J Appl Electrochem (2009) 39:1625–1632
DOI 10.1007/s10800-009-9853-y

ORIGINAL PAPER

Novel and efficient electrochemical way for silver nanoparticles deposition onto solid conductors: a new concept of metal-silver cathodes

Jacques Simonet

Received: 19 December 2008 / Accepted: 20 February 2009 / Published online: 11 April 2009

Abstract The deposit of very small silver particles onto a very large palette of solid electronic conductors was achieved by means of the cathodic reduction of alkyl iodides RIs in the presence of a suspension of silver–palladium alloy particles (diameter >250 µm). The potential applied to the conductor is so that RIs are not directly reduced at its surface. The observed cathodic reaction is then the discharge of silver grains reacted in surface and covered by a transient assigned to be [RAg^+, I^-]. The main heterogeneous products are homo-dimers R–R while the deposition of silver aggregates of very small size (nanometric scale) occurs onto the conductor. By this way, the efficient silverization of many surfaces is possible. Stable layers of Ag particles were made onto many solid surfaces like platinum, palladium, copper, nickel, iron, gold, graphite, and glassy carbon. Preliminary evidences for the use of those new silvered electrodes are presented.

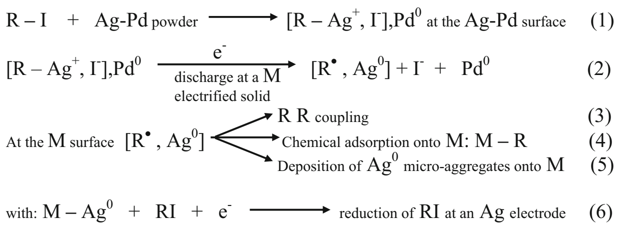
Keywords Silver-cathodes · Silver–palladium nanoparticles · Alkyl iodides · Fluidized bed electrolyses

1 Introduction

The facile and stable modification of electrode surfaces remains now a days a challenging domain in the field of organic electrochemistry [1–3]. Then, solid surfaces like graphite and glassy carbon have been intensively modified by means of several modes of grafting: use of carboxylic groups existing [4] or created by chemical or electrochemical oxidation of carbons, additions of free radicals [5, 6], galvanostatic deposits of metals. The electrodeposition of fonctionalized polymers [7] appeared to be promising ways to modify interfaces, especially when those polymers can themselves bear specific redox groups or organometallic centers, strategically important in the field of electro-catalysis [8]. Additionally, deposition of very small metallic particles (at the micro and the nanoscale) at electrodes surfaces is certainly a field in growing expansion [9]. The nature of deposits, the control of the size of particles, the chemical and mechanical stability of these produced interfaces is essential for the specific use of these electrodes. Several modes of deposition for metallic nanoparticles were reported. More specifically, many recipes for forming silver nano-particles (essentially based on the reduction of silver salts) are available [10–15] in a recent literature.

The growing interest for silver electrodes [16–21] and their catalytic possibilities prompted us to consider new modified silver interfaces in particular by the use both of palladium metal and a silver–palladium alloy [22–25]. As a complement to these recent discoveries, it is here reported a new and facile mode for deposition at solid conducting surfaces of *extremely small* silver particles based on the reaction of alkyl iodides RI with silver and silver–palladium alloy. As summarized in Scheme 1, silver strongly doped by palladium (Ag–Pd form) reacts fast with RIs to afford transients written as [RAg^+, I^-] at a potential that does not permit the regular cleavage of RI. The reduction of this structure was shown affording the concomitant formation of a free alkyl radical $R^\bullet$ (followed by the formation of its coupling form R–R) and Ag^0. The principle of the present study is based on the use of a suspension of small silver grains readily covered by [RAg^+, I^-]

J. Simonet (✉)
Laboratoire MaCSE, Université de Rennes 1, UMR 6226
Campus de Beaulieu, 35042 Rennes Cedex, France
e-mail: jacques.simonet@univ-rennes1.fr



Scheme 1 proposed mechanism for the deposition of Ag^0 nanoparticles onto an electrified conductor M *via* Ag–Pd

salt that can discharge at a any solid electronic conductor. The presented reaction is interesting owing to its easiness, the compactness of silver deposits as well as the large palette of substrates potentially candidates to be efficiently modified through this new mode of silverization.

2 Experimental

2.1 Chemical doping of silver particles by palladium and characterization of the produced surface

The purpose of the present work was to achieve the reduction of primary alkyl halides (principally iodides) thanks to a 3D electrode constituted of a fine suspension of silver–palladium alloy grains constantly electrified (and then maintained) at a given potential by an inactive central cathode at which organic halides cannot be reduced fast. In other words and owing to recent results, the standard system was an electrified carbon rod in contact with a relatively dense Ag–Pd alloy suspension. As shown below, the fixed cathode could be also made of different metals.

The modification of silver grains by palladium was simply obtained by contact of smooth silver metal (at the state of plate, electrode surfaces or powder) with a fresh aqueous acidic solutions of a palladium salt. This mode of palladization of silver has been already reported. In concrete terms, one gram of $Pd(SO_4) \cdot 2H_2O$ (Alfa Aesar) was dissolved in 100 mL of 0.1 N H_2SO_4 solution. In the contact of this solution, silver metal, is progressively covered after a few tens of seconds by a shiny layer. The surface reaction corresponds to the displacement of Ag^0 by palladium cations. Palladium nitrate and chloride could be used as well in solution with corresponding acids. The procedure of palladization gave a quasi-instantaneous dull deposit onto the smooth Ag surface apparently due to the displacement of silver by palladium ($E°$ (Pd^{2+}/Pd) = 0.92 V/ENH and $E°$ (Ag^+/Ag) = 0.799 V/ENH). The layer thickness looked strongly dependent on the time of contact with the palladium solution. With $PdCl_2$, the contact time is much shorter than with sulphate and nitrate.

The characterizations of the as-produced layers were carried out by a combined SEM, HRTEM, EDS study. This was fully described in previous papers [24]. It is recalled that 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 Energy Dispersive Spectroscopy analysis (EDS). Since the displacement reaction occurs whatever the silver substrate used, TEM characterizations were directly performed using a homemade silver sample-holder (silver grids being not commercially available). The EDS analysis (not shown here) indicates an alloy composition of 80% Ag and 20% Pd.

In order to be used as a 3D electrode, a silver powder (size of grains: 250 µm Aesar) was reacted with Pd salts (sulphate or nitrate) under violent shaking for 10 min. After reaction and decantation, the formed Ag–Pd powder considered now as a new substrate was rinsed with water, then alcohol and at last acetone. Finally, the powder was dried in a oven at 60 °C during 1 h. Under such conditions, the Ag–Pd powder was easily re-used or re-activated with a Pd salt according the same recipe. The thickness of the AgPd at silver grains was not determined. However, by analogy with previous works relative to the formation of Ag–Pd at massive silver, a thickness is expected to be several micrometers. Obviously, the thickness of the additional layer depends on the contact time with the Pd^{++} solution. Figure 1 displays the morphology of modified silver grains that appears like a concretion of small size elements apparently amorphous. These particles, with an average size of the order of 1 µm, are assigned to Ag–Pd micro-structures highly reactive with alkyl halides.

It also appeared of interest to produce in the course of this study, solid electrodes modified in surface by Ag–Pd particles. These electrodes were obtained at different metallic substrates by galvanostatic deposits of silver from a solution of $AgNO_3$ (10 g L^{-1} in a 0.1 N HNO_3 solution). The imposed current was of the order of 0.5 mA mm^{-2}, and the average amount of electricity was in all cases 1.2 millicoulombs mm^{-2}. If necessary, the silvered layer was transformed into an Ag–Pd layer by contact with a palladium salt solution (see above).

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 ($TBABF_4$) and tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) into different dipolar solvents. The purity of these salts (at least 98%) was considered suitable to achieve experiments, and they were used without any further purification. These salts were purchased from Aldrich. Used solvents were dimethylformamide (DMF) and acetonitrile

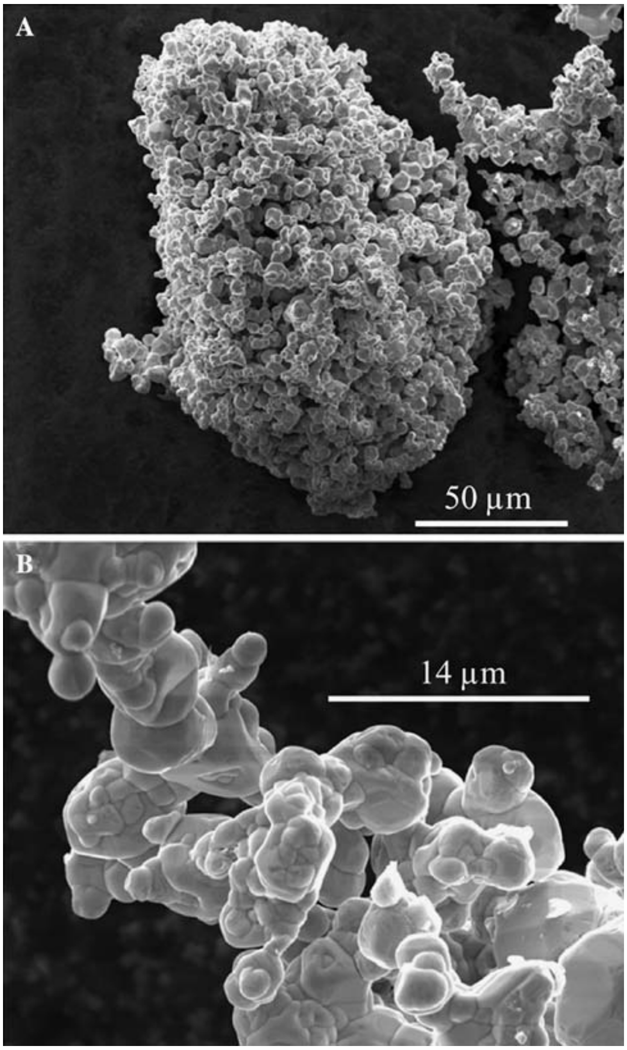


Fig. 1 Morphology of silver grains (size: 250 μm) after treatment with $PdSO_4$ showing the appearance of micro-particles of AgPd alloy

(quality for analyses) purchased from SDS and propylene carbonate (quality for syntheses) purchased from Merk. It is worth mentioning that procedures given hereafter do not require especially dry solutions. However, if one wish to reach potentials lower than −2 V, 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. For that, the use of activated neutral alumina is necessary according to an experimental procedure already reported [9]. All electrochemical experiments were performed under inert atmosphere (bubbling of dry argon).

2.3 Electrochemical instrumentation and procedures

All potentials are given versus aqueous Saturated Calomel Electrode (SCE). The electrochemical instrumentation has been described in previous publications.

2.4 Working electrodes

All electrodes used in voltammetry had an apparent surface area of 0.8 mm^2. Glassy carbon, palladium, nickel, copper, iron, and platinum disks when used as smooth substrates and were always carefully polished with silicon carbide paper (Struer) or with Norton polishing paper (type 02 and 03) before a silver deposit was made. Before use, the electrodes were twice rinsed with water then alcohol and finally acetone. Lastly, they were dried with a hot air stream.

2.5 Coulometries and electrolyses

Coulometric measurements and electrolyses of alkyl iodides in the presence of the Ag–Pd powder were carried out using three-electrode system cells with a catholyte volume about 5–10 ml. The two compartments are separated by a glass frit (weak porosity). The experiments were completed on small substrate amounts of RI (typically 0.1 millimol). Efficient argon bubbling was completed in all cases in the course of voltammetries and coulometries.

2.6 Chemicals

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

3 Methodology

The present method used for a thin silver deposit onto solid conductors (carbon, graphite, platinum, gold, palladium, tin, iron, nickel, copper and many other metals) is simply derived of a previous report devoted to the cathodic reduction of primary alkyl iodides (RI) at a new kind of electrode: massive silver covered with a fine layer of Ag–Pd [24]. In the present study, a fine Ag–Pd powder is efficiently dispersed in a liquid electrolyte. A solid conductor (carbon or metal) at which the reduction of the RI compounds (owing to a high activation energy) is much less easy than this observed at an Ag–Pd electrode, is put forward to electrify the Ag–Pd particles. Thus, the likely process is detailed in Scheme 1. A preliminary reaction (Eq. 1, Scheme 1) occurs between Ag–Pd particles and RI. As shown below, the apparent role of Pd only permits to strongly activate the reaction of silver towards the C–I bond. The contact with the solid electrode permits the discharge of the superficial reactive layer (Eq. 2, Scheme 1). At this stage, the free alkyl radical $R^\bullet$ is formed and the potential applied to the solid fixed electrode is not negative enough to allow its fast reduction. Under these conditions, the homo-coupling was pointed out to occur (Eq. 3, Scheme 1). In the meanwhile, chemisorption of the radical is also believed to happen (Eq. 4, Scheme 1). The radical formation appears to be the key point of the process: it permits to liberate an atom of silver at (or in the immediate vicinity of) the electrode. If the scheme is correct, it is expected that a silvered electrode (in principle *only* covered by very small silver aggregates) may be produced. As a matter of fact, after a certain amount of electricity has passed, the regular reduction of RI at a silvered cathode (Eq. 6, Scheme 1) is expected to become the major process. Experiments described hereafter allow verifying those proposals and precise important points relative to the nature of the produced silver layers as well as their capability to show unforeseen electrocatalytic properties (when compared to those of smooth silver).

4 Results

4.1 Voltammetries

Preliminary evidence on the silverization of solid conductors is fully displayed by Fig. 2. Thus, 1-iodooctane first reduced at glassy carbon exhibits (curve A) a two-electron step as expected [27] at a potential near −2 V versus SCE. Let us point out that the half-peak potential $E_{p/2}$ is not constant upon repetitive scans and is progressively shifted toward more negative potentials possibly due to a surface inhibition presumably provoked by a progressive formation of weakly soluble dimer at the interface. If some Ag–Pd powder is added to the solution and efficiently stirred prior scans, the voltammetric peak progressively moves towards less negative potentials (curves B). Metallic electrodes (like iron and gold, curves C and D, respectively) display a similar behavior to that of glassy carbon. A shift of about 1 V could be observed. Sometimes, several scans are necessary to get a well define and totally reproducible step: it is the case of iron, presumably because of the discharge of Ag–Pd grains (Eq. 2, Scheme 1) is made difficult owing to the presence of superficial oxide and requires quite negative potentials to trigger the silver deposition. On the contrary, gold obviously permits a silver deposit from the first voltammetric sweep. In a similar way, Fig. 3 shows rather comparable results: 1-iodooctane does not exhibit any reduction step at smooth gold and nickel while the silverization process allows to get a sharp peak ($E_{p/2} = -1.23$ V, first scan, while glassy carbon without silver gives under the same conditions –1.83 V).

In Fig. 4, voltammetric responses of 1-iodohexane are given at glassy carbon, (A), smooth silver (B_1) and Ag–Pd (B_2) electrodes. The deposit of Ag–Pd at a silver surface displays the best activation for the C–I cleavage: $E_{p/2} = -1.12$ V. If now a potentiostatic reduction of the same solution is achieved at −1.3 V in the presence of a small amount of strongly stirred Ag–Pd powder, the RI compound is totally reduced after 1.2 F mol^{-1} (no response of the RI compound at the carbon electrode within the range −1.8 to −2.2 V as displayed by curve C). The analysis by means of GC/MS of the resulting solution shows the formation of the homo-dimer in a quasi-quantitative way. Thus, the indirect reduction of RI by means of the inorganic Ag–Pd mediator (powder) does not show a quantitative electrical yield while the Ag–Pd alloy, if directly deposited onto the glassy carbon interface, allows the process to be totally completed after an electricity consumption of sharp 1 F mol^{-1}.

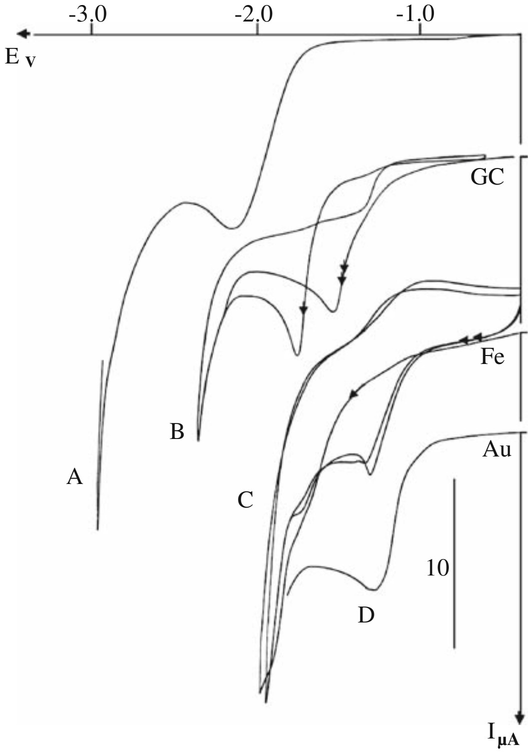


Fig. 2 Voltammetric responses of 1-iodooctane (concentration: 6 mmol L^{-1}) in 0.1 mol L^{-1} $TBABF_4$/DMF. Scan rate: 50 mV s^{-1}. Reference electrode: aqueous SCE. All cathode surface areas: 0.8 mm^2. (A) Response at a glassy carbon electrode (first and second scans). (B) Response at the same electrode after dispersion of an Ag–Pd powder (20 mg) in the electrolytic solution. Scan immediately after the stopping of the stirring. (C, D) Responses at iron (3 scans) and gold (1 scan) substrates, respectively, after a mechanical dispersion of the Ag–Pd powder in the solution

4.2 Silverization procedures onto metallic substrates

Voltammetries shown in Fig. 5 may summarize the procedure defined to silverize different metallic interfaces. For those deposits of silver onto iron, copper, and gold were achieved in another cell. The procedure, clearly displayed

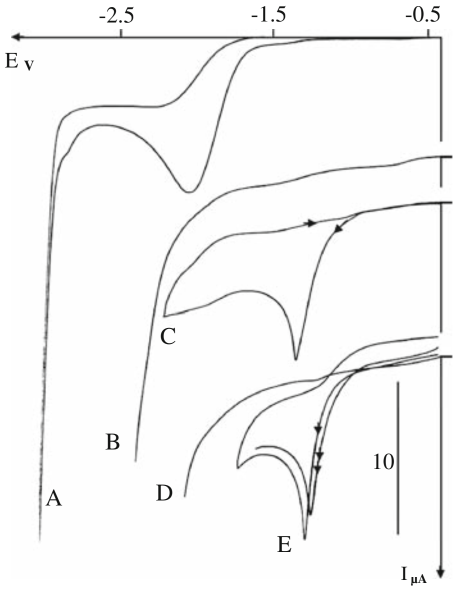


Fig. 3 1-iodooctane (concentration: 6 mmol L^{-1}) in solution in 0.1 mol L^{-1} $TBABF_4$/DMF. Responses of solid electrodes before and after silverization process thank to Ag–Pd powder dispersion in solution. Modified electrodes were sonicated for 10 min. All electrode surface areas: 0.8 mm^2. Scan rate: 50 mV s^{-1}. Reference: SCE. (A) Use of a non-modified glassy carbon electrode. (B, C) Responses at a smooth gold electrode before and after silver deposit. (D, E) Responses at a smooth nickel electrode also before and after silverization

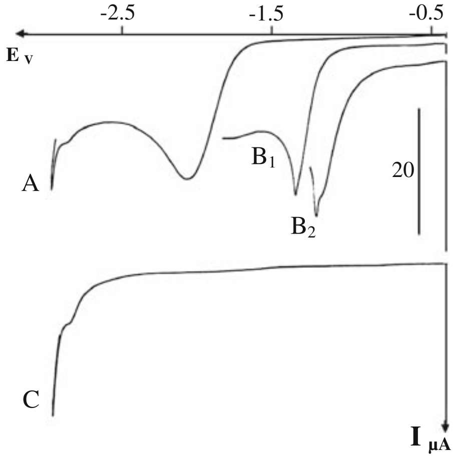


Fig. 4 Voltammetric responses of 1-iodohexane (concentration: 13 mmol L^{-1}) dissolved in DMF containing 0.1 mmol L^{-1} $TBABF_4$). Scan rate: 50 mV s^{-1}. Reference: SCE. Surface area of used electrodes: 0.8 mm^2. (A) Glassy carbon. (B_1, B_2) Responses at smooth silver and Ag–Pd electrode respectively, the latter obtained by treating smooth silver in $PdCl_2$ solution during 10 s. (C) Potentiostatic reduction of the solution at −1.3 V at graphite in the presence or Ag–Pd powder (45 mg). After 10 min, the reduction was totally completed (1.2 F mol^{-1}) and the disappearance of the iodide has been checked (curve C) thanks to a voltammetry at a glassy carbon electron

in the caption of Fig. 5, is very simple: a solution of DMF with a tetraalkylammonium salt, a RI like 1-iodobutane, a small amount of Ag–Pd powder, and an applied potential of −1.0 V. Under stirring, the current at the microelectrode (area: 0.8 mm^2) may easily reach 50 μA. In principle, it increases owing to the presence of the progressive silver heterogeneous deposit that makes the electrode more and more reactive towards the alkyl iodide. By convention, the electrode silverization was stopped after an amount of electricity of 2×10^{-2} C has passed through the cell. These very small amounts of electricity authorize the use of undivided cells. Galvanostatic procedures completed until the same total electricity consumption is reached can be used as well.

Electrodes modified using these procedures were sonicated for 10 min. The silver deposit was found to be chemically and mechanically quite stable. Silvered electrodes could be used and re-used several times without noticeable discrepancies. In Fig. 5, currents found with the different electrodes tested are quite equivalent. It is however questioning that [gold–silver] produced interface

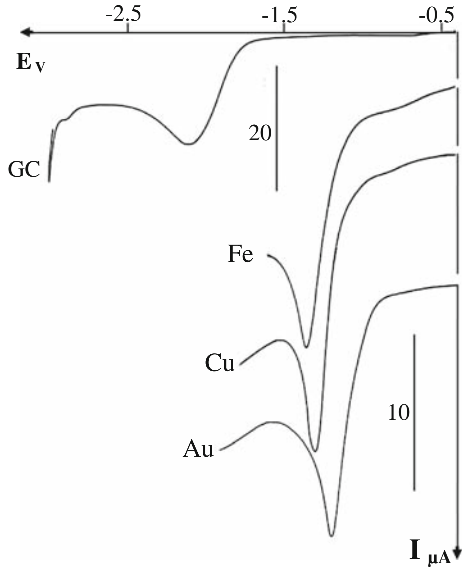


Fig. 5 Voltammetries of 1-iodobutane (concentration: 10 mmol L^{-1}) at several silverized electrodes. Area of electrodes: 0.8 mm^2. Reference electrode: SCE. Scan rate: 50 mV s^{-1}. Voltammetry at glassy carbon (GC) corresponds to a basic response without any silver deposit. With the other electrodes, iron (Fe), copper (Cu), and gold (Au), the silverization was completed in another cell according to the following recipe: 1-iodobutane (13 mmol L^{-1}) is dissolved in a solution of $TBABF_4$ in DMF. After addition of about 20 mg Ag–Pd powder, the solution is efficiently stirred and one applies to the electrode, a potential of −1.0 V. The current obtained is of the order of 50 μA. Silverization was stopped after total electricity amount of 2×10^{-2} C. Electrodes were sonicated in water for 10 min, and then rinsed with alcohol, acetone and dried under hot air stream. It is remarkable that limit currents are equal, but peak potentials are slightly different. In the given examples, the "catalytic" effect decreases according to Au/Ag > Cu/Ag < Fe/Ag. The implication of the solid substrate in the electrocatalytic activity has not been demonstrated so far

gives a more efficient catalysis than other solid substrates. So, what is actually the structure of the silver layer?

4.3 Structure of the deposit: a layer of pure silver nano-particles

Until now, only silver deposits onto large areas of glassy carbon and copper were achieved. Macroscopic views are shown in Fig. 6. With small amounts of electricity, shiny white deposits were obtained. The mass increase is, in all cases, extremely small and suggests that the thickness of the layer is, at the maximum, of a few tens of nanometers. EDS analyses of the external layers revealed the *exclusive* presence of silver: no trace of palladium could be detected (Laffont-Dandras L, unpublished observations). Figure 7 displays the compactness of such produced silver layers especially when the electricity amount is not too small. (See image B). Obviously, there is a very great discrepancy between what is obtained with quite comparable amounts of electricity, (i) by means of electrolysis of $AgNO_3$ (Ag crystals dispersed onto the metallic surface) and (ii) the use of the technique developed in this work and reported in Fig. 7. It is likely that the silver layer corresponds to the formation of a conglomerate of *very small sized* silver amorphous particles. The high compactness of all produced layers under quite comparable experimental conditions forbad getting a precise idea on the size of particles. By comparison, Fig. 8 exhibits the structure change after reduction of a RX compound of a layer of Ag–Pd *previously* deposited onto glassy carbon. Specifically, this layer was modified by the reduction of an alkyl halide (here 1-bromoheptane). The produced layer is *exclusively* formed by silver particles. It is striking that a uniform and compact layer of particles was produced. The size of particles is quite regular and equal to about 100 nm. Lastly, the use of silver grains instead Ag–Pd powder was tested to produce silver nano-particle through another process. These experiments afford also particles of small size (See Fig. 9, case of 1-iodopropyl-3-phenyl reduced in propylene carbonate) but no compact film was obtained by this method.

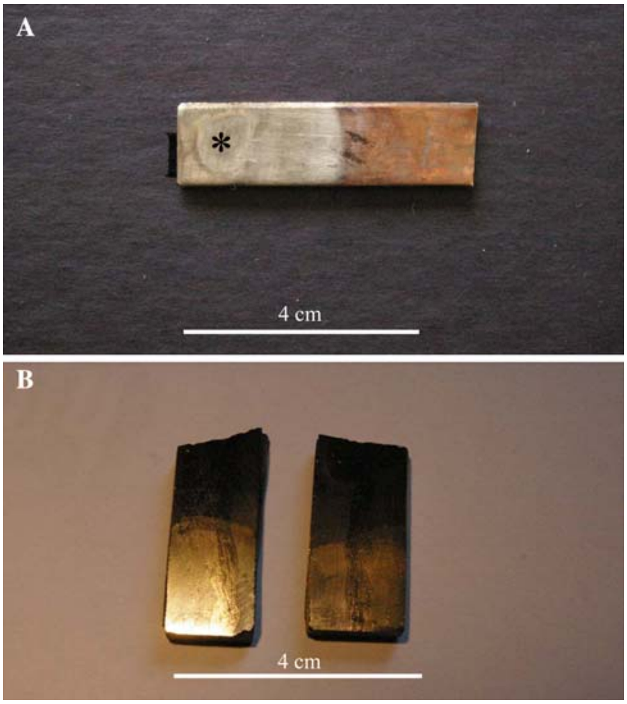


Fig. 6 Silverization of solid conductors by reduction of 1-iodobutane in the presence of Ag–Pd powder. See text. Applied potential: -1.3 V. **a** Deposit of Ag nano-particles onto copper (silverization of the left part (*) of the sample). Amount of electricity: 2 C cm^{-2}. **b** Deposits of silver onto pieces of glassy carbon. The shiny aspect of the produced silverization depends on the amount of electricity used. The right sample corresponds to an amount of electricity of 1 C cm^{-2} while the left one needed 2.5 C cm^{-2}. With the three samples, the mass increase was found to be extremely small (<<0.5 mg)

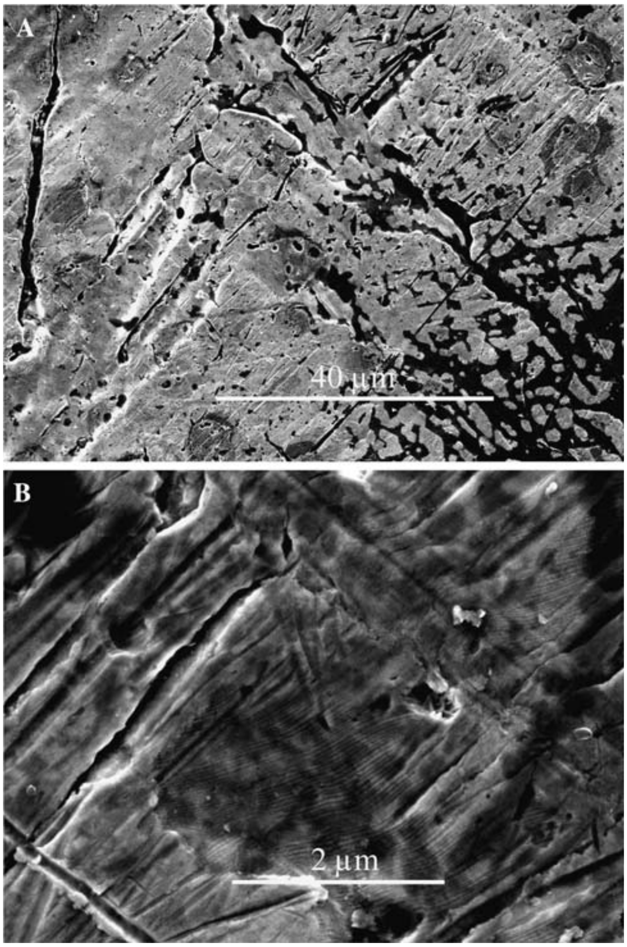


Fig. 7 Two SEM images (**a**) and (**b**) after a reduction of 1-iodooctane (concentration: 10 mmol $L^{-1)}$ at a glassy carbon electrode in the presence of Ag–Pd powder (100 mg). Volume of solution: 5 ml. Electrolyte: DMF + 0.1 mol L^{-1} $TBABF_4$. Electrolysis potential: -1.35 V. Amount of electricity: 5 C cm^{-2}

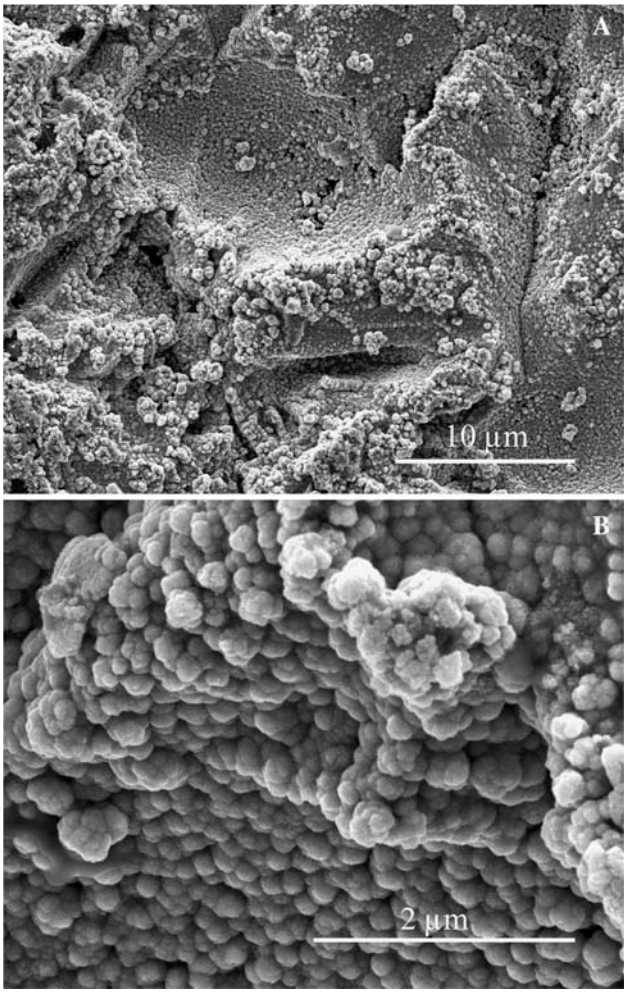


Fig. 8 SEM images (two magnifications (**a**) and (**b**) after reduction of 1-bromoheptane at a glassy carbon modified by a thin layer of Ag–Pd). Electricity amount: 7 C cm^{-2}. Spheroids are pure made of silver. There is almost no loss of cathode mass after reduction

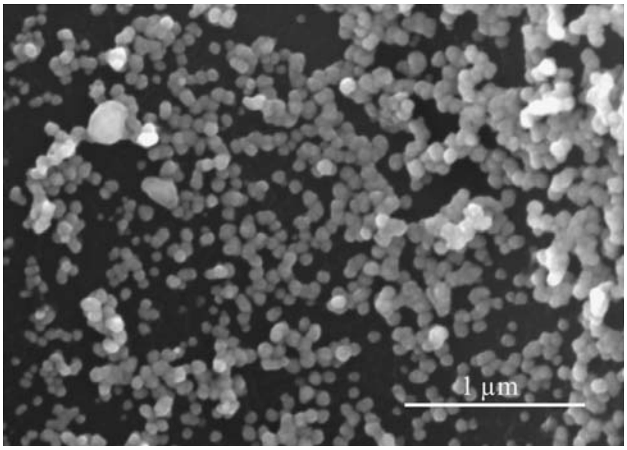


Fig. 9 Electrolysis of 1-iodopropyl-3-phenyl (concentration: 12 mmol L^{-1}) in propylene carbonate containing 0.1 mol L^{-1} $TBABF_4$ in the presence of Ag powder (particle size: 250 µm). Applied potential: −1.65 V. Amount of electricity: 2 C cm^{-2}

Let us note that also regular particles (about 50 nm) are obtained, but found to be totally dispersed onto the conductor surface. The reason of the obtaining silver particles of quite equal size is not understood so far. It seems clear however that the use of Ag–Pd powder remains by far the best way to get very compact silver layers constituted of extremely small particles.

4.4 Evidence for the formation of a new electrocatalytic surface

For that, these new-electrodes M-Ag NP has preliminary been tested thanks to a comparative study relative to alkyl bromides RBr, known to be moderately active [25] at most of solid electrodes. The example displayed in Fig. 10 concerns 1-bromobutane reduced at several solid electrodes. The potential and the peak current obtained at a glassy carbon electrode ($E_{p/2} = -2.23$ V, curve A) were compared to different kinds of silvered surfaces. Under the conditions of Fig. 10, smooth silver (curve B) does not exhibit a large catalytic effect ($E_{p/2} = -1.99$ V) while the silvered gold electrode covered of Ag nano-particles (Au–Ag NP) appears to be much more efficient (E = −1.53 V). If the latter surface shows a nice efficiency to reduce RBrs, the best electrode (Fig. 10, curve D) remains by far the one covered with a Ag–Pd layer ($E_{p/2} = -1.18$ V). The potential shift is spectacular ($\Delta E = +1.05$ V) associated to a clear diminution of the peak current (two-fold decay). With this electrode, the RBr cleavage process turns clearly (as previously shown [25]) to a one-electron process since the transient $R^{\bullet}$ free alkyl radical is not reduced at the potential required for the first electron transfer. Such

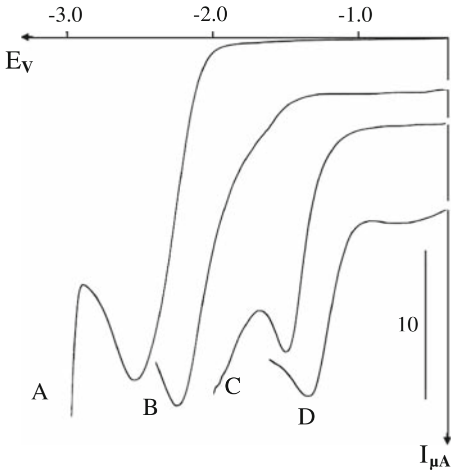
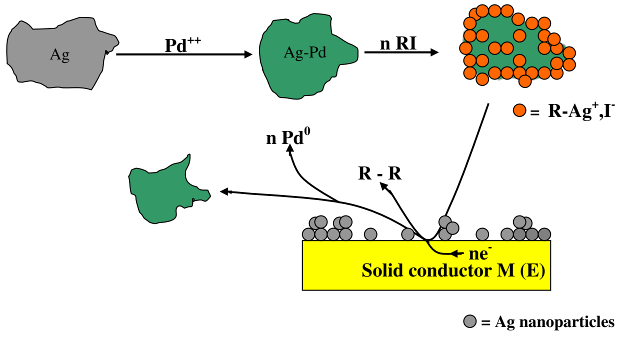


Fig. 10 Voltammetric curves of 1-bromobutane (concentration: 12 mmol L^{-1}) at several cathode surfaces (areas: 0.8 mm^2). Electrolyte: DMF + 0.1 mol L^{-1} $TBABF_4$. Scan rate: 50 mV s^{-1}. Reference: aqueous SCE. (A) Response at glassy carbon. (B) Use of smooth silver. (C) Silvered surface by deposit of nano-particles (see text). (D) Response at a silver cathode modified by a layer of Ag–Pd

electrodes permit the formation of homo-dimers R–R. This reaction was recently reported [26] with alkyl iodides. On the contrary, M-Ag NP electrodes less efficient than Ag–Pd electrodes appear to be within an intermediate position presumably because the free alkyl radical is partly reduced. The observed step is precisely located within a range quite close to the reduction standard potentials reported for most of $R^{\bullet}$ under very comparable experimental conditions [28].

5 Conclusion

It was shown that the deposit of nano-particles of very small size (presumably <10 nm) onto conducting solids could be achieved by employing a very simple procedure. The key point was first the easy formation of an Ag–Pd powder directly from a commercial silver powder treated at room temperature with a palladium salt. The electrolysis (using the known technique of fluidized bed electrolyses) of alkyl iodides by means of an indirect reduction using Ag–Pd grains allows the deposit of nano-particles onto a solid electrified conductor. A sketch (Scheme 2) pictures the electrochemical process and summarizes the different pathways. It underlines substrates and products globally implied in the whole process. Deposits of silver according to this way are possible onto a very large palette of metals (e.g. from gold to zinc). The deposit of silver according to this procedure is also feasible in matrixes of porous organic polymers at the level of their n-doped state. Therefore, this method allows the formation of a new kind of chemically modified interfaces: essentially a metal covered with Ag nano-particles that appear much more reactive for achieving cathodic cleavage reactions than smooth silver electrodes themselves. Since a large palette of solid substrates may be silvered by this method, further developments are foreseeable for this kind of *cheap silver electrodes*. Lastly, the facility and the low cost of the procedure permit to expect some applications in the field of practical works in Electrochemistry Laboratories.



Scheme 2 A proposal for the formation of Ag nano-particles and aggregates at an electrified conductor inert towards RI compounds at the applied potential (E). Note that the conversion Ag $\Longleftrightarrow$ Ag–Pd is not completed inside the electrochemical cell

Acknowledgments The author wishes to deeply thank Dr. Philippe Poizot (Université Jules-Verne, Amiens) for his constant and helpful interest in the building of new electrodes. His contribution was also fully appreciated in SEM technique for the analysis of silver layers.

References

1. Lund H, Hammerich O (eds) (2001) Organic electrochemistry, 4th edn. M. M. Dekker, New York
2. Schafer HJ (2004) In: Bard AJ, Stratmann M (eds) Encyclopedia of electrochemistry. Wiley-VSH, Weinheim
3. Shono T (1991) Electroorganic synthesis. Academic press, San Diego
4. Bernier P, Lefrant S (1997) Le carbone dans sous ses états. Gordon and Breach Publ, Amsterdam
5. Coulon E, Pinson J (2001) Langmuir 17:7102
6. Pinson J, Podvorica F (2005) Chem Soc Rev 34:429
7. Steckhan E (2001) In: Lund H, Hammerich O (eds) Organic electrochemistry. M. M. Dekker, New York, p 1103
8. Holliday JR, Timothy MS (2005) Chem Commun 23
9. Simonet J (2008) Electrochem Commun 11:134
10. Li N, Bai X, Zhang S, Zheng L, Gao Y, Zhang J, Ma H (2008) J Disper Sci Technol 29(8):1059
11. Veerabadran NG, Price R, Lvov YM (2008) PMSE Preprints 99:566
12. Wang H, Lou Y, Northwood DO (2008) J Mater Process Tech 204(1–3):327
13. Logar M, Jancar B, Suvorov D, Kostanjsek R (2007) Nanotechnology 18(32):325601/1
14. Li Y, Kim YN, Lee EJ, Cai W, Cho SO (2006) Nucl Instrum Meth B 251(2):425
15. Starowicz M, Stypula B, Banas J (2006) Electrochem Commun 8(2):227
16. Mussini PR, Ardizzone S, Gappelletti G, Longhi M, Rondinini S, Doubova LM (2003) J Electroanal Chem 552:213
17. Rondinini SB, Mussini PR, Crippa F, Sello G (2000) Electrochem Comm 2:491
18. Ardizzone S, Cappelletti G, Lioudmila M, Mussini PR, Passeri SM, Rondinini S (2003) Electrochim Acta 48:3789
19. Rondinini S, Vertova A (2005) Electrochim Acta 49:4035
20. Fiori G, Rondinini S, Sello G, Alberto C, Cirja M, Conti L (2005) J Appl Chem 35:363
21. Paddon CA, Bhatti FA, Donohoe TJ, Compton RG (2007) J Phys Org Chem 20:115
22. Simonet J (2005) Electrochem Comm 7:74
23. Poizot P, Laffont-Dantras L, Simonet J (2008) Electrochem Comm 10:864
24. Poizot P, Laffont-Dantras L, Simonet J (2008) J Electroanal Chem 622:204
25. Poizot P, Laffont-Dantras L, Simonet J (2008) J Electroanal Chem 624:52
26. Poizot P, Jouikov V, Simonet J (2008) Tetrahedron Lett (in press)
27. Peters DG (2001) In: Lund H, Hammerich O (eds) Organic electrochemistry, vol 8. M. M. Dekker, New York, p 341
28. Occhialini D, Daasberg K, Lund H (1993) Acta Chem Scand 47:1100