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Discharge cavitation during microwave electrochemistry at micrometre-sized electrodes

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Microwave induced activation of electrochemical processes at microelectrodes (ca. 0.8 μm diameter) immersed in aqueous electrolyte media is shown to be driven by (i) continuous stable cavitation (giving rise to Faradaic current enhancements by up to three orders of magnitude) and (ii) transient discharge cavitation on the μs timescale (giving rise to cathodic plasma current spikes and more violent surface erosion effects).

Electrochemical processes at platinum microelectrodes are investigated and it is demonstrated that cavitation effects are time and microwave intensity dependent. By pulsing the microwave field and by resolving processes on a sub-microsecond timescale, the cavitation bubble activity and electrical discharge processes at the electrode surface in the presence of microwaves are monitored. Using ultrafast electrochemical equipment, significant current spikes of micro-second duration are observed independent of the applied potential and independent of other underlying electrode processes.

Microwave chemistry[1] offers considerable advantages over conventional heating methods in particular when applied under non-conventional conditions e.g. at elevated pressure, solvent-free, or for substrate-bound reagents.[2] In electro-chemistry microwave activated processes have been demonstrated in a flow cell system at microelectrodes and with microwave radiation (self-)focused into a small region close to the diffusion layer at the electrode|solution interface.[3] Microwave heating applied at metal disc electrodes can result in an "antenna" effect with strong microwave focusing effects and therefore highly localised heating of the liquid at the tip of the electrode.[4,5] This results in convection, vapour bubble nucleation, cavitation, dielectrophoretic liquid jet formation,[6] and boiling close to the electrode surface.[7] Up to now, electrical discharge phenomena have not been observed during microwave electrochemistry.

Electrical discharge is a well known tool for the quick delivery of high levels of energy into solution phase and electrical discharge triggered cavitation processes have been previously studied[8] and exploited.[9] Electrical discharge and plasma phenomena during microwave application are well known in gas phase systems.[10] Electrical discharges and plasmas in the absence of microwaves have also been observed at electrodes immersed in aqueous media with high applied potential.[11]

Here, processes are investigated at the tip of small electrodes immersed into aqueous electrolyte solution and in the presence of microwave radiation. The experimental procedure has been described before[12] and is based on a conventional three electrode electrochemical system where only the working electrode is exposed to the microwave radiation.† Fig. 1 shows typical voltammetric current signals obtained at a 0.8 μm diameter platinum disc electrode immersed in 10 mM $Ru(NH_3)_6^{3+}$ in aqueous 1 M KCl. The $Ru(NH_3)_6^{3+/2+}$ redox system is observed as a well-defined one-electron redox process with a half wave potential of $E_{1/2} = -0.1$ V vs. SCE (see Fig. 1A). The mass transport controlled limiting current, $I_{lim} = -1.4$ nA, is consistent with the expression $I_{lim} = 4nFDrc$ (where n is the number of electrons transfered per molecule diffusing to the electrode surface, F is the Faraday constant, D is the diffusion coefficient, r is the electrode radius, and c is the bulk concentration of redox active reagent[13]).
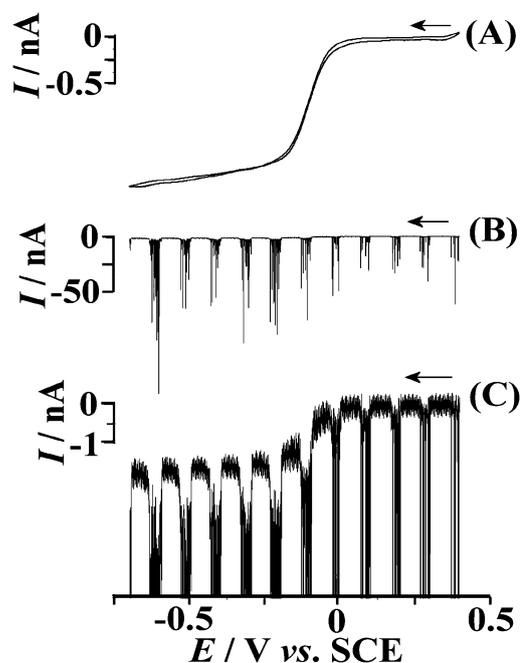

Fig. 1 Voltammetry responses (scan rate 20 mV s⁻¹) obtained for reduction of 10 mM $Ru(NH_3)_6^{3+}$ in aqueous 1 M KCl at a 0.8 μm diameter platinum disc electrode: (A) in the absence of microwave radiation, (B) in the presence of microwaves with 3.4 mA magnetron anode current, and (C) as in B but with expanded current scale.

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In previous reports and at platinum electrodes of typically 25 μm diameter, when increasing the microwave power a gradual increase in microwave enhanced mass transport was observed.[14] Here, at a platinum electrode of 0.8 μm diameter, the effects introduced by microwaves are more dramatic. At relatively low microwave power (3.4 mA magnetron anode current) pulses of microwave radiation (2 s on, 3 s off) immediately result in sharp current spikes (cathodic) which are observed in both the Faradaic current region (<0 V vs. SCE) and in the capacitive current region (>0 V vs. SCE). At a slightly lower microwave power (3.2 mA magnetron anode current) no effects are observed. This threshold effect is likely to be associated with the onset of a non-linear process such as cavitation. Similar current spikes are also observed in aqueous 1 M KCl in the absence of the redox system (not shown). Fig. 1C shows that also the anticipated increase in Faradaic current occurs during microwave pulses. However, the voltammetric signals are not resolved due to the limited instrumental time resolution.

Next, the experiments in the absence and in the presence of $Ru(NH_3)_6^{3+}$ redox system were repeated with a fast potentiostat and oscilloscope.‡ Fig. 2 shows typical chronoamperometry current signals obtained for a higher microwave power (12 mA magnetron anode current) and with a time axis where $t = 0$ corresponds to the beginning of the microwave pulse. Fig. 2A shows a typical chronoamperometric current obtained at 0.4 V vs. SCE where no Faradaic current from the $Ru(NH_3)_6^{3+}$ reduction process should occur. With a "delay time" of ca. 11 ms a dense set of sharp current "spikes" is observed each with typically a couple of microsecond duration. The same observation was made in aqueous 1 M KCl in the absence of $Ru(NH_3)_6^{3+}$. A closer look at these current "spikes" reveals a highly regular pattern (not shown) where the frequency and duration of the "spikes" is dependent on the microwave power. Fig. 2B shows a similar set of "spikes" superimposed on the Faradaic current at a potential of −0.6 V vs. SCE. The Faradaic current component shows a mass transport limited current of ca. −1.2 μA consistent with a close to three orders of magnitude enhancement as reported previously.[15] The nature of the process driving this mass transport enhancement has been linked to the presence of dynamic vapour bubbles (similar to stable cavitation). However, the nature of the current spikes remains to be resolved. An inset in Fig. 2B clearly demonstrates the regular pattern of superimposed current spikes. Increasing the microwave power causes (i) the current spikes to become shorter in duration (less than 1 μs), (ii) the frequency of spikes to increase, and (iii) the delay before the onset of the enhanced currents to shorten. Under these conditions processes at the electrode surface are violent and they may be described as discharge cavitation (similar to violent transient cavitation). Microelectrodes are easily damaged/broken during these experiments in particular at elevated microwave powers. The fact that the current "spikes" are always cathodic (at least over the studied range of potentials and conditions) and that they occur independently of the applied potential suggests a non-Faradaic origin such as a plasma discharge. The experiments when repeated in aqueous 1 M KCl without redox system also result in these sets of cathodic "spikes"

independent of the applied potential at the working electrode. The presence of the substantial Faradaic current component (see Fig. 2B) suggests enhanced mass transport from cavitation and/or bubble dynamics independent from the "spike" phenomenon. The charge under "spikes" is typically 20 pC and therefore one order of magnitude higher compared to those expected for typical surface capacitance values. Also, current spikes due to capacitive charging would be expected to change sign with scan direction.[16]

In order to further interpret these results the conditions during the experiments have to be considered. A vacuum degassing step is employed to avoid gas bubbles forming and
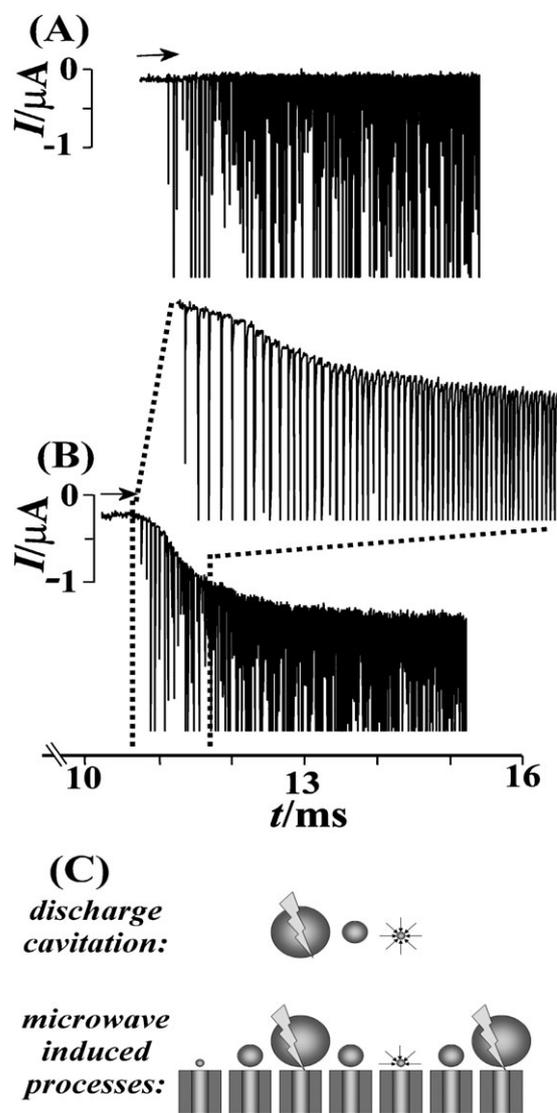

Fig. 2 Chronoamperometry data obtained with a 0.8 μm diameter Pt disc electrode immersed in aqueous 1 M KCl containing 10 mM $Ru(NH_3)_6^{3+}$ in the presence of microwave radiation (12 mA magnetron anode current, pulsed) (A) in the capacitive potential region (ca. 0.4 V vs. SCE) and (B) in the Faradaic potential region (ca. −0.6 V vs. SCE). The time axis shows the time after switching on the microwave pulse. (C) Schematic depiction of homogeneous discharge cavitation versus microwave induced surface discharge cavitation.

blocking the electrode. The delay (*ca.* 11 ms) before the onset of the microwave enhanced currents is likely to be associated with the initial formation of a dynamic vapour bubble at the electrode surface. This vapour bubble once formed creates highly dynamic conditions and it allows all cavitation phenomena to occur. The time it takes for a cavitational bubble collapse at an electrode surface under acoustic cavitation conditions—a couple of microseconds—has been studied by Maisonhaute *et al.*[17] These acoustic cavitation events are very similar to "spike" events shown in Fig. 2B except that they are Faradaic in nature. It is therefore plausible that these spikes are associated with violent bubble collapse and cavitation following a discharge from the electrode into the bubble vapour phase. A schematic comparison of "discharge cavitation" and "microwave induced discharge processes" is shown in Fig. 2C. In "discharge cavitation" a high voltage discharge is employed to trigger the formation of a vapour bubble in a liquid which is followed by a violent collapse (homogeneous cavitation). Microwave induced discharge processes occur in the vicinity of the electrode and the discharge only accompanies the vapour bubble induced process. The amount of electricity in this discharge, several pico-Coulomb based on Fig. 2B, corresponds to electrons injected into the vapour bubble. The increase in discharge frequency and decrease in discharge duration upon increasing the microwave power could be associated with the thickness of the hydrodynamic boundary layer. The chemical effects of this discharge process are currently not known.

In conclusion, focusing microwave energy at the tip of micrometre-sized metal electrodes creates powerful localised microwave fields which lead to phenomena such as (i) localised heating and vapour bubble formation, (ii) vapour bubble oscillation and stable cavitation, and (iii) electrical discharge with more violent transient cavitation. The chemical effects of the resulting plasma current flow and the experimental control of the discharge effect will require further study.

Notes and references

1 H. M. Kingston and S. J. Haswell, *Microwave-Enhanced Chemistry, Fundamentals, Sample Preparation, and Applications*, American Chemical Society Publication, Washington, 1997.
2 A. de la Hoz, A. Diaz-Ortiz and A. Moreno, *Chem. Soc. Rev.*, 2005, **34**, 164.
3 I. J. Cutress, F. Marken and R. G. Compton, *Electroanalysis*, 2009, **21**, 113.
4 U. K. Sur, F. Marken, B. A. Coles, R. G. Compton and J. Dupont, *Chem. Commun.*, 2004, 2816.
5 L. Rassaei and F. Marken, *Chim. Oggi*, 2009, **27**, 41.
6 A. Boika and A. S. Baranski, *Anal. Chem.*, 2008, **80**, 7392.
7 L. Rassaei, R. G. Compton and F. Marken, *J. Phys. Chem. C*, 2009, **113**, 3046.
8 P. Sunka, *Phys. Plasmas*, 2001, **8**, 2587.
9 B. Sun, M. Sato and J. S. Clements, *J. Phys. D: Appl. Phys.*, 1999, **32**, 1908.
10 V. Cirkva and M. Hajek, *J. Photochem. Photobiol., A*, 1999, **123**, 21.
11 K. Azumi, T. Mizuno, T. Akimoto and T. Ohmori, *J. Electrochem. Soc.*, 1999, **146**, 3374.
12 M. A. Ghanem, M. Thompson, R. G. Compton, B. A. Coles, S. Harvey, K. H. Parker, D. O'Hare and F. Marken, *J. Phys. Chem. B*, 2006, **110**, 17589.
13 B. B. Katemann and W. Schuhmann, *Electroanalysis*, 2002, **14**, 22.
14 U. K. Sur, F. Marken, N. Rees, B. A. Coles, R. G. Compton and R. Seager, *J. Electroanal. Chem.*, 2004, **573**, 175.
15 R. G. Compton, B. A. Coles and F. Marken, *Chem. Commun.*, 1998, 2595.
16 E. Maisonhaute, P. C. White and R. G. Compton, *J. Phys. Chem. B*, 2001, **105**, 12087.
17 E. Maisonhaute, C. Prado, P. C. White and R. G. Compton, *Ultrason. Sonochem.*, 2002, **9**, 297.
18 C. Amatore, E. Maisonhaute and G. Simonneau, *Electrochem. Commun.*, 2000, **2**, 81.