

Available online at www.sciencedirect.com



Electrochimica Acta 50 (2005) 2331-2341

electrochimica Actu

www.elsevier.com/locate/electacta

# Building up an electrocatalytic activity scale of cathode materials for organic halide reductions

C. Bellomunno<sup>a</sup>, D. Bonanomi<sup>a</sup>, L. Falciola<sup>a,1</sup>, M. Longhi<sup>a,1</sup>, P.R. Mussini<sup>a,\*,1</sup>, L.M. Doubova<sup>b,1</sup>, G. Di Silvestro<sup>c</sup>

<sup>a</sup> Department of Physical Chemistry and Electrochemistry, University of Milano, Via Golgi 19, 20133 Milano, Italy <sup>b</sup> IENI-CNR, Corso Stati Uniti 4, 35127 Padova, Italy

<sup>c</sup> Department of Organic and Industrial Chemistry, University of Milano, Via Venezian 21, 20133 Milano, Italy

Received 2 March 2004; received in revised form 18 June 2004; accepted 8 October 2004 Available online 21 November 2004

### Abstract

A wide investigation on the electrochemical activity of four model organic bromides has been carried out in acetonitrile on nine cathodes of widely different affinity for halide anions (Pt, Zn, Hg, Sn, Bi, Pb, Au, Cu, Ag), and the electrocatalytic activities of the latter have been evaluated with respect to three possible inert reference cathode materials, i.e. glassy carbon, boron-doped diamond, and fluorinated boron-doped diamond. A general electrocatalytic activity scale for the process is proposed, with a discussion on its modulation by the configuration of the reacting molecule, and its connection with thermodynamic parameters accounting for halide adsorption. © 2004 Elsevier Ltd. All rights reserved.

*Keywords:* Organic electrocatalysis; Organic halide reduction; Halide adsorption; Specifically interacting cathode materials; Non-interacting cathode materials (GC, BDD, FBDD)

### 1. Introduction

Surprisingly enough, careful investigations of organic electrocatalytic processes are still very rare, in spite of their intrinsic great potentialities, and unlike the many extensive investigations having been carried out so far on inorganic electrocatalytic processes. This lack can be explained by the fact that many major research groups are now concentrating on urgent topics connected with fuel cell development [1], but also by the intrinsic complexity of *organic* electrocatalysis:

(a) with respect to non-electrocatalytic organic electrochemical processes, because the electrode must be regarded not as an inert electron source (appropriate e.g. for investigations on the intrinsic reactivity of the organic substrate), but as an interacting partner for the reacting molecule, and therefore must be included in the reaction intermediate. In other words, electrocatalytic processes involve inner-sphere electron transfers [2] requiring to take into account not only the substrate intrinsic reactivity, but also specific adsorption/desorption effects, concerning not only the substrate but also the solvent and the supporting electrolyte [3];

(b) with respect to inorganic electrocatalysis, because of the structural complexity of the reacting molecule (the chemical environment surrounding a given active group not only modulates its intrinsic reactivity, but also the electrocatalytic effect exerted on it by the electrode material [4]).

Therefore, a correct investigation on a given organic electrocatalytic process should necessarily be an extensive, systematic, "multivariate" search, requiring to change one by one many parameters (the electrode material, the surface morphology, the structure of the organic molecule, the solvent, the supporting electrolyte), while keeping the others constant. A

<sup>\*</sup> Corresponding author. Tel.: +39 02 50314211; fax: +39 02 50314300. *E-mail address:* patrizia.mussini@unimi.it (P.R. Mussini).

<sup>&</sup>lt;sup>1</sup> ISE member.

<sup>0013-4686/\$ –</sup> see front matter © 2004 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2004.10.047

partial example is provided by the recent work of some of us concerning the electrocatalytic activity of silver for the reduction of organic halides, and including investigations on the effects of morphology and state of the active surface [5,6], of the molecular structure [4] and of the supporting electrolyte in constant acetonitrile solvent [3].

Actually the electrocatalytic reduction of organic halides RX, assumed [4] to proceed via an attenuated radical intermediate involving three "actors",  $R \cdots X \cdots Me$  (quite similar to the one featuring as activated complex in atom-transfer radical polymerizations [7]) appears an ideal model case for a detailed study of organic electrocatalysis. In fact

- the reduction of organic halides is a key process in organic chemistry;
- many authoritative research groups have thoroughly investigated both specific adsorption of halide anions onto metal electrodes (e.g. [8,9]) and non-electrocatalytic reduction of organic halides [10];
- other authoritative research groups have recently applied computational chemistry methods to the problem of specific halide adsorption [11,12];
- organic halide reductions have already been carried out, several times and with interesting results [10,13–18], on electrocatalytic cathode materials, but such works were predominantly application-oriented, rather than aimed to a systematic investigation of the underlying mechanism.

An exception to the above limitations is the recent, brilliant work by Langmaier and Samec [19], which, although prompted by a specific applicative problem, i.e. the electroanalytical determination of anaesthetic halothane (2bromo-2-chloro-1,1,1-trifluoroethane) in human and animal metabolism, actually features an extensive research on the electrochemical reduction of the above substrate on many cathodic materials and several media, providing convincing mechanistic schemes and interpretations of the trends of both reduction potentials (in connection with Me $\cdots$ X bonding energies) and reduction currents (in connection with solvent viscosities). However, many aspects of the above work should be modified in the perspective of a truly general investigation on RX electrocatalytic reductions, especially the following ones:

- the target molecule is a very specific one (a bromide of high intrinsic reactivity, and featuring no less than four other different halide atoms on its two-carbon backbone);
- (2) all the cathode surfaces are prepared along a single, simple standard procedure of mechanical + electrochemical polishing, irrespective of specific requirements of the different metals tested;
- (3) the experiments are predominantly carried out in 1 M NaOH in water or methanol, i.e. in media powerfully interacting with many of the tested cathodes;
- (4) above all, the electrocatalytic effect of a given cathode material is conveniently evaluated in terms of positive shift of peak potential with respect to a cathode mate-

rial assumed free of electrocatalytic effects, such as the glassy carbon one [4], while the authors considered only electrocatalytic materials in their investigations.

In this context, the present work is aimed to achieve a *general* treatment of the effects of the cathode material in the electrocatalytic reduction of organic halides, along the following methodological guidelines:

- three model organic bromides have been chosen among those tested in our cited previous screening [4] (acetobromoglucose, a glycosyl bromide; benzyl bromide; and 8bromooctanol, an alkyl bromide for which silver displays a marked catalytic effect probably on account of the presence of the hydroxy group acting as "adsorption auxiliary" [4]), plus halothane for comparison with Langmaier and Samec's work;
- nine cathode materials have been selected (Pt, Zn, Hg, Sn, Bi, Pb, Au, Cu, Ag), having widely different electronic properties and therefore showing very low to very high affinity for halides in specific adsorption experiments [8], and each surface has been prepared and/or activated along specific procedures;
- all experiments have been carried out in the same medium, i.e. acetonitrile (ACN) + 0.1 M tetraethylammonium perchlorate TEAP or tetraethylammonium tetrafluoborate TEATFB, having proved to be the least specifically interacting media for organic halide reduction in our previous screenings on silver [3,4,6];
- among the tested cathodes three possible non-catalytic reference materials have been included, i.e. glassy carbon (GC), a popular electrode for mechanistic investigations of outer-sphere electron transfers to organic halides (e.g. [20]) and the even more inert boron doped diamond (BDD) and fluorinated boron doped diamond (FBDD).

## 2. Experimental

The model organic bromides (Fig. 1)  $\alpha$ -acetobromoglucose ABG 1 (FLUKA), benzyl bromide BzBr 2 (Aldrich), 8-bromooctanol 3 (Aldrich), and halothane 4 (Aldrich), were used as received with the exception of ABG which was purified from CaCO<sub>3</sub> (added in traces as a stabilizer by the producer) by filtration in diethyl ether. Voltammograms were recorded for each substrate and cathode material in ACN (Merck HPLC grade, water  $\leq 0.05\%$ ) + 0.1 M TEAP (or TEATFB (Fluka), because of recent limitations on perchlorate availability in our country; in any case, in a parallel work on the medium effect on the electrocatalytic reduction of organic halides [21] we verified that the two supporting electrolytes result in no significant differences in the CV patterns for a given system), at three concentrations (0.001, 0.002 and 0.003 M) and at scan rates ranging  $20-500 \text{ mV s}^{-1}$ . The cyclovoltammetric investigations were carried out on carefully deaerated solutions in a cell thermostated at 298 K, by an Autolab PGSTAT 12 or an Auto-





AcO

AcO

AcO

AcO

Fig. 1. The model organic halides selected for this investigation.

lab PGSTAT 30 potentiostat/galvanostat (EcoChemie, The Netherlands) run by PCs with GPES software and equipped with a Metrohm 663 VA Stand. The reference electrode was the aqueous saturated calomel one (SCE), while the counter electrode was either a carbon or a platinum one. To allow intersolvental comparison along the IUPAC ferrocene criterion [22] the half-wave potential of ferrocene  $E_{1/2} = (E_{p,c} + E_{p,a})$  was measured on a GC electrode in our ACN + 0.1 M TEATFB medium against our aqueous SCE, yielding 0.394 V.

Controlled-surface *polycrystalline silver electrodes* were prepared on Pt wire supports (diameter: 0.05 cm, length: 1 cm) by silver electrodeposition against a silver foil anode in six-electrode batches from a 10 g dm<sup>-3</sup> KAg(CN)<sub>2</sub> bath at a current density i=2 mA cm<sup>-2</sup> for 15 h, followed by 5 min sonication in the operating solvent in a Bransonic 221 ultrasound bath. This procedure affords reproducible, controlled surfaces [5].

*Polycrystalline copper cathodes* were freshly prepared on Cu wire supports (diameter = 0.05 cm, length = 1 cm) by copper electrodeposition from a CuSO<sub>4</sub> bath at i = 0.5 mA cm<sup>-2</sup> for 15 min, followed by 5 min sonication in the operating solvent.

Gold cathodes were ultrapure gold wires (length = 1.5 cm, diameter = 0.1 cm), or a gold disk (Metrohm 6.1204.140, diameter = 0.2 cm), polished both mechanically, with wet alumina on filter paper, and electrochemically, by cycling in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

*Lead cathodes* were thin lead plates  $(1 \text{ cm} \times 0.5 \text{ cm} \times 0.05 \text{ cm}; \text{Aldrich 99.95\%})$  suspended by small platinum alligator clamps, with the working surface delimited by Teflon<sup>TM</sup> ribbon; they were mechanically polished, and then activated by immersion in 0.5 M H<sub>2</sub>SO<sub>4</sub> at -0.55 V for 20 min, followed by repeated immersions in boiling CH<sub>3</sub>COONH<sub>4</sub> solution, and by verification of open circuit potential in 0.5 M H<sub>2</sub>SO<sub>4</sub> [23]. The background CV usually featured a typical oxide reduction peak at about -1.5 V (SCE) in the first cycles, which however disappeared upon prolonged cycling. Substrate additions were made only then, and with concurrent nitrogen flowing.

*Bismuth cathodes* were spindle-shaped pieces (length = 1–1.5 cm; maximum diameter ~0.2 cm; Aldrich 99.999%) suspended by small alligator clamps, with the working surface delimited by Teflon<sup>TM</sup> ribbon; they were activated by polarization in a saturated KI solution with 1% HCl (5 min, 0.7 A cm<sup>-2</sup>) [24].

*Mercury cathodes* were either a Metrohm E410 HDME (drop surface [determined by weight] =  $0.022 \text{ cm}^2$ ), or the SDME 6.1246.020 included in the above Metrohm stand (drop surface [determined by weight] =  $0.0046 \text{ cm}^2$ ).

*Tin cathodes* were wires (length = 1 cm, diameter = 0.1 cm, Aldrich 99.999%) polarized in a  $20 \text{ cm}^3 30\%$  HClO<sub>4</sub> + 80 cm<sup>3</sup> CH<sub>3</sub>COOH solution (40 s,  $0.6 \text{ A cm}^{-2}$ ), then kept at -1.7 V (SCE), in a 0.0015 M Na<sub>2</sub>SO<sub>4</sub> solution for 30 min [25].

Zinc cathodes were wires (Aldrich 99.995%, length = 1 cm, diameter = 0.05 cm) submitted to galvanostatic steps (0/0.2 A cm<sup>-2</sup>, 5 s each, total time 2 min) in a 50% H<sub>3</sub>PO<sub>4</sub> solution, then kept for 20 min at -1.4 V (SCE) in the working solution [26].

*Platinum cathodes* were ultrapure platinum wires (length = 1 cm, diameter = 0.05 cm) polished both mechanically, with wet alumina on filter paper, and electrochemically by 30 s steps (-0.25/0/1.5 V), followed by cycling in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

*Glassy carbon cathodes* were either an AMEL GC disk electrode (diameter = 0.25 cm) or a Metrohm 6.1204.110 GC disk electrode (diameter = 0.2 cm). They were polished by wiping with acetone and then with the working solvent (a procedure affording reproducible results for our systems; sonication proved useless).

Boron-doped diamond cathodes and fluorinated borondoped diamond cathodes were 0.225 and 0.36 cm<sup>2</sup> plates, respectively (courtesy of A. De Battisti and S. Ferro, University of Ferrara; the characterization of such electrode materials is reported in [27,28]) glued by colloidal graphite (Leit-C) to a Pt wire and embedded into a concrete matrix (Saratoga Unistop, selected for its satisfactory inertness to acetonitrile) leaving it to dry for several days before use. The electrodes were polished by wiping with acetone and then with the working solvent.

### 3. Results and discussion

# 3.1. The problem of the reference, non-catalytic cathode material

As it has been shown in a former work on silver cathodes [4], the molecular structure surrounding a given active group powerfully modulates not only its intrinsic reactivity, but also the electrocatalytic activity of the cathode in the process, since even groups not involved in the faradaic process can influence both the extent and mode of specific adsorption. For example, the electrocatalytic activity of silver for the reduction of bromides featuring one or more "adsorp-

tion auxiliaries" such as hydroxyl, phenyl, and (additional) halide groups is even two or three times greater than with the analogous, purely aliphatic bromides [4]. To estimate the extent of the electrocatalytic effect of a given cathode material Me in the reduction of a given substrate, normalized with respect to the substrate intrinsic reactivity, it is convenient to consider the first reduction peak potential difference  $\Delta = (E_{p,Me} - E_{p,Ref})$ , where the "Ref" subscript denotes an inert reference material that can be regarded purely as an electron source. It should be underlined that the mechanism of the reduction reaction can be different on the different electrodes. according to the possibly different reaction intermediates, as it is, inter alia, implicit in the concept of catalysis; nevertheless the above difference is significant, since it accounts for the difference in activation energy for the uptake of the first electron via any reaction mechanism. Now glassy carbon (GC), a popular electrode for mechanistic investigations of outer-sphere electron transfers to organic halides [20], could be a convenient candidate for the inert reference electrode, but its inertness has been questioned on account of the significant amount of oxygenated functions usually present on its surface [29]. The more recently appeared boron doped diamond (BDD) electrode looks a more appropriate inert reference candidate, being predominantly hydrogen-terminated, which makes it inter alia rather inert to adsorption while retaining reversible to quasi-reversible electron transfer for inorganic model redox couples such as  $Fe(CN)_6^{-3/-4}$ ,  $Ru(NH_3)_6^{+2/+3}$ , and  $IrCl_6^{-2/-3}$  [30]. Moreover, the fluorinated boron-doped diamond (FBDD) has very recently been introduced, featuring a consistent number of fluoride atoms on its surface, which results in a more hydrophobic character and therefore in significant deactivation of the hydrogen evolution reaction in water [31]; for similar reasons we foresaw that FBDD should be even less favourable to halide reduction, since the F adatoms could have a repulsive effect on the approaching halide leaving group of the reacting molecule.

Therefore as a preliminary step to the comparison of the electrocatalytic materials, we have studied the electrochemical activity of our model substrates on the above three carbonbased electrodes, GC, BDD, and FBDD. The results are summarized in Table 1 and visualized in Figs. 2–5. It appears that

- the potential window available in ACN + 0.1 M TEAP (or TEATFB) on the diamond electrodes (BDD, FBDD) is slightly wider on the negative side, 100–200 mV, than on GC; such background (normalized with respect to the electrode surface) features on diamond-based electrodes a generally lower capacitance than on GC, as it happens in water [30];
- the CV characteristics are, whenever observable, single, irreversible peaks;
- the intrinsic reactivity of the four tested bromides (accounted for by the peak potentials on the non-catalytic electrodes) follows the order halothane  $4 \ge$  benzyl bromide  $2 \gg$  acetobromoglucose  $1 \gg 8$ -Br-octanol 3, a sequence following the substrates'  $S_N1$  character in nucle-

#### Table 1

CV features (peak potentials  $E_p$ , peak current densities  $i_p$  normalized with respect to concentration  $c = 0.003 \text{ mol dm}^{-3}$ ) obtained in solvent ACN at  $0.2 \text{ V s}^{-1}$  for the reduction of the four model organic bromides on the three cathode materials tested as non-specifically interacting reference materials

	GC	BDD	FBDD
Acetobromoglucose 1			
Supporting electrolyte	TEAP	TEATFB	TEATFB
$E_{\rm p}$ (V)	-2.491	-2.672	-2.97
$E_{\rm p} - E_{\rm p,GC}$ (V)	0	-0.181	-0.48
$(-i_p/c)$ (A cm <sup>-2</sup> mol <sup>-1</sup> dm <sup>3</sup> )	0.398	0.283	
Benzyl bromide 2			
Supporting electrolyte	TEATFB	TEAP	TEATFB
$E_{\rm p}$ (V)	-1.910	-2.326	-2.584
$E_{\rm p} - E_{\rm p,GC} (\rm V)$	0	-0.416	-0.674
$(-i_p/c)$ (A cm <sup>-2</sup> mol <sup>-1</sup> dm <sup>3</sup> )	0.748	0.623	0.555
8-Bromooctanol 3			
Supporting electrolyte	TEAP	TEAP	
$E_{\rm p}$ (V)	-2.79	No signal	before background
Halothane 4			
Supporting electrolyte	TEATFB	TEATFB	TEATFB
$E_{\rm p}$ (V)	-1.827	-2.195	$-2.37 (0.5 \mathrm{V  s^{-1}})$
$E_{\rm p} - E_{\rm p,GC} (\rm V)$	0	-0.336	
$(-i_p/c)$ (A cm <sup>-2</sup> mol <sup>-1</sup> dm <sup>3</sup> )	0.73	0.68	0.287

ophilic substitution. In particular, the intrinsic reactivity of the latter compound is so low that no wave can be observed before the background on the less active diamond electrodes;

the reduction potential sequence on the three carbon-based electrodes follows (excepting compound 3, of such a low intrinsic activity that its reduction can be observed only on the GC electrode) the sequence GC > BDD > FBDD(possibly a sequence of decreasing Lewis acidity of the reacting surfaces). The last features can be convincingly justified in terms of BDD (and even more FBDD) being less specifically interacting than GC with the reacting substrate on account of the increasing H (and F) versus O(H) ratio. FBDD appears by far the less active surface, but probably the hydrogen-terminated BDD is the more appropriate inert reference, considering that the fluorinated FBDD surface can even exert a repulsive effect on the approaching halide leaving group of the reacting molecule. Anyway, in the development of an electrocatalytic activity scale as described below, we will use GC as the reference electrode since its behaviour approaches that of BDD, and it is the only carbon-based electrode on which all the four molecules tested exhibit a reduction peak in the observable window.

*The electrocatalytic activity scale*: To enlighten the existing relationship between the cathode material and its electrocatalytic effect on the target process, we have studied the reactivity of the above four model molecules on nine cathode materials, showing very low to very high affinity for halides in specific adsorption experiments [8]: Zn, Pt, Hg, Sn, Bi, Pb, Au, Cu, Ag, each one being prepared along the specific procedure described in Section 2.



Fig. 2. CV features for the reduction of substrate acetobromoglucose 1 on different cathode materials, recorded at  $0.2 \text{ V s}^{-1}$  scan rate, in ACN + 0.1 M TEAP (or TEATFB) medium.

Table 2

CV features (peak potentials  $E_p$ , peak current densities  $i_p$  normalized with respect to concentration  $c = 0.003 \text{ mol dm}^{-3}$ ) obtained in solvent ACN for the electrocatalytic reduction of model substrate *acetobromoglucose* at  $0.2 \text{ V s}^{-1}$  on the cathode materials tested as electrocatalytic materials for the target reaction plus the glassy carbon reference electrode, for comparison

Cathode	$D^{\circ}_{298(\mathrm{M}-\mathrm{Br})} (\mathrm{kJ}\mathrm{mol}^{-1})$	Geometric surface (cm <sup>2</sup> )	0.1 M supporting electrolyte	$E_{\rm p}\left({\rm V}\right)$	$-i_{\rm p}/c ~({\rm A}{\rm cm}^{-2}{\rm mol}^{-1}{\rm dm}^3)$	$E_{\rm p} - E_{\rm p,GC} ({\rm V})$
Ag	293	0.161	TEATFB	-1.284	0.60	1.163
Pb	247	1	TEAP	-1.835	0.20	0.656
Au	220.3	0.636	TEAP	-1.844	0.40	0.647
Cu	338	0.159	TEATFB	-1.880	0.32	0.611
Hg	72.8	0.022	TEAP	-1.933	0.41	0.558
Sn	>565	0.385	TEAP	-1.938	0.22	0.553
Bi	267	0.942	TEATFB	-2.082	0.42	0.409
Pt	142	0.19	TEAP	-2.23	0.57	0.26
Zn	309	0.143	TEAP	No signal		
GC		0.049	TEAP	-2.491	0.40	0

Bonding energies  $D_{298(M-Br)}^{\circ}$  (kJ mol<sup>-1</sup>) [19,33], are also quoted.

Table 3

CV features (peak potentials  $E_p$ , peak current densities  $i_p$  normalized with respect to concentration  $c = 0.003 \text{ mol dm}^{-3}$ ) obtained in solvent ACN for the electrocatalytic reduction of model substrate *benzyl bromide* at  $0.2 \text{ V s}^{-1}$  on the cathode materials tested as electrocatalytic materials for the target reaction plus the glassy carbon reference electrode, for comparison

Cathode	$D^{\circ}_{298(\mathrm{M-Br})} (\mathrm{kJ}\mathrm{mol}^{-1})$	Geometric surface (cm <sup>2</sup> )	0.1 M supporting electrolyte	$E_{\rm p}$ (V)	$-i_{\rm p}/c ~({\rm A}{\rm cm}^{-2}{\rm mol}^{-1}{\rm dm}^3)$	$E_{\rm p} - E_{\rm p,GC} (\rm V)$
Ag	293	0.161	TEATFB	-1.047	0.71	0.863
Hg	72.8	0.022	TEAP	-1.465	0.30	0.437
Pb	247	1	TEAP	-1.531		0.379
Bi	267	0.942	TEATFB	-1.594		0.316
Au	220.3	0.636	TEAP	-1.635	0.54	0.275
Cu	338	0.206	TEATFB	-1.686	1.08	0.224
Sn	>565	0.385	TEAP	-1.867	0.23	0.043
Zn	142	0.143	TEAP	-1.902		0.008
Pt	309	0.157	TEAP	Backgrou	nd anticipation, $\sim -2.2  \text{V}$	
GC		0.049	TEATFB	-1.910	0.75	0

Bonding energies  $D_{298(M-Br)}^{\circ}$  (kJ mol<sup>-1</sup>) [19,33], are also quoted.

Table 4

CV features (peak potentials  $E_p$ , peak current densities  $i_p$  normalized with respect to concentration  $c = 0.003 \text{ mol dm}^{-3}$ ) obtained in solvent ACN for the electrocatalytic reduction of model substrate 8-*bromooctanol* at 0.2 V s<sup>-1</sup> on the cathode materials tested as electrocatalytic materials for the target reaction plus the glassy carbon reference electrode, for comparison

Cathode	$D^{\circ}_{298(M-Br)}$ (kJ mol <sup>-1</sup> )	Geometric surface (cm <sup>2</sup> )	0.1 M supporting electrolyte	$E_{\rm p}\left({\rm V}\right)$	$-i_{\rm p}/c \;({\rm A}{\rm cm}^{-2}{\rm mol}^{-1}{\rm dm}^3)$	$E_{\rm p} - E_{\rm p,GC} ({\rm V})$
Ag	293	0.161	TEAP	-1.572	0.55	1.215
Pb	247	1	TEAP	-2.201	0.13	0.586
Au	220.3	0.636	TEAP	-2.31		0.473
Hg	72.8	0.022	TEAP	No signa	l before background	
Pt	142	0.19	TEAP	-2.38	0.57	0.387
GC		0.049	TEAP	-2.787	0.30	0

Bonding energies  $D^{\circ}_{298(M-Br)}$  (kJ mol<sup>-1</sup>) [19,33], are also quoted.

Table 5

CV features (peak potentials  $E_p$ , peak current densities  $i_p$  normalized with respect to concentration  $c = 0.003 \text{ mol dm}^{-3}$ ) obtained in solvent ACN for the electrocatalytic reduction of model substrate *halothane* at  $0.2 \text{ V s}^{-1}$  on the cathode materials tested s electrocatalytic materials for the target reaction plus the glassy carbon reference electrode, for comparison

Cathode	$D^{\circ}_{298(\mathrm{M}-\mathrm{Br})} (\mathrm{kJ}\mathrm{mol}^{-1})$	Geometric surface (cm <sup>2</sup> )	0.1 M supporting electrolyte	$E_{\rm p}$ (V)	$-i_{\rm p}/c \;({\rm A}{\rm cm}^{-2}{\rm mol}^{-1}{\rm dm}^3)$	$E_{\rm p} - E_{\rm p,GC} ({\rm V})$
Hg	72.8	0.015	TEATFB	-0.851, -0.998	1.05	0.976
Ag	293	0.161	TEATFB	-1.120	0.96	0.707
Pb	247	1	TEATFB	-1.229	1.09	0.598
Cu	338	0.2	TEATFB	-1.274	0.91	0.560
Au	220.3	0.314	TEATFB	-1.431	0.67	0.396
GC		0.049	TEATFB	-1.827	0.73	0

Bonding energies  $D_{298(M-Br)}^{\circ}$  (kJ mol<sup>-1</sup>) [19,33], are also quoted.

The results are summarized in Tables 2 (substrate acetobromoglucose), 3 (substrate benzyl bromide), 4 (substrate 8bromooctanol) and 5 (substrate halothane) and synopsized in the corresponding Figs. 2–5.

The reduction processes are both chemically and electrochemically irreversible; increasing the substrate concentration from 0.001 to 0.003 M usually (but not always) results in a negative potential shift of a few to many tenths of mV per decade (according to the cathode/substrate system), consistently with the observations by Langmaier and Samec for the halothane case in other reaction media [19], which they ascribed to significant specific adsorption of the substrate on the cathode surface. The current densities obtained on the different cathode materials (always featuring a linear dependency on  $v^{0.5}$ , typical of diffusional, not adsorptive, peaks) are generally very similar (especially in the ABG and halothane cases), a good agreement when considering the wide range of forms and dimensions of the electrodes tested and the fact that current densities have been calculated by normalization of the currents against the *geometric* area, since reliable criteria for active surface determination were unavailable for many cathode materials. However, some significant exceptions do appear, and can be ascribed to partial surface deactivation, or to the active surface differing significantly from the geometric one, or to specific effects such as the formation of an organometallic product (especially some Hg and Pb cases resulting in more complex signals). On the average the current densities show an increase in the sequence ABG < Br-Octanol  $\approx$  BzBr < halothane, possibly connected with the increasing diffusion coefficients of the tested substrates (con-





sistently with their decreasing bulkiness and hydrophilicity). Moreover, dealing with irreversible peaks, the reaction mechanism should be also taken into account; however, in our case all the model bromides should undergo a first concerted dissociative electron transfer, which should be the rate determining step according to many authoritative works in the literature [32–37].

From our "electrocatalytic activity parameter"  $\Delta = (E_{p,Me} - E_{p,GC})$  a scale of electrocatalytic activity can be deduced for each model substrate, the four scales being plotted together in Fig. 6. It is evident that

• silver is by far the most catalytic cathode material for the target process, resulting in a dramatic anticipation of the reduction potential (i.e. lowering of the activation energy for the uptake of the first electron) with respect to the non catalytic reference material, the relevant  $\Delta$  values ranging 0.6–1.3 V according to the bromide molecular structure;

- both Cu and Au, preceding and following Ag in the same group of the periodic table, feature average catalytic activities ( $\Delta = 0.3-0.7$  V);
- a similar, average catalytic activity range ( $\Delta = 0.3-0.7$  V) is provided by a series of metals belonging to the following two groups in the periodic table and having strong tendency to organometallic compound formation (Hg, Pb, and to a lesser degree, Bi, Sn);
- low catalytic effects, or no effects at all, are obtained on Pt and Zn, which never gave well defined peaks;
- of course, having taken GC as the reference material, BDD and FBDD result in increasingly negative *∆* values.

It is worthwhile noticing that the best electrocatalytic materials in the scale in Fig. 6 include the materials resulting the most efficient catalysts in the preparative works available in the literature, even concerning very different halides (e.g. geminal polychlorides in environmentally oriented papers,



Fig. 4. CV features for the reduction of substrate 8-bromooctanol **3** on different cathode materials, recorded at  $0.2 \text{ V s}^{-1}$  scan rate, in ACN + 0.1 M TEAP (or TEATFB) medium.

such as [13,14,18]). This confirms the general validity of our scale for the process under study.

Besides the above general features common to all model substrates, the electrocatalytic effects significantly depend, in both their extents and sequence, on the molecular structure surrounding the active bromide group, as it is evident considering the last columns in Tables 2-5 (where for each substance the cathode materials are listed in decreasing order of our "electrocatalytic activity parameter"  $\Delta$ ) and also looking at Fig. 6. For instance, catalytic effects for the reduction of benzyl bromide are significantly and constantly lower (by from one-third to one-half) with respect to catalytic effects for the reduction of glycosyl bromide ABG and of bromooctanol; lower electrocatalytic effects are obtained for halothane, too, featuring a remarkable smoothing of the silver activity and an equally remarkable enhancement of that of mercury: actually, it is the first halide case so far encountered (including our former parallel Hg/Ag screening of about 40 organic halides [4]) where silver is not the most electrocatalytic cathode, and it must be connected with the formation of an organometallic compound, as it is evident from the relevant peak shape.

It is worthwhile underlining that, as expected, intrinsic reactivity and electrocatalytic effects are not necessarily proportional: halothane and benzyl bromide, although resulting *much more intrinsically reactive* than ABG and bromooctanol (considering the scale of reduction potentials on the inert reference cathode), result in *significantly lower electrocatalytic effects*. In fact the molecular structure is likely to modulate the electrocatalytic capability of the metal according with one or more of the following features:

• its higher or lower cooperation in the specific adsorption of the reacting molecule [4], and its effects on the distance and accessibility of the reaction site with respect to the cathode surface;

- its effects on the stability of the three-actor (Me · · · X · · · R) reaction intermediate typical of the electrocatalytic process;
- its possible promoting formation of organometallic products (several evident examples of which appear in Figs. 2–5);
- its possible effects on concurrent coadsorption or desorption of solvent and/or supporting electrolyte.

The higher electrocatalytic effects on ABG and bromooctanol could therefore be connected with them both featuring oxygen-containing groups acting as adsorption auxiliaries [4], although also the phenyl group of benzyl bromide and the chloride atom of halothane can specifically interact with the electrode surfaces. Of course the adsorption of other groups should be such to support and not to hinder, or compete with, the adsorption of the reacting group. Hindering or competition by neighbour halide atoms could explain the comparatively much lower catalytic effect of silver on halothane (actually a sort of hydrophobic halide bundle). A program of SERS investigations is currently being planned to acquire experimental information on the adsorption geometry of our model molecules on such SERS-active electrocatalytic surfaces as Ag, Au, and Cu.

Considering the above many factors affecting the reaction mechanism it is evident that finding out a quantitative relationship justifying the experimental electrocatalytic activity scale shown in Fig. 6 should indeed not be an easy task. Of course a key ad hoc parameter must be the  $X \cdots Me$  or  $X^- \cdots Me$  adsorption energy, as it is in well known, inorganic electrocatalytic processes leading to the so popular and useful "volcano-like" plots.

Computational electrochemistry groups are certainly aware of this important problem. Significantly, authoritative



Fig. 5. CV features for the reduction of substrate halothane 4 on different cathode materials, recorded at  $0.2 \text{ V s}^{-1}$  scan rate, in ACN + 0.1 M TEATFB medium.

theoretical studies have recently appeared, dealing with the problem of computing adsorption energies, charge distributions, halogen bonding energies, equilibrium bonding distances, and adsorbate charge for Me<sub>n</sub>–X or Me<sub>n</sub>–X<sup>-</sup> systems (Ignaczak and Gomes [11], Koper and Van Santen [12]). Unfortunately, both works refer to vacuum; this surely accounts for the calculated metal—halide affinity sequences being mostly in contraddiction with experimental results obtained in adsorption, reactivity (including our works) and SERS investigations. Actually, in his cited work [12], Koper underlines that, since water stabilizes a negative charge on the halide, the electrostatic interaction of a solvated halide with a metal surface will be substantially different from the halogen/halide interaction at the metal/vacuum surface. Moreover, the metal work function  $\Phi_{M}$  should be modified into  $\Phi_{M'}$  as suggested by Trasatti [38].

Therefore, at present, thermodynamic parameters on halide ion adsorption in solution can be derived only by experimental data, particularly spectroscopic X–Me bonding energies. In their pioneer work [19] Langmaier and Samec, starting from the assumption of a reaction mechanism hinging on an adsorptive rate determining step followed by uptake of the first electron, come to predict a volcano-like relationship between the reduction potentials obtained on the tested metals and the relevant X–Me bonding energies, derived from a tabulation of spectroscopic results [39]. In their particular, non-standard case (see the discussion in Section 1), referring to halothane in water



Fig. 6. The experimental electrocatalytic activity scale (referred to the non-catalytic GC assumption) of the tested cathode materials Me for the reduction of four model organic bromides in ACN with TEAP or TEATFB supporting electrolytes.

or methanol with NaOH supporting electrolyte, such relationship actually appears approximately verified, so that they even manage to discuss it in terms of coverage degrees, being optimal on silver on account of its intermediate halide bonding energies among the tested metals (in analogy with the case of the hydrogen evolution reaction on platinum).

To verify if the Langmaier and Samec relationship could be generalized, we have plotted against the same spectroscopic bonding energies (referred to the silver one, as the authors did) the four  $\Delta = E_{p,Me} - E_{p,GC}$  series obtained for our model substrates in ACN solvent with the nearly inert supporting electrolytes TEAP or TEATFB. For the sake of discussion, it is useful to underline that the so obtained diagram, appearing in Fig. 7, is directly comparable with Fig. 7 in Ref. [19], the only difference being that the latter's zero level was assigned to the reduction potential of the most catalytic electrode (Ag) since these authors performed no standardization against a non-catalytic electrode. In our figure we followed our criterion instead than the authors' one since, apart from the importance of knowing the total extents of the electrocatalytic effects (rather than their level with respect to the maximum one), normalizing against the most catalytic electrode is unappropriate when more than one halide structure has to be compared, since the electrocatalytic effects of silver are different for each structure. Fig. 7 shows that

- *each* substrate corresponds to a characteristic *significantly different* both in shape and level on the electrocatalytic activity scale;
- the characteristics pertaining to substrates BzBr (circles), halothane (crosses), and Br-octanol (squares) *can be considered roughly volcano-shaped* with a maximum on silver

(but only neglecting the anomalous case of mercury); however, the same does not seem to hold for ABG (triangles), the substrate corresponding to the highest catalytic effects (even if bismuth and platinum, the most deviating points, come from rather critical CV experiments);

• mercury represents a strong anomaly, particularly concerning the halothane case (which however is very likely justified by the formation of an organometallic compound). A similar anomaly, although less remarkable, appears also in Fig. 7 in Ref. [19], although only in the case of water and not in the methanol one.



Fig. 7. The experimental electrocatalytic effects of a series of cathode materials Me for the reduction of the four organic bromide substrates ABG (triangles), BzBr (circles), Br-octanol (squares) and halothane (crosses) in ACN medium, plotted as a function of the relevant MeBr bonding energies, referred to the AgBr one.

2341

Therefore our experimental results only vaguely comply with the volcano relationship predicted by Langmaier and Samec, which is not surprising. In fact, the use of thermodynamic parameters describing adsorption of a simple halide atom or ion on the metal surfaces cannot account for the powerful modulating effect exerted by the molecular structure surrounding the reacting halide atom in an *organic* halide (a far better parameter could be provided by the  $R \cdots X \cdots$  Me bonding energies obtained from SERS experiments); nor can they account for the possible formation of organometallic compounds. Moreover, the reaction mechanism postulated by the above authors [19] is, by their own admission, a simplified one, neglecting desorption or coadsorption of solvent and supporting electrolyte.

### 4. Conclusions

Our wide screening on four different model halides now affords an experimental scale of electrocatalytic activity of cathode materials for the reduction of organic halides in a very popular and favourable solvent for this key process, acetonitrile, in combination with supporting electrolytes giving no significant adsorption competition with the target molecules. Such scale, pivoting on the adoption of a proper non-catalytic reference material, includes both features that can be considered general (silver as by far the best electrocatalytic material, the group of metals showing intermediate catalytic activity, the metals showing little or no activity, the reactivity sequence of the three possible non-catalytic electrode materials, and so on), and specific features connected to the particular molecular structure surrounding the active group (inversions in the sequence of materials having intermediate activity, evidence of formation of organometallic compounds, the unexpected performance of mercury in the halothane case, and so on). This justifies the only partial compliance of the experimental results with the Langmaier and Samec scheme, not to mention the necessity of including solvent and supporting electrolyte in the assumed reaction mechanism. The next logical steps towards a more complete elucidation of the process will therefore include a screening on the role of the solvent and supporting electrolyte, preparative experiments on chosen (substrate + solvent + metal) systems and a program of SERS investigations on the  $R \cdots X \cdots Me$  bonds on Ag, Cu, and Au, three cathode materials that are both SERS active and electrocatalytic for the reduction of organic halides.

### Acknowledgements

The financial support of Italy's MIUR (FIRB and COFIN) is gratefully acknowledged. Moreover, the authors would like to thank Prof. A. De Battisti and Dr. S. Ferro (University of Ferrara, Italy) for the gift of the BDD and FBDD materials, and Prof. A. Gennaro and Dr. A. Isse (University of Padova, Italy) for fruitful discussions.

### References

- Electrocatalysis: from Theory to Industrial Applications, in: S. Trasatti (Ed.), Electrochimica Acta, vol. 48, 2003 (special issue).
- [2] A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, 2nd ed., Wiley, New York, 2001, p. 116.
- [3] P.R. Mussini, S. Ardizzone, G. Cappelletti, L.M. Doubova, M. Longhi, S. Rondinini, J. Electroanal. Chem. 552 (2003) 213.
- [4] S.B. Rondinini, P.R. Mussini, P. Muttini, G. Sello, Electrochim. Acta 46 (2001) 3245.
- [5] S. Ardizzone, G. Cappelletti, L.M. Doubova, P.R. Mussini, S. Rondinini, Elektrokhimija (Russ. J. Electrochem.) 39 (2002) 182.
- [6] S. Ardizzone, G. Cappelletti, L.M. Doubova, P.R. Mussini, S.M. Passeri, S. Rondinini, Electrochim. Acta 48 (2003) 3789.
- [7] K. Matyjaszewski (Ed.), Controlled Radical Polymerization, ACS Symposium Series No. 685, American Chemical Society, Washington, DC, 1998.
- [8] A. Hamelin, T. Vitanov, E.S. Sevastyanov, A. Popov, J. Electroanal. Chem. 145 (1983) 225, and literature cited therein.
- [9] M.L. Foresti, M. Innocenti, F. Forni, R. Guidelli, Langmuir 14 (1998) 7008, and literature cited therein.
- [10] H. Lund, O. Hammerich, Organic Electrochemistry, 4th ed., Dekker, New York, 2001, p. 341, and literature cited therein.
- [11] A. Ignaczak, J.A.N.F. Gomes, J. Electroanal. Chem. 420 (1997) 71.
- [12] M.T.M. Koper, R.A. Van Santen, Surf. Sci. 422 (1999) 118.
- [13] A. Kotsinaris, G. Kyriakou, C. Lambrou, J. Appl. Electrochem. 28 (1998) 613.
- [14] A. Schizodimou, G. Kyriacou, C. Lambrou, J. Electroanal. Chem. 471 (1999) 26.
- [15] M.J. Moorcroft, C. Prado, R.G. Compton, H.B. McPeak, C.E.W. Hahn, J. Electroanal. Chem. 528 (2002) 127.
- [16] Y. Hori, K. Murata, T. Oku, Chem. Lett. 32 (2003) 230.
- [17] A.A. Isse, A. Gennaro, Chem. Commun. 23 (2002) 2798.
- [18] N. Sonoyama, K. Hara, T. Sakata, Chem. Lett. (1997) 131.
- [19] J. Langmaier, Z. Samec, J. Electroanal. Chem. 402 (1996) 107.
- [20] A. Cardinale, A.A. Isse, A. Gennaro, M. Robert, J.M. Savéant, J. Am. Chem. Soc. 124 (2002) 13533.
- [21] L. Falciola, M. Longhi, F. Migliorini, P.R. Mussini, L.M. Doubova, G. Di Silvestro, J. Electroanal. Chem., in press.
- [22] G. Gritzner, J. Kuta, Pure Appl. Chem. 56 (1984) 461.
- [23] R. Amadelli, private communication.
- [24] A.N. Frumkin, M.P. Pyarnoya, N.B. Grigor'ev, U.V. Palm, Elektrokhimija 10 (1974) 1130.
- [25] L.P. Khmelebaya, B.B. Damaskin, Elektrokhimija 17 (1981) 1721.
- [26] V.V. Batrakov, A.I. Sidnin, Elektrokhimija 8 (1972) 743.
- [27] S. Ferro, A. De Battisti, J. Phys. Chem. B 107 (31) (2003) 7567.
- [28] S. Ferro, A. De Battisti, Anal. Chem. 75 (24) (2003) 7040.
- [29] R.C. Engstrom, V.A. Strasser, Anal. Chem. 56 (1984) 136.
- [30] J. Xu, M.C. Granger, Q. Chen, J.W. Strojek, T.E. Lister, G.M. Swain, Anal. Chem. 69 (1997) 591A.
- [31] G. Siné, L. Ouattara, M. Panizza, C. Comninellis, Electrochem, Solid State Lett. 6 (9) (2003) 9.
- [32] J.M. Savéant, J. Am. Chem. Soc. 109 (1987) 6788.
- [33] F. Maran, E. Vianello, G. Catelani, F. D'Angeli, Electrochim. Acta 34 (4) (1989) 587.
- [34] C.P. Andrieux, L. Gélis, M. Medebielle, J. Pinson, J.M. Savéant, J. Am. Chem. Soc. 112 (1990) 3509.
- [35] C.P. Andrieux, A. Le Gorande, J.M. Savéant, J. Am. Chem. Soc. 114 (1992) 6892.
- [36] J.M. Savéant, J. Am. Chem. Soc. 114 (1992) 10599.
- [37] A.R. Mount, M.S. Appleton, W.J. Albery, D. Clark, C.E.W. Hahn, J. Electroanal. Chem. 334 (1992) 155.
- [38] S. Trasatti, in: J.O'M. Bockris, B.E. Conway, E. Yeager (Eds.), Comprehensive Treatise of Electrochemistry, vol. 1, Plenum Press, New York, 1980, p. 65.
- [39] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 81st ed., CRC Press, Boca Raton, FL, USA, 2000.