We have developed novel apparatus for high temperature electrochemistry measurements, in which the heating is local to the measuring electrode. Two approaches are currently being used. In the first, liquid flows through a rectangular channel, in one wall of which a platinum foil electrode is embedded. The foil electrode may be heated by radiofrequency induction, so electrochemistry is carried out at the hot surface and the solution is heated by conduction and convection as it flows over the electrode. The flow pattern is altered as the hotter less viscous solution near the electrode flows more quickly, but this can be calculated (along with the effects on the chemistry due to temperature dependence of rate constants and diffusion coefficients) using a proprietary finite element fluid dynamics program[1].

The second approach employs a platinum microdisk electrode, placed in an electrochemical cell which is exposed to a strong microwave field. The presence of the metal causes the microwave field to become concentrated at the electrode, producing intense local heating in the solution just in front of the electrode. This localized “hot spot” then sets up a thermal convection flow pattern, with solution flowing fairly rapidly through the hot spot towards the electrode and then spreading out and cooling. The local conditions can be extreme; we have observed temperature rise rates of the order of 50,000 K s\(^{-1}\). In steady state, the peak temperature may considerably exceed the boiling point of the solution, but boiling does not normally occur since the convection means that the liquid passes through the hot spot and only remains at the peak temperature for some tens of milliseconds.

Again, simulation was required to solve the flow and temperature patterns in this complex system. While initial experiments were made using water (for which data is readily available), we found the trial period of the DETHERM database invaluable for locating the high temperature data (besides density and viscosity variation, it is necessary to know the behaviour of specific heat, thermal conductivity and dielectric constant) which enabled us to extend our simulations to other solvents, and a publication on this has now been accepted[2].

In a related area, we are extending the use of laser heating to fundamental studies in the field of Surface Electrochemistry. The study of the electrochemical response after the sudden increase of temperature caused by the laser contains valuable information about the structure of the electrochemical double layer (i.e., the interfacial region between the electrode and the electrolytic solution). We have shown that this response is mainly due to the disorder induced in the adlayer of solvent molecules by the increase of the temperature[3] and hence, contains information about the interaction between the solvent molecules and the electrode surface. We expect to extend these studies to non-aqueous solvents. The structure of the double layer with solvents other than water is a relatively unexplored subject which will require comprehensive information about the bulk properties of the solvent (as a function of the temperature), to study how they are affected by the presence of the electrode and how they affect the structure of the double layer. Finally, the study of the dynamic changes induced by the heating will be important from a fundamental point of view.

We were particularly impressed by the wide range of sources covered by DETHERM (e.g. internal or contract reports, dissertations) making data available which could not be retrieved from literature-only based databases. The very extensive range of data covered is also valuable; for other work in the group, we obtained figures for gas solubilities from DETHERM which we had not succeeded in locating elsewhere. The availability of this database will be important for extending our work on laser electrochemistry and the double layer.