

Microwave activation in ionic liquids induces high temperature–high speed electrochemical processes

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Received (in Cambridge, UK) 14th July 2004, Accepted 29th September 2004

First published as an Advance Article on the web 27th October 2004

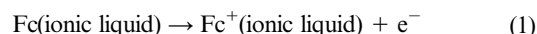
Self-focusing of intense microwave radiation at the tip of a 25 μm diameter platinum disk microelectrode immersed into the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($\text{BMIM}^+\text{PF}_6^-$) containing 1 mM ferrocene causes dramatically (two orders of magnitude) enhanced voltammetric current signals and temperatures in excess of 600 K (at the electrode surface)—extreme conditions sufficient for condensed phase pyrolysis processes to occur.

Microwave heating provides a new and versatile activation tool in chemistry and can lead to localized superheating and inverted temperature gradients.¹ Microwave activation has been employed to promote catalysis,² organic and inorganic syntheses,³ plasma reactions, analytical sample processing, and ceramic sintering. In addition to affecting homogeneous chemical processes, microwave activation has been reported to modify processes at interfaces⁴ and in heterogeneous systems.⁵ The microwave activation of processes in ionic liquids (which are good microwave absorbers) has been reported for various types of homogeneous reactions.⁶

The *in situ* microwave activation of electrochemical processes is possible in a novel electrochemical flow cell system,⁷ in which intense microwave radiation is self-focused into a small region within the diffusion layer at the working electrode surface | solution (electrolyte) interface.⁸ The methodology is complementary to thermal activation of thin wire⁹ or film electrodes,¹⁰ radio frequency heating of the electrode in a channel flow cell,¹¹ laser pulse heating,¹² and radio frequency heating of microelectrodes.¹³ Applications of microwave activated electrochemistry have been proposed in electroanalysis.¹⁴ The microwave effect at metal electrodes is highly localized, which has been demonstrated for example with microwave pulse experiments.¹⁵ Fast temperature pulses can be applied in particular at small fast responding microelectrodes. A simplistic physical model for the microwave focusing and activation effect based on Joule heating and localized low viscosity convection–diffusion has been proposed to quantitatively account for the observed electrochemical currents.¹⁶ It has been shown that in the high temperature zone at the electrode surface, mass transport is enhanced in about equal amounts by (i) the temperature effect on the rate of diffusion and (ii) by additional convection in the presence of temperature and viscosity gradients. Recently, also the quantitative treatment of the effects of focused high-intensity microwave radiation on electrochemical processes in the nonaqueous media has been reported.¹⁷

Ionic liquids¹⁸ are room temperature molten salts and are becoming widely available and recognized as solvents for ‘green’ organic syntheses due to their non-flammability and non-volatility.¹⁹ For some chemical processes significant enhancements in reaction rate, yield, and selectivity have been reported.^{20,21} In electrochemistry, ionic liquids employed as the solvent and electrolyte offer properties such as ionic conductivity, novel solvation effects,^{22,23} and a wide potential window.²⁴ A possible draw-back of ionic liquids is their relatively high viscosity,^{25,26} but this can be overcome for example by thermal activation. In this communication we are exploiting the non-volatile characteristics of ionic liquids for the *in situ* microwave activation of electrochemical processes.

Fig. 1a shows a cyclic voltammogram† for the oxidation of 1 mM ferrocene dissolved in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($\text{BMIM}^+\text{PF}_6^-$) obtained at a 25 μm diameter platinum disk microelectrode.



The oxidation is detected with a midpoint potential of 0.30 V vs. SCE, which is consistent with data reported recently for the electrochemistry of ferrocene in $\text{BMIM}^+\text{PF}_6^-$.²⁷ Under the conditions employed here, a peak-shaped voltammetric response is expected even at a 25 μm diameter disk microelectrode, because of the relatively low diffusion coefficient of ferrocene in the viscous ionic liquid environment. The peak current observed at ambient temperature is approximately 1.7 nA, proportional to the concentration of ferrocene in solution and, as expected under diffusion control, proportional to the square root of the scan rate.

Figs. 1b and c show cyclic voltammetric responses for the oxidation of 1 mM ferrocene dissolved in $\text{BMIM}^+\text{PF}_6^-$ at a 25 μm diameter platinum disk microelectrode at different microwave power settings (magnetron anode currents of 15 mA and 18 mA were applied). In the presence of microwave radiation, the peak-shaped voltammetric signal is changed into a sigmoidal current response and the steady state limiting current, I_{lim} , can be seen to be dramatically increased. Current enhancements of two orders of magnitude are readily achieved (see Fig. 1c and Table 1). It is interesting to more quantitatively explore the high temperature conditions at the electrode surface during microwave activation.

For reversible steady state voltammetric responses, data analysis is possible by plotting $\ln\left(\frac{I}{I_{\text{lim}} - I}\right)$ vs. the potential.²⁸ The slope at the midpoint potential is then related to $\frac{nF}{RT}$, where I is the current, I_{lim} is the current under limiting mass transport conditions, n is the number of electrons transferred per molecule diffusing to the electrode surface, F is the Faraday constant, R is the constant for

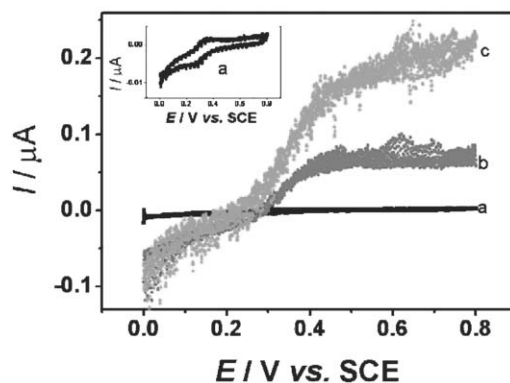


Fig. 1 Cyclic voltammograms (scan rate 0.1 V s⁻¹) for the oxidation of 1 mM ferrocene in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($\text{BMIM}^+\text{PF}_6^-$) at a 25 μm diameter platinum disk microelectrode (a) in the absence and (b,c) in the presence of microwave radiation (magnetron anode currents 15 mA and 18 mA, respectively).

Table 1 Voltammetric data (scan rate 0.1 V s⁻¹) for the oxidation of 1 mM ferrocene in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM⁺PF₆⁻) in the absence and presence of high-intensity microwave radiation focused at a 25 μm diameter Pt disc microelectrode

Magnetron anode current/mA ^a	$E_{\text{mid}}/\text{V vs. SCE}^b$	$I_{\text{lim}}/\text{nA}^c$	$T_{\text{electrode}}/\text{K}^d$
0	0.30	1.7	298 ± 2
13	0.33	22	480 ± 25
15	0.35	80	600 ± 50
18	0.36	200	750 ± 70

^a The magnetron current was used to control the microwave power.¹⁵ ^b The midpoint potential corresponds to the halfwave potential for reversible voltammetric responses. ^c The current I_{lim} corresponds to the peak current or the mass transport limited oxidation current. ^d The temperature of the electrode $T_{\text{electrode}}$ was determined from the slope, $\frac{dE}{dT}$, of the plot of $\ln\left(\frac{I}{I_{\text{lim}} - I}\right)$ vs. the potential E assuming reversible electron transfer (see text).

ideal gases, and T is the temperature in Kelvin. This analysis for voltammetric data is consistent with temperatures of 480 K and 600 K for magnetron current setting of 13 mA and 15 mA, respectively. At higher microwave power even higher temperatures are accessible (see Table 1) but the decomposition of the ionic liquid under these conditions cannot be ruled out. Ferrocene is known to be thermally extraordinarily stable with gas phase pyrolysis temperatures reported higher than 700 K.²⁹ Therefore, ferrocene is an ideal electrochemical probe to explore the conditions in ionic liquids at elevated temperatures. Under the extreme conditions employed here, other types of conventionally redox inactive systems (such as chlorinated aromatics, synthetic, or bio-polymers) may undergo decomposition and electron transfer processes. Temperatures of 600–700 K are consistent with pyrolysis or cracking conditions for many types of organic materials³⁰ and they can be readily reached in ionic liquid environments in the presence of focused microwaves. The thermal stability of the ionic liquid has been considered in the literature³¹ and decomposition may also occur at elevated temperatures but only a small zone is affected by the microwave heating and therefore conditions at the electrode can be sustained. This opens up the possibility of studying electrochemical processes under extreme conditions and to apply electroanalytical methods for systems which under conventional conditions are redox inactive. Other types of high temperature processes may also occur. For example, in spite of ionic liquids being non-corrosive, due to the presence of fluoride (and moisture) in BMIM⁺PF₆⁻, etching of the glass around the platinum microelectrode is observed after prolonged exposure to high temperature conditions.

The steady state voltammetric responses shown in Fig. 1 are enhanced due to localized heating of the liquid at the electrode surface. Switching off or pulsing the microwave power immediately causes the current to return back to the room temperature value (not shown). The limiting current I_{lim} follows an Arrhenius-type behaviour with an apparent activation energy of $E_A = 20$ kJ mol⁻¹, which is not untypical for diffusion processes. However, this activation parameter is not well-defined due to the contributions from both diffusion and convection and the unknown relationship between the current and the diffusion coefficient. The midpoint potential for the voltammetric signal follows an approximately linear dependence when plotted against the temperature at the electrode surface, $T_{\text{electrode}}$ (see Table 1). The slope of this plot, $dE/dT = 0.16$ mV K⁻¹ is small when compared to values determined for ferrocene in other more conventional solvents.¹⁷

In this preliminary report, it has been demonstrated that diffusion-convection controlled electrode processes in ionic liquid media can be locally enhanced by two orders of magnitude. In future, more work will be necessary (i) to further explore the effects of the high temperature conditions generated with microwaves in ionic liquids, (ii) to develop a more quantitative description of the physical processes within the microwave activated region, and (iii) to investigate the effect of solutes and impurities³² on the microwave enhanced electrochemical process.

F. M. thanks the Royal Society for the award of a University Research Fellowship. We are grateful for support from the EPSRC for the project "Microwave-Enhanced Voltammetry—Electrochemistry under Extreme Conditions" (GR/S06349/01).

Notes and references

† Reagents were obtained commercially (1-butyl-3-methylimidazolium hexafluorophosphate from Merck and ferrocene from Aldrich) and used without further purification. Electrochemical experiments were conducted with a μ-Autolab II potentiostat (Eco Chemie, Netherlands). For measurements in the presence of microwaves an electrochemical flow cell was employed placed into a port of a multi-mode microwave cavity (Panasonic NN-3456, 2.45 GHz).¹⁵ The three-electrode electrochemical cell consisted of a Pt counter electrode (downstream), a saturated calomel (SCE) reference electrode (upstream), and a 25 μm diameter working electrode (Micro Glass Instruments, Greensborough, Victoria, Australia). A test with a radiation meter (Apollo XI microwave monitor, Apollo Ltd.) confirmed the design to act as a filter minimising microwave radiation leakage from the cavity. The microwave intensity was controlled via the anode current of the magnetron. During experiments, a slow flow of ionic liquid (ca. 0.12 mL min⁻¹) through the electrochemical cell was maintained to minimize bulk solution heating within the cell and to avoid overheating of the inlet and outlet solution.

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