

dioxygen(g), but an honestly phrased fractional excess over the total power delivered to the electrochemical cell itself.

The electrochemical cells sit in a thermostated water bath. Typically, two cells are run at the same time, with constant current provided by a regulated power supply. An isothermal-flow calorimeter is used to determine the power dissipated in the cell. Crudely put, a constant-displacement pump provides a flow of the calorimetric fluid (water in the most recent experiments) at a rate of about 1 ml/min, but the actual water flow is measured much more accurately than the constancy of the pump by having the water delivered to a beaker that rests on the platen of an electronic scale, so that over almost all measuring intervals the mass of the water is measured accurately. An automatic "siphon" occasionally empties the beaker, so that the measurement is inaccurate over a small fraction of the intervals.

From the mass flow and the known specific heat of water, the power transfer to the water could be calculated if one knew the temperature rise. This is determined by measuring the inlet temperature with two platinum resistance thermometric devices (RTD) and measuring the outlet temperature within the calorimeter housing by two additional RTD. To minimize heat transfer to the surrounding thermostated bath, the calorimeter is immersed in a single-ended metal Dewar flask. Water from the thermostatic bath enters and descends along the inner wall of the flask, entering the calorimeter at the base and having the temperature measured by two RTD at that point. After passing outside the coiled compensating heater which encloses the electrochemical cell, the water begins its exit from the cell through a small venturi aperture, in order to mix the streamlines, and has its temperature measured by two additional RTD at the exit.

A sensing current of 0.5 mA is fed to each RTD for a couple of seconds every four minutes. All measurements are taken by a Keithley digital multimeter. The multimeter was time shared to measure all of the parameters electrically.

In the absence of excess heat, the energy communicated to the electrochemical cell would be determined by the product of the known magnitude of stabilized current supplied, and the voltage measured at the base of the electrochemical cell. Because that voltage fluctuates with time and with current density, the experimental configuration has been designed to reduce the dependence of the entire calorimeter upon the linearity of the individual calorimetric measurements. This has been achieved by modifying the power to the compensating heater in each interval, so that a desired total power is achieved through the sum of the power input to the electrochemical cell and that input to the compensation heater. This is done by averaging the Pd/Pt cell voltage over a brief interval during the previous 4-minute measuring period, and then commanding the heater current to provide a value of supplementary power that is sufficient to obtain the nominal 12 W (or 30 W) or whatever is the target total power for the next 4-minute portion of the experiment.

Therefore, the output temperature should be nominally constant. More particularly, the measured total power (cell plus compensating heater), as determined by the measured calorimetric fluid mass flow and temperature rise, should be constant with time, except for the 4-minute delay in compensating power. Measurements of excess power are therefore in principle straightforward, based on the value of the power required from the compensation heater in order to obtain the desired total power delivered to the calorimetric fluid.