from high-pressure sources. Other mechanisms for the release of hydrogen may be operative as well. The gas bubbles in these solutions are much smaller than those obtained with fritted-gas-dispersion tubes, and many appear to have formed within the solution. For such fine gas dispersion, the hydrogen must leave the electrode in a highly energetic

form. It is conceivable that much of the hydrogen may leave the electrode as molecular hydrogen or possibly as free radicals and that the gas subsequently forms in the solution.

ENTHALPY OF EXPANSION AND GAS WARMING

If the hydrogen isotope has a very high enthalpy as it loses thermal contact with the cathode, then this provides a means for pumping energy from outside to inside the cell along the cathode lead. The electrolysis is usually conducted at a low confining pressure where the enthalpy of the hydrogen at the end of the expansion is near its ideal gas value. The difference in enthalpy is converted to kinetic energy, which may be absorbed by the surrounding electrolytic solution. Owing to the very small size of the gas bubbles formed in these solutions and the high thermal conductivity of gases of the isotopes of hydrogen, almost complete energy exchange with the solution is feasible before the gas reaches the surface of the solution. The state of the hydrogen when it loses thermal contact with the electrode cannot be determined with certainty. Oates et al.[10] determined excess values of the thermodynamic properties for alloying palladium with the isotopes of hydrogen in the range of gas-to-metal atom ratios of 0.0 to ~0.75; however, reliable methods are not currently available for extrapolating these results to ratios near 1.0 that Fleischmann et al.[1] indicated were necessary for observation of excess power. The upper limit of the cooling of the cathode can be estimated by assuming hydrogen gas is released at, effectively, a very high pressure in the rate-limiting step of the cathode process.

In the following results, the power for steady expansion of the gas was determined with values of the enthalpy of compressed hydrogen calculated by Driessen and Griessen.[11] Column 2 of Table I shows ΔH_{xs}, the enthalpy difference for expansion of hydrogen at 300 K from the high pressure P to a low pressure where the gas is ideal. The values for deuterium are not significantly different from those for hydrogen, so the thermal effects are essentially the same for either isotope. The power produced per ampere of electrolytic current is shown in column 3. The values in column 3 are also equal to the ratio of the power that can be produced by gas expansion to the power to transfer current from the cathode to the anode at 1 V. Using the Pons et al. procedure for calculating excess power,

$$\dot{Q}_{xs}/\dot{Q}_{in} = (d\Delta H_{xs}/dt)/I(V - V_{chem}) \ ,$$

where

V = voltage across the cell

V_{chem} = voltage for the electrochemical reaction in the cell

I = current

$\dot{Q}$ = power.

Column 4 shows the relative temperature of a gas bubble for an adiabatic expansion. These temperature differences are dramatic, but both the mole and the volume fractions of gas bubbles in the solution are small enough for the solution to serve as a very large heat sink for cooling the gas bubbles. The principal component in this heat sink is water, and its molar heat capacity is 2.6 times that of gaseous hydrogen at 300 K and 0.1 MPa.

TABLE I

Thermal Quantities Associated with Adiabatic Expansion of Hydrogen for Maximum Thermal Conduction
Along Cathode Leads at 300 K

P (MPa)	ΔH_{xs} (kJ/mol)	$(d\Delta H_{xs}/dt)/I$ (W/A)	$T_{gas}-T_{el}$[a] (K)	ΔT(platinum)$/I$[b] (K/A)
0.1	0.0	0.0	0.0	0.0
100	1.45	0.008	50	1.3
200	3.03	0.016	104	2.8
300[c]				
500	7.39	0.038	254	6.9
1 000	13.84	0.072	476	12.8
2 000	25.04	0.130	860	23.2
3 500[d]				
5 000	52.35	0.271	1 799	48.6
5 304[e]				
100 000	464.55	2.41	15 964	431.0

[a]Temperature change for adiabatic expansion of H_2.
[b]Temperature gradient produced by power in column 3 on a 1-mm-o.d. × 1-cm platinum conductor.
[c]Nominal tensile strength of annealed hydrogen-absorbing metals.
[d]Tensile strength of high-strength materials of construction.
[e]Solidification pressure of H_2.

TEMPERATURE GRADIENT ON ELECTRICAL LEAD, UPPER BOUND

As a consequence of energy being removed from the cathode by the released hydrogen isotopes, the cathode must cool, but a steady state must be reached during the electrolysis. The energy removed by the hydrogen isotopes must be resupplied either by the solution or from outside the solution (and cell) along the electrical lead to the cathode.

Calculation of the temperature profile around the cathode depends on factors specific to each experiment. An upper bound can be estimated for the gradient if all of the energy associated with the gas expansion is released without bursts and is conducted from outside the cell to the cathode along its electrical lead. Column 5 shows the temperature gradient required to conduct the power in column 3 between ends of a 1-mm-diam × 1-cm-long platinum electrical lead that has infinite heat sinks at each of its ends and has a mean temperature of 300 K. The thermal conductivity of platinum at 300 K is 0.711 W/cm (Ref. 7). These temperatures suggest that sensible differences in temperature should exist between the regions of entry to the calorimetric cell for untempered electrical leads to the cathode and anode.

CONCLUSIONS

The excess powers shown in column 3 are the same magnitude as those reported in many calorimetric reports of excess power generated during the electrolysis of D_2O solutions on palladium cathodes.[4] In these experiments, the currents ranged from 0.1 to 10 A, and $V - V_{chem}$ was of the order of 1 V; however, exact matching of these to experimental results cannot be done because information is not available for exact specification of the effective pressures required to load the cathode during any particular experiment.

The calculated gas temperatures show that boiling of the electrolyte can arise from the gas expansion. Burst release of the gas can produce a temperature gradient along the electrical lead several times those calculated, but such values are not inordinate and could go unnoticed owing to the difficulty in probing the temperature of bare electrical leads carrying high currents. If highly pressurized cavities deep within the cathode rupture in a manner that permits the metal to make good heat exchange with the expanding gas, then the metal temperature will rise rapidly during such transient events. These short-duration temperature rises are interruptions of the steady removal of energy by gas expansions that are not restricted by passage through small fissures.

As a final reiteration, cathode release of hydrogen at a high chemical potential can cause conduction of significant amounts of energy along the cathode lead during electrolysis of water. Calorimetric measurements to show excess power generation from nuclear reactions induced in these experiments should have adequate provisions for eliminating heat pumping action from this potential source.

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