Microwave activation of electrochemical processes at microelectrodes

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Electrochemical experiments at platinum microdisc electrodes are shown to be possible in an environment of intense microwave radiation and a considerable current enhancement observed for the ferrocyanide/ferricyanide redox couple in aqueous 1 M KCl is shown to be Faradaic in nature consistent with a rapid heating effect causing the temperature in the liquid phase at the electrode/solution interface to locally superheat.

By combining the use of a source of activation with the range of known electrochemical methodology new types of experiments and in some cases novel applications of electrochemistry, *e.g.* in photoelectrochemistry and in sonoelectrochemistry, have been developed. The interaction of microwave radiation with electrochemical systems, that is with redox and chemical processes at solid/liquid and liquid/liquid interfaces, is to date unexplored, although the interest in microwave enhanced chemistry[1] and the use of microwave radiation and microwave technology have become widespread over the recent decades. The use of *low* power microwave radiation in electrochemical systems is of considerable importance in areas of research such as *in-situ* electrochemical EPR[2] (typically X-band, 9.5 GHz) and microwave reflectance characterisation[3] of semi-conducting electrodes. The activation of the electrochemical system due to absorption of microwave radiation can in these cases usually be ignored due to the rather low intensities involved. However, microwave radiation is known to interact not only with molecules in the gas phase but also with condensed materials and interfaces with sufficient dielectric loss, ε',[4] and may therefore be employed to activate an electrochemical system.

An 800 W, 2.45 GHz domestic multi-mode microwave oven has been modified† to supply constant power or pulsed microwave radiation of variable power and to allow an electrochemical cell to be inserted into a high intensity region. In Fig. 1 a schematic drawing of the experimental arrangement is shown. In Fig. 2(a)–(c) voltammograms for the one electron oxidation of 2 mM $Fe(CN)_6^{4-}$ at a 25 μm diameter Pt disc electrode in aqueous 1 M KCl are shown. The observed limiting current, I_{lim} = 6.4 nA, is slightly higher than that expected for the known diffusion coefficient, $D(Fe(CN)_6^{4-}) = 0.63 \times 10^{-9}$ m^2 s^{-1},[5] presumably due to micro-electrode imperfection. The expression for quasi-steady-state voltammetry at a microdisc electrode[6] has been shown to be $I_{lim} = 4nFDcr$. In this expression n denotes the number of electrons transferred per molecule, F, the Faraday constant, c, the concentration, and r, the radius of the electrode. Pulsed microwave radiation can be seen to induce current pulses which are superimposed on the quasi-steady-state current response.

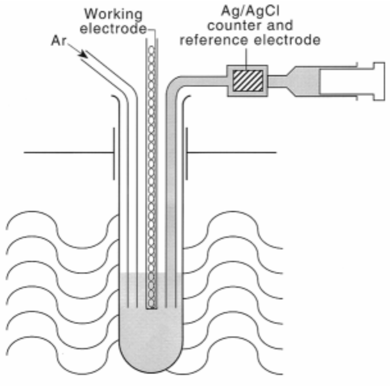

Fig. 1 Schematic representation of the electrochemical cell used for experiments in the presence of microwave radiation.

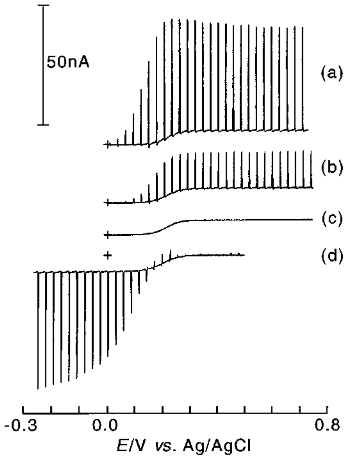

Fig. 2 Voltammograms obtained for (a)–(c) the oxidation of 2 mM $Fe(CN)_6^{4-}$ and (d) the reduction of 2 mM $Fe(CN)_6^{3-}$ in aqueous 1 M KCl at a 25 μm diameter Pt disc electrode and with a scan rate of 10 mV s^{-1}; 0.6 s microwave pulses with (a) and (d) 24 W and (b) 16 W microwave intensity.

In Fig. 2(a) the effect of 24 W (absorbed microwave power, see Table 1) microwave pulses of 0.6 s duration is shown. Current pulses are observed at potentials well negative of those of the current response in the absence of microwave radiation. The equilibrium potential for the $Fe(CN)_6^{4-/3-}$ redox couple is known to be affected by the temperature and data for the equilibrium potential–temperature dependence determined in the same cell over a 70 °C range and with the temperature of the reference electrode kept constant at 25 °C suggest a linear dependence with $dE/dT = -1.53$ mV K^{-1} consistent with published data.[7] Therefore at higher temperature the current response for the oxidation of $Fe(CN)_6^{4-}$ is expected to occur at a more negative potential in qualitative agreement with the

Table 1 The rate of microwave heating of 5 cm^3 water or aqueous solution in the electrochemical cell placed in a high intensity area of the modified microwave oven

	Pure water		1 M aqueous KCl	
Microwave power level	Rate of heating/ K s^{-1}	Absorbed energy[a]/W	Rate of heating/ K s^{-1}	Absorbed energy[a]/W
A	0.15	4	0.26	7
B	0.40	10	1.0	24
C	0.77	18	1.7	41
D	1.1	28	3.4	83
E	1.8	43	4.7	113

[a] Calculation based on a calibration procedure in which joule heating with a resistor is used to induce a temperature change.

Table 2 The temperature measured potentiometrically after *ca.* 0.2 s in a solution of 5 mM $Fe(CN)_6^{4-}$, 5 mM $Fe(CN)_6^{3-}$, and 1 M KCl at a 25 μm diameter Pt disc electrode when a 0.6 s pulse of microwave radiation is applied

Microwave pulse intensity/W	7	16	24	33
Temperature/°C	60 ± 6	87 ± 9	120 ± 12	150 ± 15

experimental observation [Fig. 2(a)]. From the current trace in Fig. 2(a) it can be concluded that the temperature of the bulk solution is not significantly affected by the pulsed microwave radiation. The current immediately returns to the expected value, I_{lim}, after each microwave pulse. The rate of heating observed independently in an experiment monitoring the bulk solution temperature was 1 K s^{-1} for the 24 W microwave intensity setting (see Table 1). Therefore it appears to be possible that the intensity of the microwave radiation is considerably higher at the electrode/solution interface compared to the average intensity experienced by the solution phase. A lower microwave intensity of 16 W induces a smaller current response as shown in Fig. 2(b). More importantly, microwave pulses of 24 W intensity applied to the reduction process of 2 mM $Fe(CN)_6^{3-}$ in 1 M KCl at a 25 μm diameter Pt disc electrode [Fig. 2(d)] also induce current jumps superimposed on the quasi-steady-state voltammetric response with complementary features. The cathodic current increases by a similar factor compared to the increase of the anodic current [Fig. 2(a)] and the shift of the half wave potential towards more negative potentials upon irradiation with microwaves is apparent. From this observation and from the linear dependence of both the quasi-steady-state current and the microwave enhanced current on the concentration of the redox reagent it can be concluded that the observed current for the $Fe(CN)_6^{4-/3-}$ redox couple in 1 M KCl in the presence of microwave radiation is purely *Faradaic*.

In order to achieve a more quantitative description of the heat pulse induced by microwave radiation at the electrode/solution interface the temperature can be estimated potentiometrically based on the equilibrium potential for a solution of 5 mM $Fe(CN)_6^{4-}$, 5 mM $Fe(CN)_6^{3-}$, and 1 M KCl under zero current condition. This measurement allows the temperature at the electrode/solution interface to be measured simultaneously with applying microwave pulses and data for the observed trend are given in Table 2. These data are valid only for the 25 μm diameter Pt disc electrode and cell geometry used in this set of experiments. However, the data suggest an approximately linear dependence of the microwave intensity absorbed by the bulk solution and the heating induced by the microwave radiation focused by the micro-electrode. Further, for short periods of time superheating of the solution phase can be observed.

The diameter of the working electrode also is a crucial factor in determining the magnitude of the heating effect. In experiments with a 50 μm diameter Pt disc electrode higher microwave intensities were required in order to give similar temperature jumps compared to those observed at the 25 μm diameter Pt disc electrodes. In experiments conducted with a 1 mm diameter Pt disc electrode the heating effect remained negligible even at the highest microwave intensity settings. In general, the temperature measured at the electrode strongly depends on (i) the microwave intensity, (ii) the cell geometry and positioning of the electrode, (iii) the type of solvent and solute used and produced during the course of the electrode reaction. The use of organic solvent systems is possible and the parameter characterising the microwave absorption has been shown to be the dielectric loss.[4]

The 0.6 s pulse which has been employed in the experiments shown in Fig. 2 is sufficient for thermal equilibrium to be achieved, at least locally at the electrode surface. With the knowledge of the approximate temperature at the electrode/solution interface it is possible to calculate the mass transport limited current based on the temperature dependence of the diffusion coefficient of $Fe(CN)_6^{4-}$. The limiting current observed for the oxidation of 2 mM $Fe(CN)_6^{4-}$ in 1 M KCl shows an Arrhenius type increase consistent with an activation energy of 14.3 kJ mol^{-1} and in agreement with Walden's rule[8] and literature data.[5] The expected mass transport controlled limiting current for the oxidation of 2 mM $Fe(CN)_6^{4-}$ at 120 °C can be calculated to I_{lim} = 26 nA. In the corresponding voltammogram [Fig. 2(a)] the observed limiting current is 50 nA and therefore higher. For a temperature of 90 °C the limiting current for the oxidation of 2 mM $Fe(CN)_6^{4-}$ is expected to be 18 nA which is slightly lower than the experimentally observed current in the presence of microwave radiation of 20 nA [Fig. 2(b)]. Therefore under conditions employed in Fig. 2 the temperature jump induces a current response with transient characteristics especially for very large temperature jumps. Further indications for the non-steady-state behaviour are the microwave induced *anodic* current in Fig. 2(d) at 0.22 V *vs.* Ag/AgCl for the reduction of $Fe(CN)_6^{3-}$ and the maximum observed at 0.24 V *vs.* Ag/AgCl for the microwave induced current associated with the oxidation of $Fe(CN)_6^{4-}$ [Fig. 2(a)].

The time scale for a steady-state current to be achieved at a microdisc electrode within ε% has been shown[9] to be approximately $t_\varepsilon = 10^4 r^2/\pi^3 \varepsilon^2 D$. In this expression the time t_ε is related to the electrode radius, r, and the diffusion coefficient, D. For a microdisc electrode of 25 μm diameter the expected time scale for the transient current to settle within 5% of the steady-state current is in the order of 2 s. Therefore the time scale for current transient after a temperature jump is expected to be larger compared to the time scale needed for the temperature to settle.

It has been shown both that microwave activation is an interesting new tool for enhancing and controlling processes in electrochemical systems and that electrochemical detection may be employed for microwave induced chemical processes.

Notes and references

† The intensity distribution in a Panasonic NN-3456 multi-mode microwave oven with modified electric power supply and fitted with a water load was mapped. A hole through the cavity wall extended by a 14.7 mm inner diameter brass tube, 50 mm long, which acted as a waveguide below cutoff, allowed a 1.41 cm diameter electrochemical cell to be inserted into a high intensity region (Fig. 1). A special working electrode design with a range of Pt disc electrodes of 25, 50, and 1000 μm diameter sealed into glass was used to prevent both radiation from escaping through the inlet and sparking. The lead-out from the micro-electrode was in the form of a helix made by winding 0.19 mm diameter platinum wire on a 0.46 mm diameter mandrel with 28 turns per cm. A test with a radiation meter (Apollo XI microwave monitor, Apollo Ltd.) confirmed this design to act as a filter and to stop microwave radiation from being conducted out of the cavity. In electrochemical experiments an Autolab PGSTAT 20 system (Eco Chemie, NL) was used for recording voltammetric and microwave intensity data. Reagents of analytical grade purity and demineralised water of conductivity not less than 18 MΩ cm were used. If not stated otherwise experiments were conducted under an inert atmosphere of argon and at a temperature of 25 ± 2 °C.

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