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# Palladized silver as new cathode material: Evidence of a one-electron scission for primary alkyl iodides

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## A B S T R A C T

Silver electrodes modified by “palladization” thanks to an immersion in acidic solutions of Pd<sup>2+</sup> salts, exhibit exceptional catalytic capabilities especially in the cleavage of primary alkyl halides used as standard systems in order to evaluate the catalytic activity. Such chemically modified surfaces characterized by the formation of an Ag/Pd-based alloy showed large potential shifts compared to the use of glassy carbon or even smooth silver cathodes. Specifically, these palladium-doped silver surfaces were successfully used for cleaving carbon–iodine bonds. Thus, preliminary results have revealed that palladized silver electrodes behave quite differently from smooth silver and showed exceptional catalytic capabilities. Cathodic reductions were achieved in dimethylformamide, acetonitrile, and propylene carbonate. While smooth silver cathodes generally entailed two-electron cleavage reactions (evidence of two clearly separated steps in propylene carbonate), palladized silver interfaces always yield catalytic cleavages of carbon–iodine bonds according to single one-electron processes with the transient formation of a free alkyl radical leading to homo-coupling processes.

## Keywords:

Cathode material  
Palladium silver alloy  
Silver electrodes  
Cleavage of carbon–iodine bonds  
Homo-coupling

## 1. Introduction

The discovery of ideal and multi-purpose electrodes in the field of organic electrochemistry remains nowadays an important goal to specifically achieve new reactions in which the heterogeneous character of the electrode surface could play a crucial role [1]. Basically, the use of mercury is now banned for environmental reasons [2] whereas both cost and weak hydrogen over-voltage make the use of platinum within the cathodic domain difficult. Alternately, different carbon surfaces such as graphite or glassy carbon provide universal solid working electrodes but their neutrality towards electrochemical ions insertion and their tendency to graft electro-generated species were often mentioned (e.g., like highly reactive free radicals within a well defined potential range) [3]. Similarly, electrodes covered with functionalized conductive polymers could be used in interfacial synthesis by mimicking the principle of organic chemistry on solid support [4] especially when organo-metallic centers and/or metallic micro aggregates are incorporated into the matrix. Consequently, some new insights in electrochemical synthesis may be linked to the development of solid electrodes with very specific properties. Following this approach, pure silver [5] as well as other solid metal electrodes modified by adatoms [6] could offer interesting prospects when tailored for specific reactions.

Especially within the cathodic range, two-electron cleavage reactions are of importance in organic synthesis because some of them can be applied to deprotection processes [7]. However, the success in achieving such deprotections by reductive scission reactions depends on the electrochemical potential necessary to cleave these carbon–heteroatom bonds. Most of the reported reactions of this type occurs at potentials lower than  $-2$  V vs. SCE, and consequently does not allow the use of aqueous or even wet organic solvents at most polarized solid metals.

The group from Rennes underlined during the past three years the interest in using smooth palladium and palladized surfaces [8] to improve the ease of carbon–halide bonds scission [9], in particular those of alkyl iodides. More recently, the use of palladium associated with copper was successfully developed [10–12]. In the present preliminary paper, we similarly develop an easy way to produce a thin layer of an Ag/Pd alloy particularly useful to strongly speed up bonds scission often described as having high activation energy to achieve the first electron transfer [13–18]. Thus these new modified electrodes have been simply formed by chemical palladization of both smooth silver and silvered solid conducting substrates, the latter being produced simply by electrodeposition of Ag<sup>0</sup>. Here are gathered the first results on the cleavage of a large series of primary alkyl iodides RI. Reactions on palladized silver substrates are compared to those currently observed at glassy carbon electrodes. The advantages of these Ag–Pd surfaces in terms of catalytic character, stability, simplicity of

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use and formation are preliminarily underlined. The use of such interfaces is presented in terms of potential shifts, chemical stability of the surface, and catalytic efficiency. Our results were also compared to the use of smooth silver recently developed [19–24] using, however, organic tertiary and benzylic halides already known to be more reactive than the ones studied in the present work.

## 2. Experimental

### 2.1. Chemical doping of silver by palladium and characterization

The modification of silver by palladium at the nanometric scale was simply obtained by contact of smooth silver metal with a fresh aqueous solution of palladium sulphate in sulphuric acid. One gram of  $\text{Pd}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$  (Alfa Aesar) was dissolved in 100 mL of 0.1 N  $\text{H}_2\text{SO}_4$  solution. After a few seconds, a shiny layer progressively covered the silver surface due to the displacement of  $\text{Ag}^0$  by palladium cations. Palladium nitrate could be used as well. The layer thickness appeared to strongly depend on the time of contact with the palladium solution.

Characterization of the as-produced layers was carried out by a combined SEM, HRTEM and EDS study. Morphology of the layer formed onto the electrode was first investigated by SEM using a FEI QUANTA F200P coupled with an Oxford Link ISIS instrument for EDS analysis. The TEM and HRTEM imaging were performed using a FEI TECNAI F20 S-TWIN whereas the elemental composition was also determined by EDS analysis at nanometer resolution. Since the displacement reaction occurs whatever the silver substrate used, TEM characterizations were directly performed using a homemade silver sample-holder (silver grids for microscope commercially unavailable). The diffraction patterns were performed using the selected area diffraction (SAED) mode or by Fourier transform of the HRTEM imaging.

In order to be used as an electrode (micro- or working-electrode), the metallic substrate was rinsed with water, then alcohol and at last acetone. Finally each electrode was dried with a hot air flow during about 30 s. Under such conditions, electrodes were easily re-used and gave coherent data providing they were rinsed according to the above procedure. Along this study, the resulting electrolysis products such as free radicals are suspected to be more or less strongly adsorbed onto the surface, and disturb the following experiments.

It also appeared of interest to make electrodes from silvered surfaces. These electrodes surfaces were obtained by galvanostatic deposits of silver from a solution of  $\text{AgNO}_3$  ( $10 \text{ g L}^{-1}$  in a 0.1 N  $\text{HNO}_3$  solution). These deposits, elaborated onto glassy carbon, smooth silver or platinum, were achieved thanks to fixed current electrolyses ( $0.5 \text{ mA mm}^{-2}$ ). Silver deposition corresponded to electricity amounts between  $10^{-3}$  and  $4 \times 10^{-3} \text{ C mm}^{-2}$ .

### 2.2. Electrochemical procedure; salts and solvents

In all of the experiments, the supporting salt concentration was fixed at 0.1 M. In this study, the results mainly concern the solutions of tetra *n*-butylammonium tetrafluoroborate ( $\text{TBABF}_4$ ) and tetra *n*-butylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) into different dipolar solvents. The purity of these salts (at least 98%) was considered suitable to achieve experiments, and was used without any further purification. These salts were purchased from Aldrich. The used solvents were dimethylformamide (DMF) and acetonitrile (quality for analyses) purchased from SDS and propylene carbonate (PC) purchased from Merck (quality for syntheses). It is worth mentioning that procedures given hereafter do not require especially dry solutions. However, if one wishes to reach potentials as

low as  $-2 \text{ V}$  vs. Saturated Calomel Electrode (SCE), the solution needs to be dried more efficiently to limit the hydrogen evolution (reduction of the remnant water), and therefore increase the electrical yield of the overall organic cleavage. All electrochemical experiments were performed under inert atmosphere thanks to a bubbling of dry argon.

### 2.3. Electrochemical instrumentation and procedures

All potentials are given vs. aqueous Saturated Calomel Electrode (SCE). The electrochemical instrumentation has been described in previous publications [9,10].

### 2.4. Working electrodes

All the electrodes used in voltammetry had an apparent surface area of  $0.78 \text{ mm}^2$ . Silver, glassy carbon, pure palladium and platinum disks when used as substrates were always carefully polished with silicon carbide paper (Struer) or with Norton polishing paper (type 02 and 03). Before use, the electrodes were twice rinsed with water then alcohol and finally acetone. Lastly, they were dried in a hot air stream. Palladized platinum and palladized glassy carbon electrodes – used for comparison – were obtained by means of a galvanostatic deposit from a solution of palladium chloride (e.g.,  $\text{PdCl}_2$  at the concentration  $10 \text{ g L}^{-1}$  in aqueous 0.1 N HCl). In general, such galvanostatic deposits correspond to amounts of electricity from  $10^{-3}$  to  $2 \times 10^{-2} \text{ C cm}^{-2}$  with currents of the order of a few hundreds micro-amps. The procedure of palladization gave a quasi-instantaneous dull deposit onto the smooth silver surface apparently due to the displacement of silver by palladium ( $E^\circ(\text{Pd}^{2+}/\text{Pd}) = 0.92 \text{ V/NHE}$  and  $E^\circ(\text{Ag}^+/\text{Ag}) = 0.799 \text{ V/NHE}$ ) concomitantly with an unexpected reaction leading to a specific Ag–Pd interface. The determination of the resulting alloy is described hereafter (see Section 3).

### 2.5. Coulometry and electrolyses

Coulometric measurements and electrolyses of alkyl iodides were carried out using three-electrode system cells with a total catholyte volume of about 5–10 mL. The anodic compartment was separated by a fritted glass of weak porosity. The experiments were completed on small substrate amounts (typically 0.1 mM). In order to avoid the disturbance resulting from the possible presence of silver oxide, which could depend on the history of solid substrate, a pre-electrolysis of the solution was systematically achieved prior to adding the RX compound to the cell. Efficient argon bubbling was completed in all cases in the course of voltammetries and coulometries, and enabled quite a good reproducibility of data especially in voltammetry.

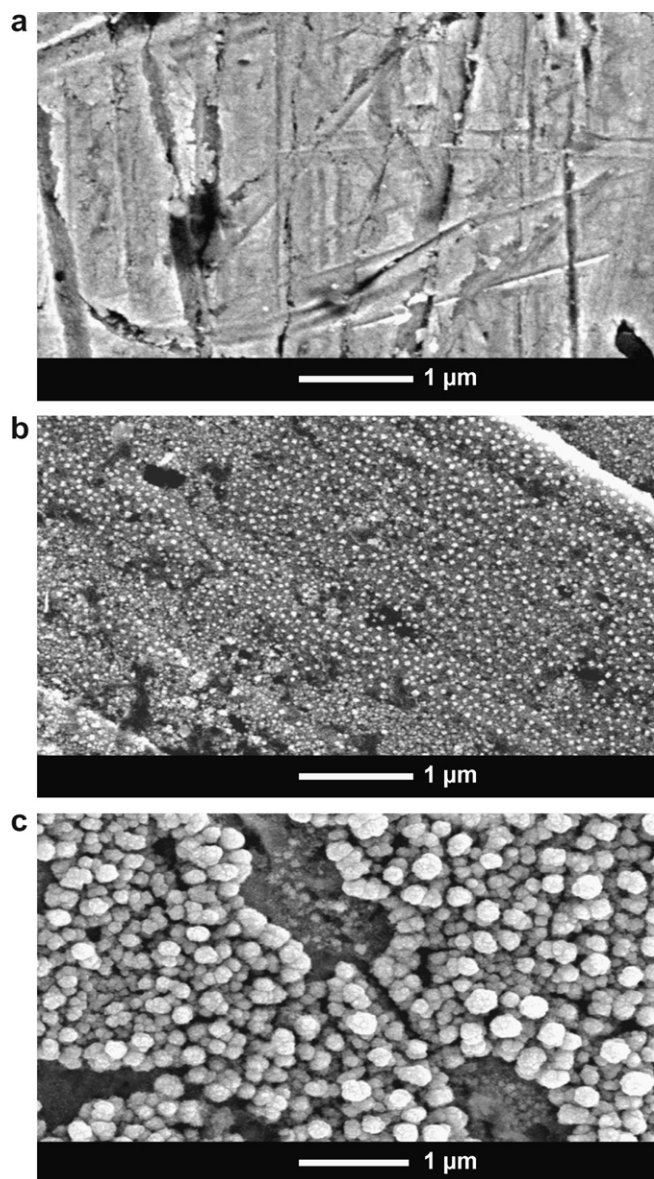
### 2.6. Chemicals

All the alkyl halides studied in the present work were obtained from Aldrich, with a minimum purity of 95%. They were used as such.

## 3. Results and discussion

### 3.1. Textural and structural characterization of the Ag–Pd interface

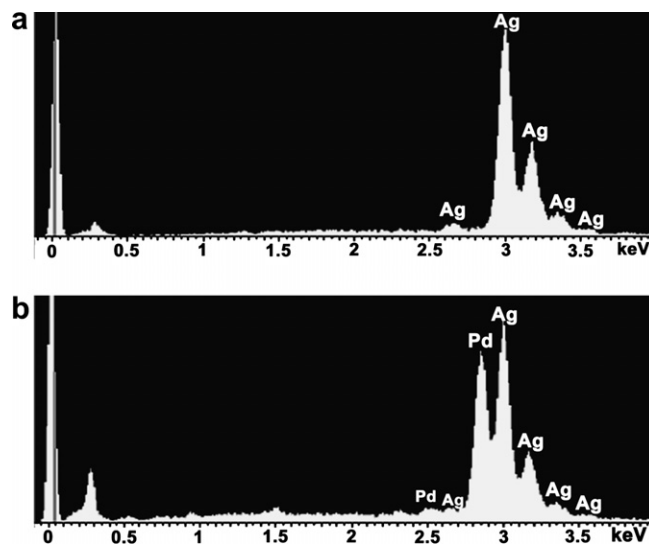
With quite short times of contact (e.g., less than 1 min) the as-produced layer appeared to be stable, and the sonication procedure had no visible effect on the adhesion of micro crystals covering the silver substrate. A selection of SEM images (Fig. 1) shows the spectacular surface evolution of the substrate as the “palladization”



**Fig. 1.** SEM images of (a) the pristine silver surface, (b) after immersion in a  $\text{PdSO}_4$  solution during 30 s, and (c) during 5 min.

reaction prolongs. In the initial stages of the film growth, very small grains of spheroid-like shape cover the surface of the substrate. As expected, the particle size progressively increases with much longer contact times yielding a quasi covering of the substrate after 5 min (Fig. 1c). Although Pd and Ag exhibit similar energy diagrams, EDS analyses of the layer were performed since the  $\text{Pd-L}_{\alpha 1}$  radiation, located at 2.8387 eV in energy, is not overlapped. For comparison, Fig. 2 shows two spectra, before and after surface modification, leading to the conclusion that those spheres contain palladium after the chemical treatment. However, it was difficult to evaluate the Ag/Pd ratio of spheres since the thickness of the layer is not high enough to suppress the silver substrate contribution.

So a TEM study was performed to determine the texture, the structure and the composition of this layer. The bright field image (Fig. 3a) shows a dendritic-like growth of the palladium-based layer obtained with the solution of palladium sulphate (size < 20 nm). The HRTEM image (Fig. 3b) of one part of the bright field image represents some agglomerated nanoparticles, which



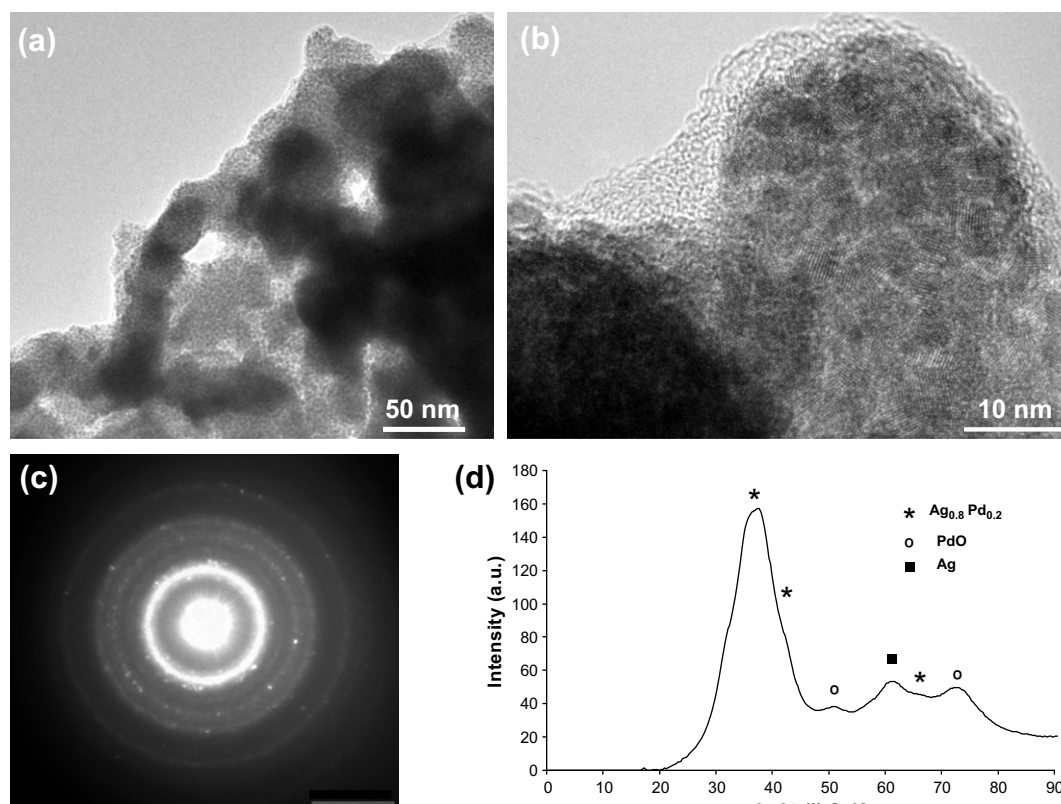
**Fig. 2.** EDS spectrum of a smooth silver sample (a) and a modified silver surface by palladium after a contact time of 5 min (b).

composed the dendrite. These nanoparticles have homogeneous morphology and dimension (around 5–10 nm) and are well crystallized. The SAED pattern (Fig. 3c) of the corresponding Fig. 3a is composed of diffraction circles due to the fact that all nanoparticles are oriented in different directions. Due to the software 'Process Diffraction', a line profile of the electron diffraction pattern enables to plot a graph similar to the X-ray diffraction (Fig. 3d), and to determine that the layer is composed of an Ag/Pd alloy [25] (lattice parameter: 4.0499(8) Å) and also of PdO and Ag. Indeed, as recently mentioned [26], Ag/Pd alloys can slightly decompose under air into PdO and Ag by oxidation. The EDS analysis (not shown here) obtained on this sample indicates systematically an alloy composition of 80% Ag and 20% Pd. As reported by Rao [27], the lattice parameter of Ag/Pd alloys changes with temperature, which is in good agreement with the alloy composition that we have found (i.e.,  $\text{Ag}_{0.8}\text{Pd}_{0.2}$ ) since the beam heating is around 200 °C.

### 3.2. Cathodic reduction of primary alkyl iodides at silver and palladized silver interfaces

Electrochemical data found for Ag–Pd surfaces with a series of primary alkyl iodides (see Table 1, propylene carbonate being chosen as solvent due to the lack of disturbing inhibition phenomena) were quite similar to those previously reported for other kinds of Pd-based surfaces such as palladized platinum or palladized glassy carbon [8]. As underlined in Table 1, it seems clear that the potential shift regarding the reduction step at an Ag–Pd surface is significant by comparison to both glassy carbon ( $\Delta E > 0.9$  V) and smooth silver ( $\Delta E > 0.1$  V). This effect does not depend much on the length of the alkyl chain. For comparison, voltammetries at smooth silver in different solvents were found to be often complex probably because a non-conducting layer is produced by contact between silver and organic iodide (Fig. 4) in particular in both acetonitrile and DMF. This kind of inhibition to the heterogeneous electron transfer leads to a relative shift toward more negative potentials (forward scan) while the backward one gives an interesting curve-crossing, probably due to the chemical formation of the non conductive layer has no time to occur. The inhibition cause could be clarified by dipping smooth silver into the primary alkyl iodides RI (or its concentrated solution in a polar solvent like DMF): one may evidence a reaction between the metal and the iodide. Prolonged contacts (e.g., more than 30 min) bring very large





**Fig. 3.** (a) Bright Field image of the Ag/Pd alloy. (b) HRTEM picture showing the nanoparticles of the alloy. (c) SAED pattern of the TEM picture showing the polycrystalline nature of the layer. (d) Line profile of the SAED pattern characteristic of the  $\text{Ag}_{0.8}\text{Pd}_{0.2}$  alloy, PdO and Ag.

**Table 1**  
Voltammetric and coulometric data relative to some primary alkyl iodides in 0.1 M TBAPF<sub>6</sub>/propylene carbonate

Entry	RI (concentration)	Glassy carbon electrode		Smooth silver electrode <sup>a</sup>		Palladized silver electrode		Coulometric measurements			
								Ag–Pd electrode <sup>c</sup>		Smooth Ag electrode <sup>d</sup>	
		$E_p/2$ (V)	$I_p$ (μA)	$E_p/2$ (V)	$I_p$ (μA)	$E_p/2$ (V) <sup>b</sup>	$I_p$ (μA)	$E$ (V)	$Q$ (F mol <sup>-1</sup> )	$E$ (V)	$Q$ (F mol <sup>-1</sup> )
1	1-Iodopropane (10 mM)	−1.92	14.0	−1.24	12.1	−1.17	11.2	−1.6	1.1	–	–
2	1-Iodobutane (8.8 mM)	−1.93	10.6	−1.22	9.1	−1.10	8.3	−1.6	1.1	−1.2	1.1
3	1-Iodohexane (7 mM)	−1.91	8.2	−1.20	7.2	−1.14	6.6	−1.5	1.2	−1.1	1.0
4	1-Iodooctane (7 mM)	−1.91	6.1	−1.24	5.8	−1.10	6.0	−1.6	1.3	−1.2	1.1
5	1-Iodohexadecane (5 mM)	−1.83	7.4	−1.23	4.1	−1.12	5.5	−1.5	1.1	−1.3	1.0

Scan rate, 50 mV s<sup>-1</sup>. Potentials are referred to aqueous SCE. Apparent surface area of all electrodes, 0.78 mm<sup>2</sup>. The treatment of the Ag electrode was achieved by a dipping time of 1 min in Pd sulphate (see Section 2).

At −1.5 V, electrolyses achieved both in DMF and PC yield in all cases to two-electron processes,  $2 \pm 0.2$  F mol<sup>-1</sup>.

<sup>a</sup> Potential of the first peak.

<sup>b</sup> Appearance of a lone peak.

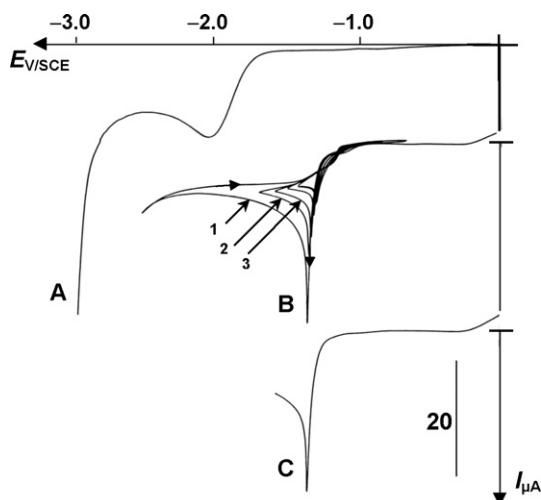
<sup>c</sup> Coulometries achieved in DMF.

<sup>d</sup> Coulometries achieved in PC.

discrepancies at the silver surface. For example, a silver surface maintained in contact of 1-iodobutane or 1-iodooctane exhibited a huge structural change as shown by SEM analysis (Fig. 5). Large black zones are widespread onto the surface, which can be assigned to adsorbed product of silver with alkyl iodide as well as produced free radicals since a huge peak of carbon is present on the EDS spectra. So, such results confirm the reactivity of silver toward RI compounds. This reaction was recently discussed [28].

The importance of silver implication depends on the contact time between Ag and RI. We can expect from these preliminary experiments that primary RIs will be slowly chemically reduced by silver. The weak but effective reducing capabilities of silver metal towards carbon–iodine bonds already permit to propose a reduction scheme (see Scheme 1) where the first and second elec-

tron transfers can be differentiated under quite well defined experimental conditions. Especially, experiments achieved in propylene carbonate enable to support the existence of a one-electron step with the formation of an alkyl free radical at the level of peak 1 (see Fig. 6, curve B and coulometry in Table 1). This first peak is followed by a second peak, which accounts for the reduction of the free radical. The potential range found for peak 2 located at around −1.5 V (Fig. 6) quite agrees with the standard potentials given by Lund [29] for a large panel of similar free alkyl radicals. In general, the second step is rather small, and it is expected that the free radicals formed during the first reduction process are strongly adsorbed at the metal surface. However, fixed potential electrolyses at smooth silver at applied potentials lower than  $E_{p2}$  enabled to demonstrate that the global reduction may reach 2 F mol<sup>-1</sup>. It is



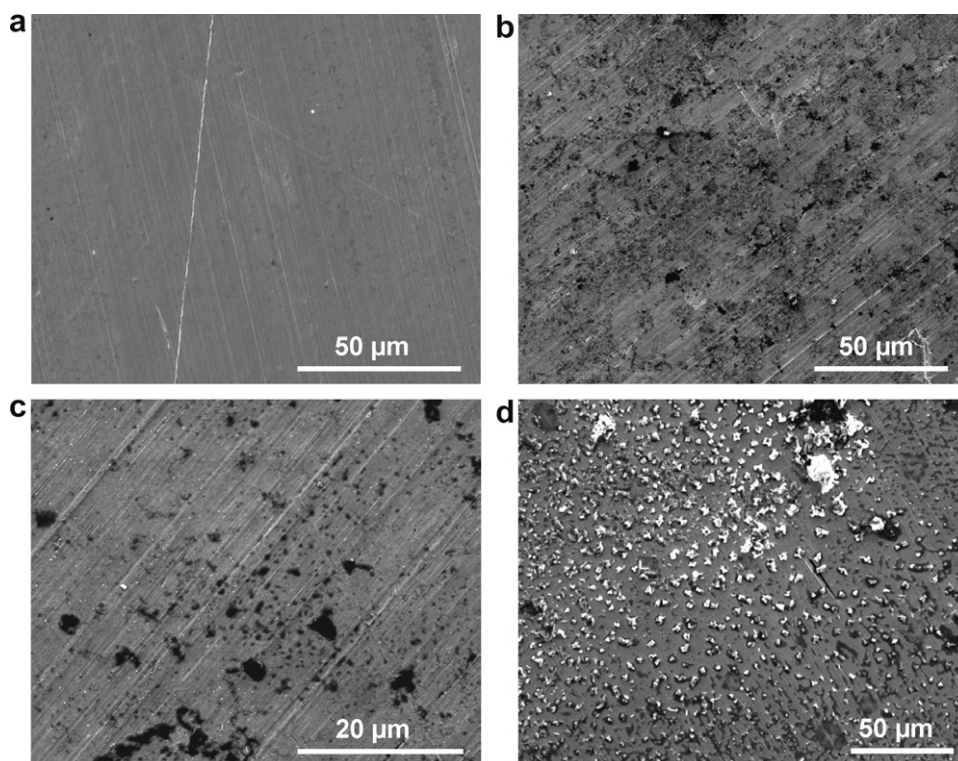
**Fig. 4.** Recurrent scans measured at a smooth silver electrode using 1-iodohexane (concentration, 2.7 mM) in 0.1 M TBAPF<sub>6</sub>/DMF. Apparent surface areas,  $S = 0.78 \text{ mm}^2$ ; Scan rate,  $50 \text{ mV s}^{-1}$ . (A) Inert glassy carbon taken as a standard. (B) Five first scans at a smooth silver electrode (sweeps between  $-0.7 \text{ V}$  and  $-2.5 \text{ V}$ ). (C) New scan immediately after the 5th sweep of (B)).

remarkable that the reduction of RI compounds can occur in two separate steps. Interestingly, examples of dimers obtained with tertiary alkyl iodides by coupling of the free radical  $\text{R}^\bullet$  at silver cathodes under comparable (but not identical) conditions can be found in a recent literature [23]. It is quite possible that adsorption of free radicals at the silver surface may inhibit their own reduction (level of peak 2). At this point, let us recall that the addition of free radicals onto metallic interfaces has frequently been observed [3,30]. The effective separation of two reduction steps with RIs could be valuable for the modification of silver surfaces. Lastly,

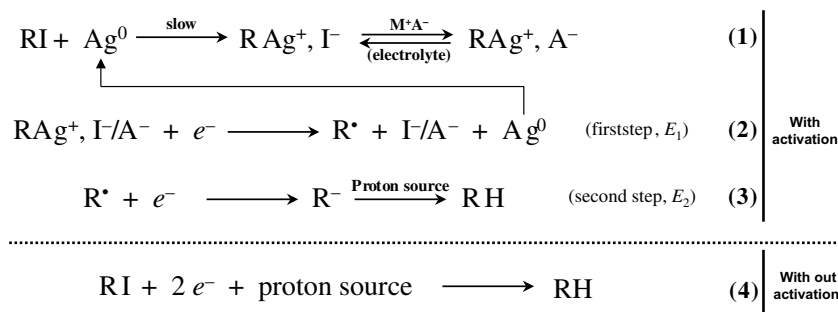
the adsorption of free radicals onto silver could cause the pre-step (to step 1) found here with all the primary alkyl iodides in propylene carbonate. If we refer to the classification by Laviron [31–33] on polarographic and voltammetric currents, this would be caused by the fast adsorption of the reduction product (i.e., free alkyl radical). Electrolyses at the level of step 1 of the modified interface by dipping of Ag in RI lead to the merging of crystals (Fig. 5d) clearly identified as dimers  $\text{R-R}$  issued from  $\text{R}^\bullet$ . Note that the example reported in Fig. 5 corresponds to 1-iodooctane; its homo-dimer hexadecane is weakly soluble in PC.

Voltammetric curves may also depend on the nature (and preparation) of the silver surface and the level of moisture present in the DMF solution. Thus, with small RI amounts dissolved in super-dry electrolyte solutions (obtained by addition in situ of neutral activated alumina), voltammetric currents show no complication brought by adsorption, and curves are well reproducible (see Fig. 7, case of 1-iodobutane). It is likely that the low level of moisture at the silver interface favors the solubility of the silver salt essentially lipophilic, and therefore strongly diminishes the occurrence of the inhibition of the first electron transfer always evidenced at large RI concentrations. This technique would, in principle, permit to monitor the alkyl iodides reduction (potential at the level of the first peak, Fig. 7B) in order to obtain a pure one-electron step. However, the use of activated alumina remains a heavy technique, and forces to a constant activation of alumina.

On the contrary, palladized silver surfaces do not exhibit any apparent chemical reaction towards RIs. As a matter of fact, only one step under diffusion controlled and proportional to the organic iodide concentration was obtained with Ag–Pd electrodes for concentrations smaller than 10 mM. Because of the absence of inhibition at the silver surface, the resulting peak was found to be shifted at less cathodic potentials towards the one already described at pure silver surface. This absence of inhibition at Ag–Pd surface with RI compounds can be related to the absence of pure silver



**Fig. 5.** SEM image of (a) the pristine silver surface, (b) after 30 min contact with 1-iodooctane, (c) after 30 min contact with 1-iodopropane, and (d) same treatment as in (b) followed by an electrochemical reduction at  $-1.4 \text{ V}$  vs. SCE.



Scheme 1.

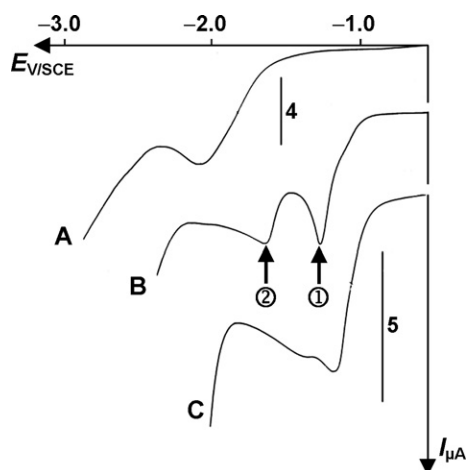


Fig. 6. Voltammeteries obtained at different working electrodes using 1-iodohexadecane (concentration, 4 mM) in 0.1 M TBAPF<sub>6</sub>/PC. Apparent surface areas,  $S = 0.78 \text{ mm}^2$ ; scan rate,  $50 \text{ mV s}^{-1}$ . (A) Glassy carbon. (B) Smooth silver with the separation of two steps 1 and 2. (C) Ag–Pd electrode.

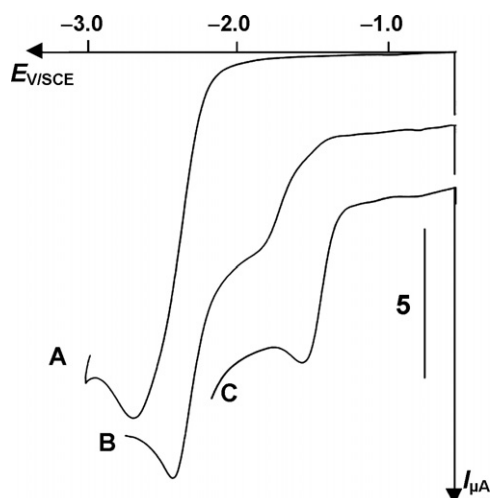


Fig. 7. Voltammeteries obtained at different working electrodes using 1-iodobutane (concentration, 9 mM) in 0.1 M TBAPF<sub>6</sub>/DMF. Super-dry conditions have been obtained by adding freshly activated neutral alumina to the electrolyte. Apparent surface areas,  $S = 0.78 \text{ mm}^2$ ; scan rate,  $50 \text{ mV s}^{-1}$ . (A) Glassy carbon. (B) Smooth silver. (C) Ag–Pd electrode.

zones at the interface. Fig. 6 with hexadecane iodide, curve C and Fig. 7, case of 1-iodobutane, curve C underline that the step current at Ag–Pd electrodes corresponds roughly to half of the current

obtained at glassy carbon, well known to enable two-electron processes (classical hydrogenolysis of the C–I bond). This point would mean that the use of palladized silver enables specific one-electron reductions. This proposal is well checked by means of coulometry at Ag–Pd cathodes (Table 1, reductions in DMF at about  $-1.5 \text{ V}$  vs. SCE, entries 2–5), which perfectly establish that RIs reduction under these conditions obeys a pure one-electron process whatever the polar organic solvent. The applied potential does not matter much since the reduction step obtained at Ag–Pd surface is the lone step and well separated from the cathodic limit at  $-2 \text{ V}$ , which is specific of such palladium surface under the defined experimental conditions. This means that free radical reduction at palladium and palladized interfaces (possibly owing to a strong chemisorption of those radicals leading to an efficient coverage of the interface) does not occur fast within a potential range until  $\sim 0.7 \text{ V}$  beyond the peak potential. These results are in full agreement with recent data [8] observed with palladized electrodes with RI compounds, whatever the mode of Pd deposition.

Additionally, the presence of a free alkyl radical is efficiently checked thanks to the spin trapping method in ESR; the latter is due to the formation of a paramagnetic nitroxide radical when the reduction was completed in the presence of nitron (*N-tert-butyl- $\alpha$ -phenylnitron*) or nitroso compounds (*tert-butyl-nitroso*). This method has been successfully developed with other palladized surfaces [11,12], and is in full agreement with a one-electron overall process (real trapping, in this case, of the free radical  $\text{R}^\bullet$  by the nitron).

Thus, the use of Ag–Pd surfaces always brought a real improvement of the catalytic effect both in potential shift and electrolysis specificity.

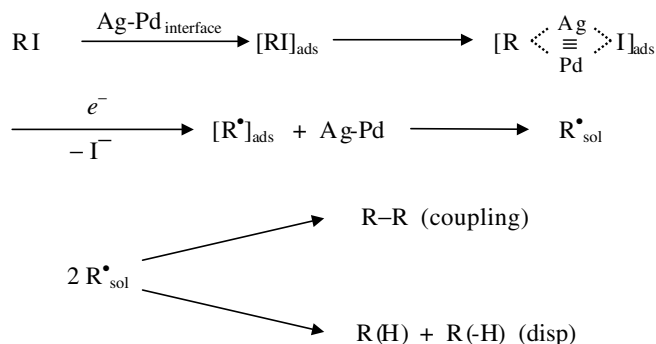
### 3.3. Reduction products at macro smooth silver and Ag–Pd cathodes

For comparison, macro-reductions were achieved both at large silver and silver–palladium surfaces (surface areas of about  $2 \text{ cm}^2$ ) with several alkyl iodides. As shown in Table 1, results in DMF containing TBA<sup>+</sup> salts confirm the one-electron character of the global cathodic process with Ag–Pd electrodes. Also at smooth silver surfaces, one-electron process can be also easily observed on the provided condition that macro-electrolyses are achieved in PC at moderate potentials (between  $-1.2 \text{ V}$  and  $-1.4 \text{ V}$  vs. SCE). Preliminary data (see Table 2) achieved with RIs are in agreement with the transient formation of a free radical  $\text{R}^\bullet$  capable to dimerize or/and disproportionate. Thus, preliminary GC–MS analyses on electrolyses mixtures showed the major formation of homo-dimers R–R and the monomers R(H) and R(H) roughly in equal amount. The specificity of silver–palladium cathodes obeys probably interfacial catalytic process put forward in Scheme 2, and based on a possible synergy between Ag and Pd. Ratios dimer/monomers vary upon experimental conditions but it should be stress that dimer yields are excellent or quasi quantitative. It seems, however, too

**Table 2**

The experimental conditions are those reported in Table 1

RI	Experimental conditions	R(H) (%)	R(-H) (%)	R-R (%)
<i>n</i> C <sub>6</sub> H <sub>13</sub> -I	Electrode: smooth silver;	3.6	3.2	93.1
<i>n</i> C <sub>8</sub> H <sub>17</sub> -I	electrolyte: PC + TBAPF <sub>6</sub> ;	2.7	5.1	92.2
<i>n</i> C <sub>10</sub> H <sub>21</sub> -I	applied potential: -1.30 V	3.2	3.3	93.4
<i>n</i> C <sub>16</sub> H <sub>33</sub> -I		7.7	6.7	85.6
Ph(CH <sub>2</sub> ) <sub>3</sub> -I		-	-	>99
<i>n</i> C <sub>8</sub> H <sub>17</sub> -I	Electrode: Ag-Pd;	-	0.1	99.9
<i>n</i> C <sub>10</sub> H <sub>21</sub> -I	electrolyte: DMF + TBAPF <sub>4</sub> ;	1.1	1.6	97.3
Ph(CH <sub>2</sub> ) <sub>3</sub> -I	applied potential: -1.25 V	-	-	>99



early to draw definitive conclusions about a mastering of the dimer production.

#### 4. Conclusions

The aim of the present work was to propose a new cathodic material in order to achieve, at moderate potentials, one-electron processes with primary alkyl iodides taken here as target substrates. Thus, for the first time, a silver-palladium alloy was used as modifier of smooth silver surfaces. Its chemical structure has been totally defined and its building is particularly easy and fast. The preliminary results relative to organic iodides listed in the present paper are extremely attractive. As a matter of fact, this new cathodic material combines two important properties: (i) the catalysis specific of silver towards primary alkyl iodides with substantial potential shifts towards data previously shown at glassy carbon [34] and (ii) the role of silver-palladium modifier for specifically orienting cleavages of carbon-iodine bonds to one-electron reduction processes. These preliminary results have pointed out that the use of such Ag-Pd electrodes could be at first considered as a source of free alkyl radicals as shown by means of coulometries, spin trapping technique, and fixed potential electrolyses. Moreover, voltammetries achieved in several dipolar solvents, showed that Ag-Pd surfaces certainly privileged obtaining of well defined one-electron reduction steps. These reduction steps were found to be generally diffusion controlled and electrolyses could be achieved stepwise. The stability of the surface appeared to be good and macro-electrolyses (current densities up to 50 mA cm<sup>-2</sup>) allowed several runs by using the same electrode. Let us stress also that the necessary promotion of Ag-Pd electrodes

needed beforehand a wider scope of the intrinsic behaviour of silver towards organic halides. Thus, the present work has additionally clarified the reason for the catalysis already observed with the alkyl iodides.

However, until now, the intrinsic reason for obtaining an electro-catalysis at such electrodes is not totally understood and the unexpected synergy [Ag + Pd] evidenced within the present work needs additional experiments. A general scope of other kinds of organic substrates (possessing chemical bond capable to cleave under electron transfer like primary alkyl bromides) is being undertaken with success.

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