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## Microwave activation of electrochemical processes: enhanced PbO<sub>2</sub> electrodeposition, stripping and electrocatalysis

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**Abstract** Microwave activation of electrochemical processes has recently been introduced as a new technique for the enhancement and control of processes at electrode|solution (electrolyte) interfaces. This methodology is extended to processes at glassy carbon and boron-doped diamond electrodes. Deposition of both Pb metal and PbO<sub>2</sub> from an aqueous solution of Pb<sup>2+</sup> (0.1 M HNO<sub>3</sub>) are affected by microwave radiation. The formation of PbO<sub>2</sub> on anodically pre-treated boron-doped diamond is demonstrated to change from kinetically sluggish and poorly defined at room temperature to nearly diffusion controlled and well defined in the presence of microwave activation. Calibration of the temperature at the electrode|solution (electrolyte) interface with the Fe<sup>3+/2+</sup> (0.1 M HNO<sub>3</sub>) redox system allows the experimentally observed effects to be identified as predominantly thermal in nature and therefore consistent with a localized heating effect at the electrode|solution interface. The microwave-activated deposition of PbO<sub>2</sub> on boron-doped diamond remains facile in the presence of excess oxidizable organic compounds such as ethylene glycol. An increase of the current for the electrocatalytic oxidation of ethylene glycol at PbO<sub>2</sub>/boron-doped diamond electrodes in the presence of microwave radiation is observed. Preliminary results suggest that the electrodisolution of solid microparticles of PbO<sub>2</sub> abrasively attached to the surface of a glassy carbon electrode is also enhanced in the presence of microwave radiation.

**Keywords** Voltammetry · Lead · Stripping · Microwave · Thermal activation

### Introduction

Microwave activation of electrochemical processes has recently been shown [1, 2] to allow rapid heat pulses or continuous high-temperature conditions [3] to be achieved and applied in situ. The focusing effect of the metallic electrode located in the microwave field causes the formation of a considerable thermal gradient and a “hot spot” within the diffusion layer directly in front of the electrode surface [4]. Owing to the absorption of microwave energy predominantly in the solution phase and the rapid heat conduction in the metal, the electrode surface remains relatively cold compared to the “hot spot” in solution [4]. The resulting microwave-induced changes in electrochemical processes are dominated by thermal activation and solution convection induced by the temperature gradient. The application of microwave activation in organic (for example, see [5, 6, 8] and for a review [7]) and analytical [9] chemistry has been shown in several cases to be the key to fast and efficient processes, and similar benefits may be expected for microwave-enhanced electrochemical processes. In particular, recent studies by Gründler et al. [10, 11, 12, 13, 14] demonstrate the importance of purely thermal effects in electroanalysis.

Boron-doped diamond electrodes have been employed in a range of demanding electrochemical problems [15, 16, 17] and often offer advantages over other types of carbon-based electrode materials, especially in respect to their chemical inertness, the wide accessible potential window, and the extreme hardness. In electroanalysis, for example, the detection of dopamine [18] and manganese [19] at boron-doped diamond has been reported, and in electrosynthesis, boron-doped diamond electrodes have been proposed for anodic fluorination processes [20]. Recently it has been shown that both metal deposition [21] and metal oxide deposition [22] on boron-doped diamond are possible and the deposition of PbO<sub>2</sub> at high applied potential on anodically pretreated diamond electrodes in the presence of power ultrasound

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followed by cathodic stripping has been employed for trace metal analysis [23]. Furthermore,  $\text{PbO}_2$  itself is a well-known and catalytically active electrode material (for example, see [24, 25]). By depositing  $\text{PbO}_2$  onto boron-doped diamond, a novel type of modified electrode with  $\text{PbO}_2$  reactivity and diamond properties is available, similar to the Pt-modified [26] and the  $\text{IrO}_2$ -modified [27] diamond electrodes reported recently.

In this study, preliminary results of the effect of microwave activation on the deposition and stripping characteristics for Pb metal and  $\text{PbO}_2$  are compared for a glassy carbon electrode and a boron-doped diamond film electrode grown on a tungsten substrate. For both types of electrodes, the effects have been consistently inferred as predominantly thermal in nature. These results suggest that a dramatic improvement for the analytical  $\text{PbO}_2$  deposition and stripping process is achieved on boron-doped diamond electrodes in the presence of microwave activation.

## Experimental

### Reagents

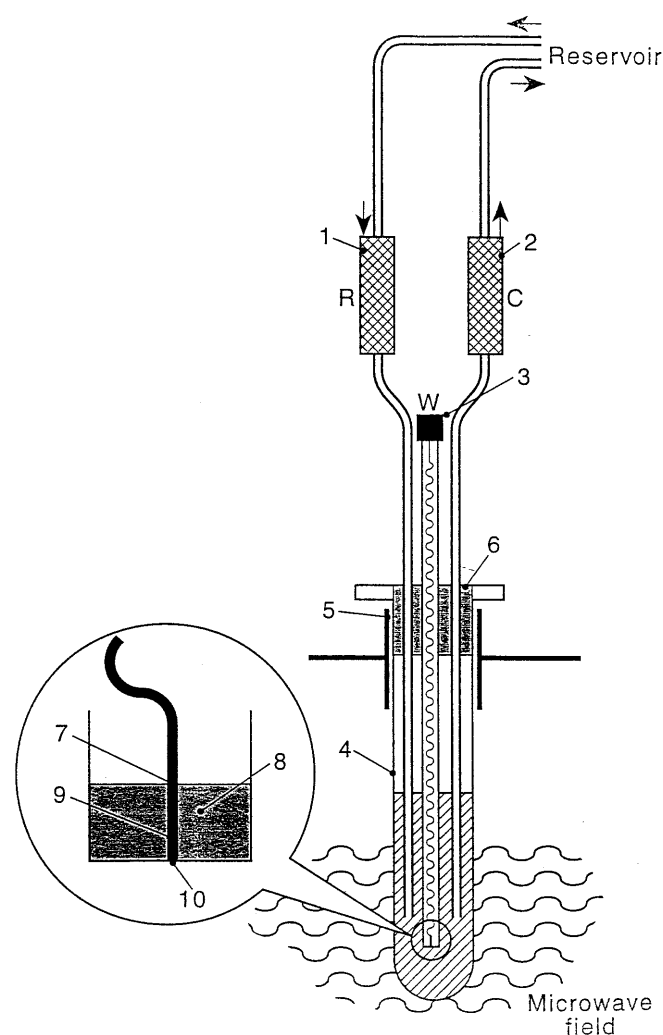
KCl,  $\text{HNO}_3$ , ethylene glycol,  $\text{Fe}(\text{SO}_4)\cdot 7\text{H}_2\text{O}$ ,  $\text{Fe}_2(\text{SO}_4)_3\cdot 5\text{H}_2\text{O}$  (all Aldrich) and  $\text{Pb}(\text{NO}_3)_2$  (BDH) were obtained in the highest commercially available quality and used without further purification. Demineralized and filtered water with a resistivity of not less than  $18 \text{ M}\Omega \text{ cm}$  was taken from an Elgastat water purification system (Elga, High Wycombe, Bucks, UK). Solutions were de-aerated with argon (Pureshield, BOC) for at least 15 min prior to undertaking experiments. All experiments were carried out at a temperature of  $28 \pm 2^\circ \text{C}$  unless otherwise stated.

### Instrumentation

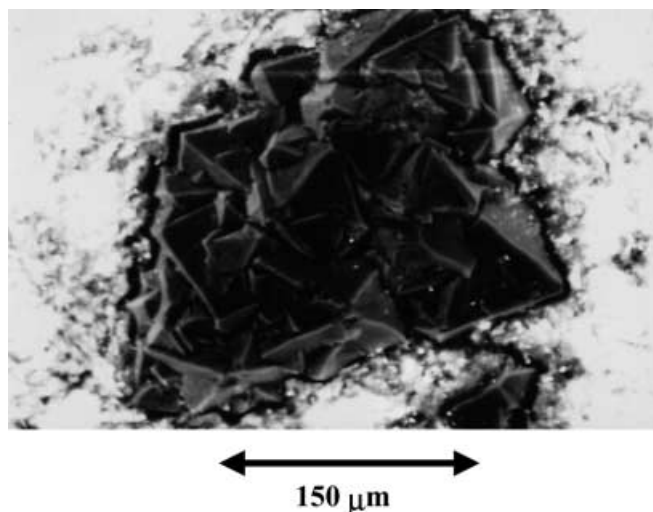
A  $\mu$ -Autolab II potentiostat system (Eco Chemie, Netherlands) was used for electrochemical experiments. The electrochemical cell (see Fig. 1) consisted of a three-electrode arrangement with a saturated calomel electrode (SCE) as reference (1), a Pt-mesh counter electrode (2) and a working electrode (3) designed to operate under microwave conditions [1, 4] (Micro Glass Instruments, Greensborough, Victoria, Australia or Scienglass, Long Hanborough, Oxfordshire, UK) and made from  $250 \mu\text{m}$  diameter Pt wire. The Pyrex glass cell (4) is inserted through a port (5) into the microwave field and closed with a Teflon lid (6). In order to change the working electrode material, either a  $250 \mu\text{m}$  diameter glassy carbon rod (5 mm length) or a  $150 \mu\text{m}$  diameter tungsten rod (9) (5 mm length) coated with a boron-doped diamond film (10) was connected to the platinum wire with conducting silver-loaded epoxy adhesive (7) (RS) and mounted with Torr Seal (Varian Vacuum Products) (8) (see Fig. 1). Excess epoxy was removed from the electrode surface by careful polishing on a fine carborundum paper. The long-term stability of the Torr Seal mounting under microwave conditions was only limited at high temperature and in the presence of aqueous solution, as the extreme heating appeared to gradually cause electrical contact of the aqueous solution phase with the tungsten substrate, which was detected as an increase in background current. For microwave activation experiments an in-house-modified multi-mode microwave oven (Panasonic NN-3456) with a modified power supply and a water energy sink was used. Changing the anode current of the magnetron controlled the microwave intensity. The cell and electrode geometry have a considerable effect on the intensity of the microwave radiation focused into the region close to the electrode surface. The effect of the cell fill height and electrode positioning were found to be

crucial and optimized by maximizing the electrochemically (chronopotentiometrically) detected thermal effect, detected as a shift in equilibrium potential of the  $\text{Fe}^{3+}/2^+$  redox couple ( $4 \text{ mM Fe}^{3+}$ ,  $4 \text{ mM Fe}^{2+}$ ,  $0.1 \text{ M HNO}_3$ ). Before operation the integrity of the system was tested for leaking microwave radiation with a radiation meter (Apollo XI microwave monitor).

For the solid state voltammetric electrodisolution study of  $\text{PbO}_2$  (Aldrich), microparticles were abrasively attached (for example, see [28]) to the  $250 \mu\text{m}$  diameter glassy carbon electrode by gently rubbing the electrode over the solid sample (ca. 3 mg) placed on a filter paper (Whatman). The synthesis of polycrystalline boron-doped diamond films on tungsten substrates (doping level approx.  $10^{20}$ – $10^{21} \text{ cm}^{-3}$ ) has been described recently [29, 30]. The surface of these electrodes is partially oxidized by cycling the potential in pH 2 phosphate buffer solution [30]. An image of the diamond electrode mounted in Torr Seal and exposed by polishing (see Fig. 2) shows crystals with typically  $50 \mu\text{m}$  size and an overall electrode diameter of approximately  $250 \mu\text{m}$ . Electrodes were characterized by Raman spectroscopy (Dilor Labram spectrometer with 20 mW He-Ne laser) and SEM imaging (JEOL JSM-5200 system).



**Fig. 1** Schematic drawing of the electrochemical cell used for in situ microwave-activated voltammetry and the design of the tip of the electrode (see Experimental)

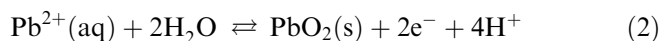


**Fig. 2** SEM image (backscatter mode) of a boron-doped diamond film electrode deposited onto a 150  $\mu\text{m}$  diameter tungsten wire and mounted in epoxy

## Results and discussion

Microwave radiation self-focused into the region in the vicinity of an electrode surface causes a localized activation effect on electrochemical processes, predominantly due to heating [4]. In previous studies, metal electrodes, e.g. gold, platinum and mercury, have been employed to study the effect of the intense microwaves on diffusion, deposition and stripping processes [3]. However, carbon-type materials and especially boron-doped diamond are preferable or essential for some electroanalytical applications. A modification of the platinum working electrode is possible by attaching a wire of 5 mm length and suitable diameter of a new electrode material (see Fig. 1). In Fig. 2 an SEM image of the exposed surface of the polycrystalline boron-doped diamond film electrode grown onto a 150  $\mu\text{m}$  tungsten wire can be seen, with an average crystal size of ca. 50  $\mu\text{m}$ . Only insignificant damage to the electrode surface is caused by the polishing procedure.

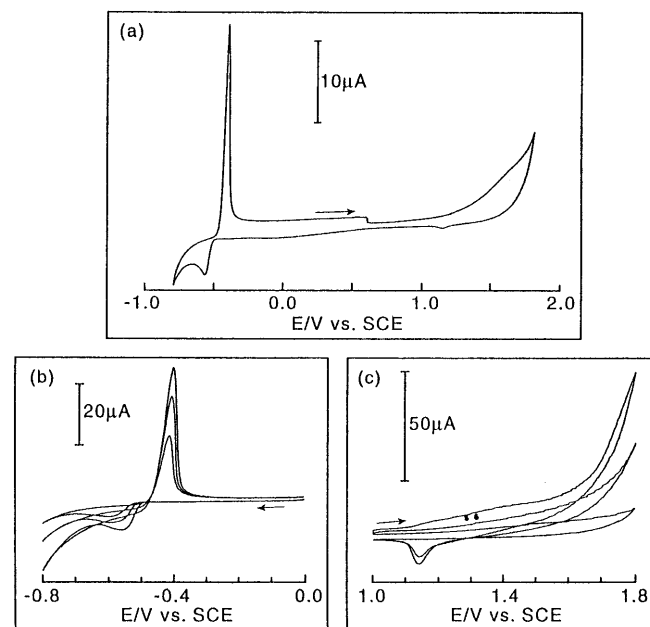
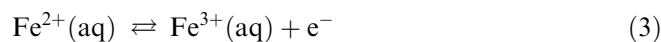
A 250  $\mu\text{m}$  diameter glassy carbon disc electrode prepared by mounting a carbon fibre in epoxy resin (see Experimental) and immersed in 2 mM  $\text{Pb}^{2+}$  in aqueous 0.1 M  $\text{HNO}_3$  allows the detection of both the cathodic deposition of Pb metal (Eq. 1) and the anodic deposition of  $\text{PbO}_2$  (Eq. 2) (Fig. 3a):



The corresponding stripping responses associated with the re-dissolution of the deposits are detected with peak potentials at  $E_{\text{p}}^{\text{ox}}(\text{Pb}) = -0.40$  V vs. SCE and  $E_{\text{p}}^{\text{red}}(\text{PbO}_2) = 1.15$  V vs. SCE. Both of these stripping responses have been employed for the analytical detection of Pb

[21, 22], with the  $\text{PbO}_2$  process having been shown to be insensitive towards oxygen and interferences [22]. However, the deposition and stripping of  $\text{PbO}_2$  on glassy carbon are observed to give only very small and poorly defined responses (Fig. 3c). The effect of microwave radiation on the deposition of Pb metal is shown in Fig. 3b. The nucleation process required during the initial stages of the deposition process is more facile in the presence of microwave radiation and the increase in the stripping response indicates a faster rate of deposition of the metal during the deposition stage. Very similar observations have been described recently for the microwave-enhanced deposition and stripping of cadmium [3]. However, the deposition of  $\text{PbO}_2$  at potentials positive of 1.4 V vs. SCE is affected far more dramatically by microwave radiation than the effect seen for metal deposition. A well-defined stripping response is observed at sufficiently high microwave power (see Fig. 3c).

As a first approximation, thermal activation is believed to be responsible for the observed electrochemical effects of microwave radiation. Hence, a calibration of the electrode surface temperature,  $T_{\text{electrode}}$ , was performed by monitoring the equilibrium potential of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple (Eq. 3) in 0.1 M  $\text{HNO}_3$  as a function of applied microwave power and during conventional heating:



**Fig. 3** Cyclic voltammograms (scan rate 0.1  $\text{V s}^{-1}$ ) obtained at a 250  $\mu\text{m}$  diameter glassy carbon electrode for the reduction and oxidation of 2 mM  $\text{Pb}^{2+}$  in aqueous 0.1 M  $\text{HNO}_3$  scanned over a potential window of **a** -0.8 to 1.8 V vs. SCE, **b** 0.0 to -0.8 V vs. SCE in the presence of microwave radiation (magnetron current 0, 30 and 50 mA) and **c** +1.0 to 1.8 V vs. SCE in the presence of microwave radiation (magnetron current 0, 30 and 50 mA)

The formal reversible equilibrium potential for this redox process is sensitive to temperature changes and a linear shift of  $dE^{\circ}(\text{Fe}^{3+/2+})/dT = 1.2 \pm 0.1 \text{ mV K}^{-1}$ , determined experimentally by monitoring the zero current potential of the cell at temperatures ranging from 20 to 90 °C, gave an estimate of the temperature in the presence of microwave radiation. Data obtained by comparing conventional heating and microwave activation are summarized in Table 1. Temperatures,  $T_{\text{electrode}}$ , determined in this way refer to temperatures at the electrode surface. Owing to the characteristics of microwave heating, the formation of considerable “inverted” thermal gradients near the electrode surface [4] is possible and  $T_{\text{electrode}}$  may only approximately describe the thermal effect induced by microwave radiation in solution. It can be seen that the microwave-enhanced voltammograms shown in Fig. 3b and c have been obtained at temperatures of approximately  $T_{\text{electrode}} = 57$  and  $73$  °C, respectively. Indeed, in voltammetric experiments, in which conventional bulk heating rather than localized microwave activation is employed, similar trends of deposition and stripping characteristics to those shown in Fig. 3 can be detected at ca. 70 °C. Nevertheless, it has recently been shown [4] that conditions in the presence of microwave activation (localized heating, considerable thermal gradients, convection) are different compared to conventional heating (no thermal gradient, stagnant solution phase) and give rise to a higher rate mass transport.

The  $\text{PbO}_2$  stripping response shown in Fig. 3c, although enhanced by microwave activation, remains small compared to the Pb metal stripping process, in agreement with sluggish kinetics and/or competing processes at the glassy carbon electrode surface. It is interesting to ask whether microwave radiation affects only the deposition process or also causes an enhancement of the stripping process. In a preliminary study, the effects of microwave radiation on the electrodisolution of  $\text{PbO}_2$  microparticles, abrasively attached [28] to the 250  $\mu\text{m}$  diameter glassy carbon electrode, have been

explored. In Fig. 4a a voltammetric curve obtained for the electrodisolution process at ambient temperature is shown. The reduction process commences at 1.15 V vs. SCE and a peak at ca. 1.03 V vs. SCE is detected. In the presence of pulsed microwave radiation a considerable enhancement is detected, suggesting that the process indeed becomes more facile in the presence of microwave activation. The broad, drawn-out shape of the current response (Fig. 4a) also suggests that the overall process for the reduction of the  $\text{PbO}_2$  microparticles in 0.1 M  $\text{HNO}_3$  is more complex and not consistent with the reversible mechanism proposed in Eq. 2, presumably due to local pH changes in the vicinity of the microparticles (for example, see [31]).

In Fig. 5, cyclic voltammograms for the oxidation and reduction of an aqueous solution of 2 mM  $\text{Pb}^{2+}$  (0.1 M  $\text{HNO}_3$ ) obtained at a boron-doped diamond electrode in the absence and presence of microwave activation are shown. The background current for boron-doped diamond is considerably smaller compared to glassy carbon and, hence, well-defined Pb metal deposition and stripping can be observed (Fig. 5a). Although the wide potential window of diamond electrodes at positive potentials suppresses competing background processes, the deposition and stripping of  $\text{PbO}_2$  on diamond is seen to proceed only slowly in the absence of microwave activation. Compared to the well-defined Pb metal stripping response at  $-0.4$  V vs. SCE, the  $\text{PbO}_2$  stripping response at 1.15 V vs. SCE is small and insignificant. However, a considerable change occurs in the presence of microwaves. The cathodic Pb deposition (Fig. 5b) is affected to a similar extent compared to the process at glassy carbon (Fig. 3b) and it is plausible to assume a thermal activation effect. The deposition and stripping of  $\text{PbO}_2$ , however, become an order of magnitude more efficient in the presence of microwave radiation. The cathodic stripping response detected at boron-doped diamond is comparable in peak current to that observed for the anodic stripping of Pb metal.

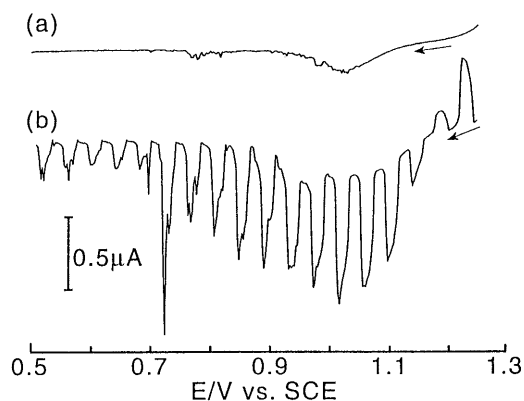
**Table 1** Data for the chronopotentiometrically detected thermal effect of microwave activation at a 250  $\mu\text{m}$  diameter glassy carbon electrode determined as the equilibrium potential  $E^{\circ}(\text{Fe}^{3+/2+})$  (4 mM  $\text{Fe}^{2+}$ , 4 mM  $\text{Fe}^{3+}$ , 0.1 M  $\text{HNO}_3$ ) or  $T_{\text{electrode}}$  as a function of magnetron current

Magnetron anode current (mA)	$E^{\circ}(\text{Fe}^{3+/2+})^a$ (mV vs. SCE)	$T_{\text{electrode}}^{b,c}$ (°C)
0	492	$28 \pm 2$
20	508	$40 \pm 2$
30	530	$57 \pm 2$
40	547	$71 \pm 2$
50	550	$73 \pm 2$
60	551	$75 \pm 2$

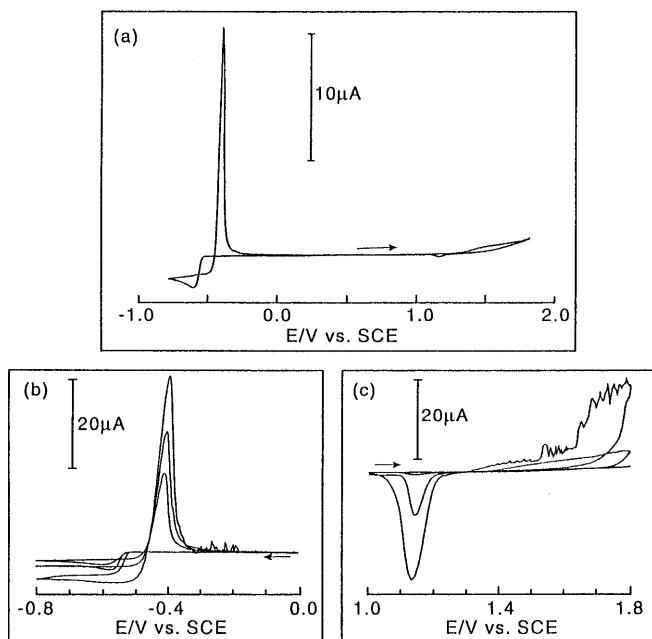
<sup>a</sup>Zero current potential

<sup>b</sup>Temperatures  $T_{\text{electrode}}$  calculated from  $E^{\circ}$  data by using  $dE/dT = 1.2 \text{ mV K}^{-1}$

<sup>c</sup>Errors estimated



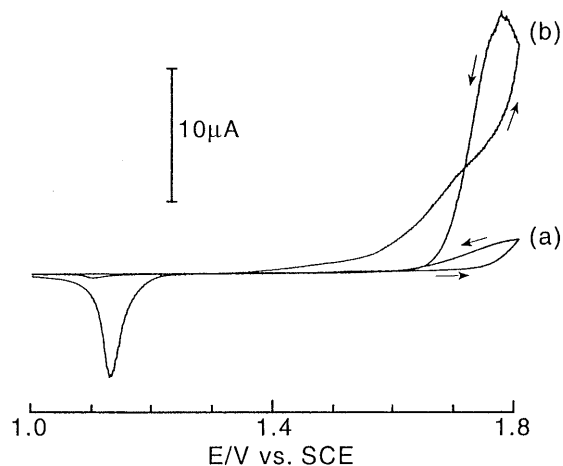
**Fig. 4** Cyclic voltammograms (scan rate  $0.1 \text{ V s}^{-1}$ ) obtained for the reduction of  $\text{PbO}_2$  microparticles mechanically attached (see Experimental) to a 250  $\mu\text{m}$  diameter glassy carbon electrode and immersed in 0.1 M  $\text{HNO}_3$  (a) in the absence and (b) in the presence of microwave radiation (pulsed magnetron current 50 mA)



**Fig. 5** Cyclic voltammograms (scan rate  $0.1 \text{ V s}^{-1}$ ) obtained at a boron-doped diamond electrode for the reduction and oxidation of  $2 \text{ mM Pb}^{2+}$  in aqueous  $0.1 \text{ M HNO}_3$  scanned over a potential window of **a**  $-0.8$  to  $1.8 \text{ V vs. SCE}$ , **b**  $0.0$  to  $-0.8 \text{ V vs. SCE}$  in the presence of microwave radiation (magnetron current  $0$ ,  $30$  and  $50 \text{ mA}$ ) and **c**  $+1.0$  to  $1.8 \text{ V vs. SCE}$  in the presence of microwave radiation (magnetron currents  $0$ ,  $30$  and  $50 \text{ mA}$ )

Therefore under conditions of microwave activation in aqueous  $0.1 \text{ M HNO}_3$ , the deposition of  $\text{PbO}_2$  becomes essentially mass transport controlled and without kinetic limitations, as opposed to the process observed in the absence of microwaves. The presence of current fluctuations at high applied microwave powers is believed to indicate the nucleation of gas bubbles in the vicinity of the electrode.

Finally,  $\text{PbO}_2$  is an important electrode material for a variety of electro-organic processes and is known to exhibit catalytic properties for several types of electro-oxidations (for example, see [32]) and oxygen-transfer processes [31, 33]. The presence of  $\text{PbO}_2$  on boron-doped diamond electrodes therefore turns a rather inert electrode material into a catalytically active modified electrode. In Fig. 6 it can be seen that the oxidation of  $10 \text{ mM}$  ethylene glycol in aqueous  $0.1 \text{ M HNO}_3$  can be achieved in the presence of  $\text{PbO}_2$ . A characteristic "current loop" indicates the onset of the ethylene glycol oxidation during the course of the  $\text{PbO}_2$  deposition and this process becomes even more pronounced in the presence of microwave radiation. Surprisingly, the  $\text{PbO}_2$  stripping process, which is of considerable importance for the sensitive analytical detection of  $\text{Pb}$ , is not strongly affected by the presence of an excess of the organic reagent. Both the deposition of the  $\text{PbO}_2$  on the boron-doped diamond electrode and the electro-oxidation of ethylene glycol appear to be largely independent and non-interfering processes in the presence of micro-



**Fig. 6** Cyclic voltammograms (scan rate  $0.1 \text{ V s}^{-1}$ ) obtained at a boron-doped diamond electrode for the reduction and oxidation of  $1 \text{ mM Pb}^{2+}$  in the presence of  $10 \text{ mM}$  ethylene glycol in aqueous  $0.1 \text{ M HNO}_3$  (**a**) in the absence and (**b**) in the presence of microwave radiation (magnetron current  $50 \text{ mA}$ )

waves. The oxidation process of the organic material must be located at the surface of the solid rather than in the solution phase via a soluble redox catalyst.

## Conclusions

In this preliminary study, it has been shown that microwave activation of electrochemical processes is possible for a range of processes and electrode materials. Kinetically limited processes, such as the deposition and stripping of  $\text{PbO}_2$ , can be activated into highly efficient or even mass transport controlled processes. The main physical basis of the microwave effect can be inferred as predominantly thermal activation localized at the electrode|solution interface, although more specific effects during electrodeposition and stripping cannot be ruled out. The advantages of microwave over conventional heating in electrochemistry may be summarized as (1) unusually high temperatures with an "inverted" temperature gradient at the electrode|solution interface, (2) an increase in mass transport caused by the formation of thermal gradients and a convective flow pattern [4] and (3) the possibility of rapid heat/microwave pulse transient studies. The use of boron-doped diamond electrodes in the presence of microwave activation appears promising, especially for the analytical use of deposition and cathodic stripping of  $\text{PbO}_2$ .

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