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Voltammetry of MicroParticles in Thin Layer

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10

Abstract: We describe a new experimental device for the characterization of electroactive
12 microparticles and of the soluble species released during their electrochemical transformation.
By using only a few microparticles, it provides, in a faster way, similar information as
14 modified carbon paste electrodes with electrolytic binders (CPEEBs) and the sensitivity and
resolution are must better. The device geometry was modelled with ferrocyanide ions and the
16 voltammograms for ferrocene, pyrolusite and hematite were compared with the literature ones
concerning CPEEBs. Finally, an alumina-supported palladium catalyst and pyrite-containing
18 argillite were successfully characterized.

20 **Keywords:** Voltammetry of microparticles, Manganese dioxide, Ferric oxide, Alumina
supported palladium, Callovo-Oxfordian argillite

22

1. Introduction

24 Voltammetry of microparticles (VMP) is a technique developed by Scholz [1] that can be
applied for the voltammetric characterization of any solid electroactive material, conducting

or not, via the mechanical immobilization of microparticles on the cross section of a current collector [2-5]. This latter is most often a graphite rod which had been previously impregnated with solid paraffin to fill up the graphite pores. VMP has the advantages over carbon paste electroactive electrodes of requiring only a few micrograms of matter to be analyzed and avoiding the use of organic binders that can influence the electrochemical behaviour of the solid compounds. However, VMP cannot provide information on the soluble species released in solution by the immobilized microparticles during their electrochemical transformation. when the electrochemical kinetics is slow and voltammetry at rapid scan rates is inoperable. To get this information today, electrochemists can utilize Carbon Paste Electrodes with Electrolytic Binders (CPEEBs), which have been developed in the seventies by the Bauer group who established a theoretical model on their working principle [6-8]. CPEEBs are prepared by mixing graphite powder with electrolytic solutions instead of non-conducting pasting liquids with traditional modified carbon paste electrodes [9]. In this way, in principle, the whole of the electroactive matter inserted in the carbon paste is electrochemically transformed and soluble species released are trapped in the carbon paste. These electrodes have been successfully used with various compounds just as well insoluble (ferrocene [6], uranium ores [11] copper sulphides [12-14], ilmenites [15], oxides of iron [16-21], copper [21] and manganese [22]) as dissolved directly in the electrolyte (FeCl_2 and MnCl_2 [22], $\text{Fe}(\text{CN})_6^{4-}$ and O_2 [6]). Ramirez et al. proposed some experimental modifications [23] and the Vittori group introduced theoretical complements on the Bauer model [24,25]. Nevertheless, when CPEEBs are employed, extremely slow scan rates (in the range of some hundredths or tenths of mV/s) and very concentrated supporting electrolytes are used in order to minimize capacitive currents. Moreover, the effective deaeration of the carbon paste is quite hard (use of vacuum and glove boxes or previous electrochemical reduction of atmospheric oxygen if possible). In addition, if the solubilization of the non-conducting electroactive microparticles

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is very slow, the faradaic current becomes of the same order of magnitude as the background current [6].

We developed an experimental device that comes from the combination of VMP and thin-layer (TL) voltammetry [26] that we called ‘Voltammetry of MicroParticles in Thin Layer’ (VMPTL) [27]. Its principle consists in entrapping a very small amount of electroactive material (some micrometric or submicrometric particles) and a TL of electrolyte solution between the cross sections of two graphite electrodes. VMPTL provides similar information as CPEEBs while maintaining the benefits of VMP. In this way, the voltammetric characterization of both the entrapped microparticles and the soluble species released by the latter can be performed with a much higher sensitivity and resolution than CPEEBs with only a few micrograms of matter. In addition, the solution can be easily deaerated before the entrapping stage by bubbling an inert gas and ten times faster scan rates can be used.

The aim of this paper is to show the potentiality and performance of VMPTL in comparison with CPEEBs. After the description of the experimental device, its functioning will be tested with the model electrochemical system $\text{Fe}(\text{CN})_6^{3-/4-}$. Then, the voltammograms recorded for ferrocene (Fc), pyrolusite (MnO_2) and hematite (Fe_2O_3) will be compared with the literature ones obtained with CPEEBs. Finally, VMPTL will be utilised for the characterization of two electroactive compounds that are at percent levels in more or less complex matrixes: metallic palladium in an alumina-supported catalyst and pyrite (FeS_2) in Callovo-Oxfordian argillite. The present approach could be also useful for studies of organic deposits, as it has been pioneered by Doménech-Carbó [28,29].

2. Experimental

2.1. The electrochemical cell

Experimental setup: some electroactive microparticles and a TL of solution are entrapped

between the cross sections of two graphite rods. The rods are mounted, with an epoxy resin (Epofix kit from Struers), in the axis of the truncated plungers of two glass syringes that allow to the rods to slide hermetically inside the end truncated syringe barrels (Fig. 1A). The rods are externally short-circuited and connected to the working electrode input of the potentiostat. The main purpose of using two short-circuited graphite electrodes opposite each other instead of only one against an insulating surface, as with classic thin layer cells, is to ensure a good electrical contact with the immobilized electroactive microparticles allowing the electrochemical transformation of the greatest possible number, if not all, of them.

Before mounting the graphite rods (3.05 mm diameter, 99.9995% metals basis from Alfa Aesar) in the truncated plungers of the syringes it is necessary to fill up the graphite pores with solid paraffin to eliminate the electrochemical response of adsorbed oxygen and to avoid the contamination of graphite by soluble species as recommended by Scholz [1].

Cell design: the cell, depicted schematically in Figure 1B, is made of Perspex and has a cylindrical shape. There is a central cylindrical conduit, containing the electrolytic medium, where are stuck horizontally with a bicomponent epoxy glue the syringe barrels where the two graphite electrodes are allowed to move. A platinum counter electrode inserted in a PTFE stopper is screwed on the basis of the cell and, according to the experiment, a silver-wire used as the quasi-reference electrode or a Ag/AgCl reference electrode are inserted in a PTFE stopper on the top of the cell. An inert gas inlet tube is also inserted in the top stopper. Depending on the position of the tube, the gas is bubbling through the solution or it maintains an inert atmosphere over its surface. The device is equipped with a metallic holder and a slight rotation about its axis allows to remove one after the other the graphite electrodes for cleaning or polishing without emptying the cell.

2.2. Use of the device

To transfer and immobilize the electroactive particles inside the TL, a few grains are applied

to the graphite surface of one of the electrodes and pressed on it with a small spatula. Then the electrode is softly struck against a glass surface before its introduction in the electrochemical cell in order to remove the particles that were badly fixed. After deaeration of the solution, the graphite electrodes are pushed up and rotated one against the other in such a way that the immobilized microparticles come in the most intimate contact with the two graphite discs. Before each experiment the surface of the electrodes is cleaned by polishing with a filter paper or with a grinding paper, if necessary.

2.3. Electrochemical measurements

Voltammetric experiments were performed with a model 174A polarographic analyzer (EG&G-PAR), which was interfaced via a computer AD card and monitored by a home-made application created by means of the TestPointTM software, or with a 'Quadstat' four-channel potentiostat used as a single three-electrode potentiostat and monitored by the EChem Software (both from EDAQ). According to the experiments, the potentials were referred to the silver quasi-reference electrode (Ag/QREF) or to the saturated Ag/AgCl electrode.

2.4. Chemicals and minerals

Potassium hexacyanoferrate(II), sulphuric and hydrochloric acids and potassium chloride, were of RP Normapur grade from Prolabo. Ferrocene purum grade, manganese(IV) oxide puriss. grade and iron(III) oxide puriss. p.a. grade were obtained from Fluka, and palladium(II) chloride from Merck. Palladium on alumina pellets loading 5 wt. % catalyst was from Johnson Matthey (see SECM characterization in Fig. 2A). The Callovo-Oxfordian argillite sample containing 0.5-1 wt. % pyrite [30] came from Bure (Meuse) in France (optical microscope picture in Fig. 2B). It was kindly provided by Prof. M. Cathelineau ('GeoRessources' laboratory - Université de Lorraine).

3. Results and Discussion

3.1. Test of the device with the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ system

A series of cyclic voltammograms obtained for 2 mM $\text{K}_4\text{Fe}(\text{CN})_6$ in 1 M KCl using scan rates from 1 to 5000 mV/s allowed us to estimate the liquid TL thickness. Some typical voltammograms recorded in the 10-100 mV/s range are displayed in Figure 3A. The analysis of the results shows that the anodic and cathodic peak separation (ΔE_p) first decreases until the scan rate (ν) is over 6 mV/s then increases (Fig. 3B). ΔE_p remains smaller than 58 mV as long as ν is lower than 40 mV/s. The plot of the anodic peak current (I_p) versus ν in a log-log representation (Fig. 3C) exhibits two linear parts with an interconnecting break point at about 100 mV/s. The slope of the first part, very close to 1, indicates a TL behaviour, $I_p = [n^2F^2VC^\circ/(4RT)]\nu$ (1). The second part has a slope very close to 0.5 according to the cyclic voltammetry theory: $I_p = [0.4463(F^3/[RT])^{1/2}n^{3/2}AD^{1/2}C^\circ]\nu^{1/2}$ (2). In these formulas, C° and D are, respectively, the concentration and the diffusion coefficient of the electroactive species, V the volume of the TL and A the surface area of the electrode. The variation of the slope of $\log I_p$ vs. $\log \nu$ is interpreted as follows: As long as the diffusion layer thickness remains wider than the distance between the graphite electrodes one observe a TL behaviour. Then, when ν becomes high enough for the diffusion layer to become smaller than the TL, the system varies with ν according to the cyclic voltammetry theory. The scan rate value at the break point (ν_{bp}) depends only on the TL thickness (l) and D . In fact, at this point, I_p can be calculated by both equations (1) and (2) and one can easily demonstrate that $l = 1.7852[DRT/(nF\nu_{bp})]^{1/2}$ (3). According to the experimental data, $\nu_{bp} = 96$ mV/s that gives 24.6 μm for l . As the VMPTL device comprises two parallel active graphite electrodes, l must be multiplied by 2 to have the real interelectrode distance, therefore, the distance is about 50 μm . Figure 4C also shows the modelling made using equations (1) and (2) with $D_{\text{Fe}(\text{CN})_6^{4-}} = 7.4 \times 10^{-6}$ cm²/s [31] for two 3.0 mm diameter electrodes put in front each other and forming

two 24.6 μm TLs; the calculated curve is in good agreement with the experimental points.

2

3.2. Comparison with literature experiments performed with CPEEBs

4 In this section the voltammograms recorded for ferrocene, pyrolusite and hematite using
VMPTL are compared with those obtained by Bauer et al. [6] and Lorenzo et al. [21,22] with
6 CPEEBs. Four i-E curves from these references have been digitized and superimposed on our
own experimental data to aid comparison.

8 3.2.1. Characterization of ferrocene

Ferrocene has been used in the very first experiments performed with CPEEBs in the
10 seventies by the Bauer group. Voltammograms for ferrocene microparticles recorded in 1.4 M
 H_2SO_4 using VMPTL, at 2 mV/s, and a CPEEB at 0.2 mV/s (from ref. [6]) are shown in
12 Figure 4A. Overall, the shape of the two curves are quite comparable in spite of a scan rate 10
times faster for VMPTL. At the first anodic scan, started from the open circuit potential
14 (OCP), the oxidation of ferrocene is spread over several hundreds of millivolts because of the
ohmic drop resulting from the bad contact between the insulating ferrocene particles and
16 graphite. In contrast, the reduction of the produced soluble ferrocenium cation gives rise to the
symmetrical cathodic peak C1 at potentials close to the thermodynamic value. The second
18 anodic scan is much less affected by ohmic drop because of the intimate contact between
graphite and the ferrocene deposited on it during the reduction of Fc^+ at C1. However, in the
20 case of CPEEB, peak A1 is far from being symmetrical because of remaining ohmic drop.
Some typical cyclic voltammograms recorded with the VMPTL device after stabilization of
22 the currents are displayed in Figure 4B. Thus, in the case of ferrocene, VMPTL provides more
rapidly similar information to the one obtained using CPEEBs and the corresponding
24 voltammograms are less affected by ohmic drop.

3.2.2. Characterization of pyrolusite

2 The voltammogram recorded with MnO₂ microparticles in 10 mM HCl using VMPTL at 5
mV/s and that displayed in ref. [22] (CPEEB, $\nu = 0.5$ mV/s) are represented in Figure 5. The
4 scans were started from the OCP in the negative direction. Both voltammograms provide
similar information, however, the voltammogram recorded using VMPTL does not suffer
6 neither from ohmic drop nor from capacitive current as that using CPEEB, in spite of a scan
rate ten times faster.

8 According to Lorenzo et al. [22], the cathodic peak C1^o, observed at the first cycle,
corresponds to the reduction of the initial MnO₂ in soluble Mn²⁺ ions ($\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow$
10 $\text{Mn}^{2+} + 2\text{H}_2\text{O}$). After the scan reversal, the opposite reaction occurs at anodic peak A1, which
is located just before the anodic limit. After another reversal of the sweep direction, the
12 cathodic signal for the reduction of MnO₂ electrochemically deposited on the graphite surface
(peak C1) is shifted towards more positive potentials with respect to peak C1^o. A careful
14 examination of the voltammogram obtained with VMPTL shows that: (i) The C1/C1^o peaks
area ratio is about 1.1 (This ratio is approximately 2.6 in the case of the CPEEB because of
16 the presence of Mn²⁺ ions in the electrolyte inside the carbon paste. According to the authors,
Mn²⁺ result from the interaction of MnO₂ with HCl, however, the corresponding chemical
18 reaction is not written and the process is unclear for us). (ii) In the VMPTL voltammogram, a
very slight signal is still present at C1^o during the second cycle that means that the MnO₂
20 reduction is not totally complete. When a CPEEB is used, it is very difficult to estimate the
amount of MnO₂ reduction at the second scan because of the probable overlapping of peaks
22 C1^o and C1.

3.3.3. Characterization of hematite

24 The voltammogram for the characterization of Fe₂O₃ in 1M KCl at pH 1 using VMPTL is
shown in Figure 6A (curve a). The potential scan ($\nu = 5$ mV/s) started from the OCP in the

negative direction. The cathodic peak C1° corresponds to the Fe₂O₃ reduction into Fe²⁺ that is
2 oxidized to Fe³⁺ during the reverse scan (peak A1). Along the second and next cycles Fe³⁺ is
reduced in Fe²⁺ (C1) and then oxidized again in Fe³⁺ (A1). This voltammogram closely
4 resembles that obtained by Encinas Bachiller et al. [21] in 1M HCl by means of a CPEEB at
0.5 mV/s. However, in the case of VMPTL, because of the lower acidity of the solution, the
6 reduction of Fe₂O₃ takes place at more negative potentials and the peak shape for the Fe^{3+/2+}
system is different. Indeed, peaks A1 and C1 related do CPEEB demonstrates pure TL
8 behaviour but are not symmetrical because of the ohmic drop, whereas those related to
VMPTL are almost symmetrical. Moreover, even if peaks A1 on both voltammograms are
10 virtually superimposable, the A1-C1 peak separation is larger in the case of VMPTL because
of the formation of FeOH²⁺ and Fe(OH)₂²⁺ species whose reduction is more difficult than that
12 of Fe³⁺ [32].

Figure 6B illustrates the comparison of the voltammograms for Fe₂O₃ recorded with VMPTL
14 ($\nu = 5$ mV/s) and CPEEB ($\nu = 0.5$ mV/s, from ref. [22]) in the same medium: 10 mM HCl. As
in the case of MnO₂, the voltammogram corresponding to VMPTL shows no ohmic drop nor
16 capacitive current if compared to that for CPEEB. However, the two voltammograms are
completely different. The one for CPEEB provides similar information as provided in the 1M
18 HCl medium. When VMPTL is used, the Fe₂O₃ reduction is far to be complete, the signal A1
for Fe²⁺ oxidation is flat while that for Fe³⁺ reduction (C1) is barely visible. This due to the
20 very low quantity of protons inside the TL. Indeed, the electrochemical reduction of hematite
according to the reaction: Fe₂O₃ + 2e⁻ + 6H⁺ → 2Fe²⁺ + 3H₂O (1) requires 2 electrons and 6
22 protons.

Indeed, assuming that in the best-case scenario the TL thickness is 100 μm, the corresponding
24 TL volume is 7×10⁻⁷ L, which contains 7×10⁻⁹ mol of protons. By integration of the
voltammetric curve in Figure 6B, we estimated at approximately 4.3×10⁻⁴ C the charge

exchanged at peak C1° and, consequently, the reduction concerns 2.2×10^{-9} mol of Fe_2O_3 that
2 require 1.3×10^{-8} mol of H^+ . Yet, only 7×10^{-9} mol are present in the TL. In this way, the pH
inside the TL will be highly alkaline (~ 12.3) after the hematite reduction, which explains the
4 $\text{Fe}^{3+/2+}$ system shape. We also made the same kind of calculations for the voltammogram
obtained with the CPEEB [22]. Given that 1.6 mg of Fe_2O_3 (10^{-5} mol) and 50 μL of 10^{-2} M
6 HCl (5×10^{-7} mol) were used for the preparation of the carbon paste there is a serious shortage
of protons for the complete reduction of hematite. We estimated that approximately 7×10^{-7}
8 mol of Fe_2O_3 were reduced at peak C1°, by integration of the voltammetric curve, which
correspond to a 0.14 C charge. It is unclear in ref. [22] if the electrode was filled with the
10 whole of the carbon paste or not. We accepted the most favourable hypothesis i.e. the totality
of the carbon past was used and therefore 5×10^{-7} mol of H^+ are present inside the electrode,
12 whereas only 7% of the initial hematite was electrochemically reduced. As the reduction of
 7×10^{-7} mol of Fe_2O_3 requires 4.2×10^{-6} mol of H^+ , the $\text{H}^+/\text{Fe}_2\text{O}_3$ ratio is much more
14 unfavourable than in the case of VMPTL and the shape of the voltammogram in Figure 8B is
totally incompatible with such a high pH value unless there is a massive introduction of H^+
16 from the solution into the paste.

Figure 6C illustrates an attempt to prevent the Fe(III) precipitation in the 10 mM HCl medium
18 by formation of the anionic complex FeCl_4^- after the addition of a massive amount of chloride
ion. This is why the series of voltammograms in Figure 6C was recorded in the 10 mM HCl +
20 1 M KCl mixture by decreasing dramatically the amount of Fe_2O_3 immobilized in the TL. In
the forward scan, the signal C1° for the Fe_2O_3 reduction is no more a sharp peak, as in Figure
22 6B, but a wide signal that is composed of two successive steps at -0.20 and -0.37 V as in
Figure 6A. After the reversal of the scan direction, a well defined anodic peak A1 is observed
24 at 0.48 V for the Fe(II) oxidation, then, following a second scan reversal, peak C1 for the
Fe(III) reduction appears at 0.42 V. However, the C1/A1 height ratio is only 0.69. During the

next cycles, the cathodic signal $C1^\circ$ remains virtually unchanged whereas peaks A1 and C1 progressively grow towards constant heights with an A1/C1 ratio about 0.77. What is notable is that it is as hematite was regenerated at every voltammetric cycle. Probably, the mechanism is complex and may involve the formation of green rusts [33]; therefore, specific investigation is required that is beyond the scope of this article.

3.3. Characterization of electroactive compounds present at percent levels in different matrices

After showing the interest of VMPTL for the characterization of pure solids, it is extended here in species that are present at very low amounts in more or less complex matrices, i.e. a palladium-based catalyst and a pyrite containing natural rock.

3.3.1. Palladium supported on alumina catalyst (Pd/Al/Cat)

The hydrogenation aromatic rings, the oxidation of methane [34] and glucose [35], the deoxygenation of inert gases [36], the fuel cells [37,38] and the combustion in gas turbines [39] are among the numerous applications of Pd/Al/Cats. In the environmental area, Pd/Al/Cats are used for the reductive dehalogenation of chlorinated hydrocarbons or the hydrogenation of aromatic compounds in groundwater [40,41] and the exhaust emissions (NO_x+CO) transformation in the automotive [42,43]. Vibrational spectroscopy has been mainly used for the Pd/Al/Cats characterization [44-47]; it showed that an oxidation phenomenon occurred on the Pd surface with formation of PdO when the catalysts were in contact with air, even at room temperature. Their regeneration requires the reduction of the oxide by gaseous hydrogen at high temperatures. Finally, the Bauer group investigated in 1992 the electrochemical characterization of palladium compounds, including palladium automotive catalysts, by means of CPEEBs [48,49].

The experiments were performed in 1 M KCl at pH 2, in order to lower the Pd° oxidation potential by the formation of palladium chloro-complexes and avoid the production of

palladium monoxide which is insoluble in all acids, including aqua regia [50,51]. The
2 speciation diagram that we plotted for 50 mM Pd(II) in 1 M KCl shows that if $\text{pH} < 2.25$ the
whole quantity of Pd(II) is under the anionic forms PdCl_4^{2-} (95%) and PdCl_3^- (5%).

4 The VMPTL voltammograms recorded at 5 mV/s for Pd/Al/Cat microparticles obtained after
grinding of the commercial pellets are displayed in Figures 9A and 9B.

6 In Figure 9A, the potential sweep was started from the OCP in the positive direction. At the
first voltammetric cycle the anodic peak A1° (0.64 V) corresponds to the oxidation of the
8 alumina-supported metallic Pd particles in PdCl_4^{2-} . After the potential reversal, the cathodic
peak C1° (0.00 V) is ascribed to the deposition on the graphite surface of Pd° that results from
10 the reduction of: (i) PdCl_4^{2-} , released at A1° and (ii) PdO originally present on the catalyst
surface (see Fig. 9B). Indeed, the peak C1° area is much greater than that of A1°
12 ($\text{C1}^\circ/\text{A1}^\circ \approx 1.7$). At the second cycle, the stripping of Pd° deposited on the graphite surface
during C1° occurs at lower potentials (peak A1 at 0.58 V) than that originally present on
14 Al_2O_3 . However, the $\text{A1}/\text{C1}^\circ$ area ratio is about 0.6; that means that either a large part of the
 Pd° formed at C1° is no more in electric contact with the graphite or the air-oxidized
16 palladium on the Pd/Al/Cat surface was at an oxidation state higher than 2. After the scan
direction reversal, PdCl_4^{2-} is reduced at peak C1 (0.02 V), which is thinner than C1° because
18 of the absence of PdO, and $\text{C1}/\text{A1} \approx 1.2$. At the third and fourth cycles, the $\text{C1}/\text{A1}$ area ratio
tends towards 1 and the voltammetric peaks height progressively decreases. This is probably
20 the result of the gradual adsorption of PdCl_4^{2-} on alumina, which, according to electrokinetic
measurements [52], is positively charged for pH values smaller than 8-9 whatever the origin
22 and the crystalline structure of Al_2O_3 . The positions of peaks C1 (0.02 V), for the PdCl_4^{2-}
reduction, and A1 (0.58 V) for the Pd° stripping on graphite have been confirmed by the
24 voltammogram recorded for 1 mM PdCl_2 in the same medium (Fig. 9C curve c). Therefore,
the kinetics of the $\text{PdCl}_4^{2-}/\text{Pd}$ system is slow. In the literature the positions of peaks A1 and

C1 are very dependent on the experimental conditions: 0.66 and 0.00 V vs. SCE, respectively, at a carbon felt in 0.1 M HCl [53], 0.36 and 0.174 V vs. SCE at a CPEEB in 2 M HCl [48], 0.67 and 0.26 V vs. SCE at a vitreous carbon electrode in 0.03 M HCl + 0.8 M HClO₄ [54]. As regards the PdCl₄²⁻/Pd standard potential, there are some inconsistencies in the literature where E° varies from 0.580 to 0.646 V vs. SHE [55-61]. The PdO reduction potential, which depends on the pH, was observed at -0.165 vs. Ag/QREF at pH 2 in the present study, -0.100 vs SCE at a CPEEB in 2M HCl [48], 0.529 V vs. the reversible hydrogen electrode (RHE) at a Pd electrode in 0.5 M H₂SO₄ [62] and 0.76 vs. RHE at a smooth Pd electrode in 1M H₂SO₄ [63]. The E°_{PdO/Pd} standard potential, ranges between 0.87 and 0.91 V vs. SHE [51,55,62,64,65]. Therefore, the normal apparent potential at pH 2 is about 0.80 V vs. SHE (~0.57 V vs. Ag/QREF).

When the voltammograms are recorded in the negative direction (Fig. 9B), at the first cycle, the broad signal C0 going from 0.1 to -0.2 V corresponds to the PdO reduction in Pd°. After reversal of the scan direction, two anodic stripping signals appear: (i) A0 for the elemental palladium deposited onto graphite surface during the PdO reduction and (ii) A1° to the Pd originally present on Al₂O₃. The (A0+A1°)/C0 peaks area ratio is about 3. Then, after the scan reversal (A0+A1°)/C1 = 1.3. At the second and third cycles, as for the voltammograms recorded in the positive direction, the heights of peaks A1 and C1 progressively decreases and their ratio tends to 1.

The voltammogram obtained with an automotive Pd catalyst using a CPEEB at a 0.25 mV/s scan rate in 2 M HCl (digitized from reference [48]) is represented in Figure 9C (curves a and b). The comparison with the VMPTL voltammograms shows that, even if the potentials of peaks A0, A1, C0 and C1 are different because of the high acidic level used with the CPEEB the interpretation is the same. Thus, the results are qualitatively similar and those for VMPTL can be obtained 20 times faster.

3.3.2. Pyrite containing Callovo-Oxfordian argillite (COx) from Bure

2 In several studies on the underground landfill of spent nuclear fuel, it is accepted that small
amounts of pyrite (~1 wt. %) will be responsible for the low redox potential of argillaceous
4 soils envisaged for the fuel storage [66]. Therefore, it is important to examine if
electrochemical techniques could be a useful tool to investigate the reactivity of minerals
6 included in these subsoils. Bure is the French site planned for the deep repository of high
activity long life radioactive waste [67]. The experiments have been performed in chloride
8 medium (10 mM HCl + 1 M KCl), because the chloride concentration in the Bure clay pore
water ranges from 0.01 to 0.5 M according to the localization of the analysed samples [68].
10 The voltammogram for COx grains entrapped in the VPMTL device is shown in Figure 10.
The potential scan was started from the OCP (0.07 V vs. Ag/QREF) in the positive direction.
12 The anodic peak A1 that appears at about 0.99 V, just before the anodic limit, is due to the
pyrite oxidation. During the reverse scan, we can see the reduction of species issued from the
14 FeS₂ oxidation: Fe(III) at peak C2 (0.40 V), and a mixture of S₈, S_x²⁻ and oxysulphur
compounds (S₂O₃²⁻, S₄O₆²⁻...) [69-71] at peak C3 (-0.50 V). In the second cycle, one can
16 remark the appearance of peak A2 (~0.59 V) for the oxidation of Fe²⁺ ions formed at C2 and
the dramatic decrease of peak A1. Therefore, almost the whole of pyrite comprised in the clay
18 has been oxidized during the first cycle. Peak C2 is superimposable to that of the first cycle. It
is difficult to have an exact estimation of the A1/C2 peak area ratio because A1 and the
20 oxidation of chloride ions are too close. However, the very approximate experimental value of
16 that we determined is in favour of the formation of oxysulphur compounds like SO₄²⁻,
22 S₂O₃²⁻, S₄O₆²⁻ ...during the oxidation of pyrite. For example, the reaction $\text{FeS}_2 + 8 \text{H}_2\text{O} + \text{Cl}^-$
 $\rightarrow \text{FeCl}^{2+} + 2 \text{SO}_4^{2-} + 16 \text{H}^+ + 15 \text{e}^-$ would lead to an A1/C2 peak area ratio of 15. Because of
24 the fundamental importance of the electrochemical characterization of COx, a more detailed
presentation will be the subject of a separate paper.

2 **4. Conclusions**

We hope that this article could convince the reader of the usefulness of VMPTL that enables
4 to characterize electrochemically not only pure solids but also compounds that are in very low
amounts in complex matrixes. As this technique provides information on the soluble species
6 formed at the surface of the immobilized electroactive microparticles, it is an efficient tool,
complementary to VMP. Moreover, VMPTL, from just a few μg of matter, gives equivalent
8 results as CPEEBs using scan rates more than ten times faster with better resolution and
higher signal-to-noise ratio, especially if the experiments are made in low conducting media.
10 The voltammograms recorded in this study with ferrocene, pyrolusite and an alumina-
supported palladium catalyst are in good agreement with the literature ones obtained using
12 CPEEBs, while those for hematite lead us to suspect a complex mechanism. Finally, VPMTL
has been successfully applied to a sample of Callovo-Oxfordian argillite.

14

5. Acknowledgements

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18

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Figure Captions

2 **Fig. 1.** The VMPTL electrochemical cell: (A) experimental setup, (B) schematic
representation of the cell design.

4 **Fig. 2.** Electroactive solids present at percent levels in different matrices: (A) Alumina-
supported palladium catalyst (scanning electron photomicrograph, back-scattered electron
6 image), (B) Pyrite-containing Callovo-Oxfordian argillite (optical microscopy photograph).

Fig. 3. Voltammetric behaviour of 2 mM $K_4Fe(CN)_6$ in 1 M KCl using the VMPTL device.
8 (A) Cyclic voltammograms for different scan rates. (B and C) Analysis of the variation of the
voltammograms characteristics with the scan rate: Separation between the anodic and
10 cathodic peak (B), Anodic peak current (C).

Fig. 4. Voltammetric characterization of ferrocene microparticles in 1.4 M H_2SO_4 using
12 VMPTL: (A) Two first cycles and comparison with CPEEB (reproduced with permission
from [6]), (B). Stabilized voltammograms for different scan rates.

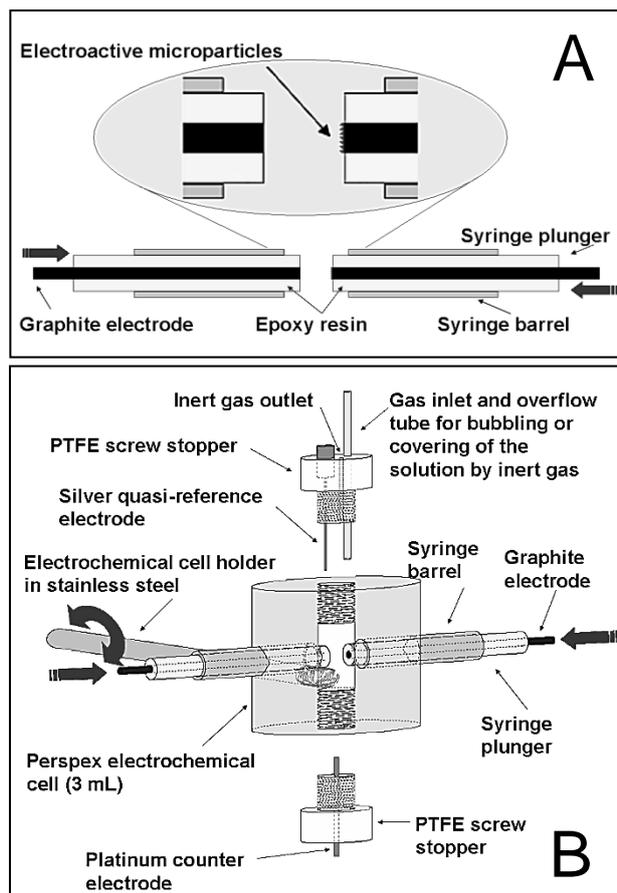
14 **Fig. 5.** Voltammetric characterization of MnO_2 microparticles in 10 mM HCl using VMPTL
and a CPEEB (reproduced with permission from ref. [22]). Scans started from the OCP in the
16 negative direction.

Fig. 6. Voltammetric characterization of Fe_2O_3 microparticles: (A) Curve (a) 1M KCl, pH 1
18 VMPTL at 5 mV/s; Curve (b) 1M HCl CPEEB, at 0.5 mV/s (reproduced with permission
from ref. [21]), (B) 10 mM HCl, VMPTL (curve a), CPEEB (curve b reproduced with
20 permission from ref. [22]).

Fig. 7. Voltammetric characterization of palladium supported on alumina catalyst (all scans started from the OCP): (A) VMPTL in 1 M KCl at pH 2, in the positive direction ($v = 5$ mV/s), (B) VMPTL in 1 M KCl at pH 2, in the negative direction ($v = 5$ mV/s), (C): curves a and b CPEEB in 2 M HCl in the negative direction (reproduced with permission from ref. [48], $v = 0.25$ mV/s) and curve c, electrochemical behaviour of 1 mM PdCl₂ thin layer in 1 M KCl at pH 2 ($v = 5$ mV/s).

Fig. 8. Voltammetric characterization of Callovo-Oxfordian argillite in 1 M KCl pH 2 using VMPTL. Scan started from the OCP in the positive direction, $v = 5$ mV/s.

Fig. 1



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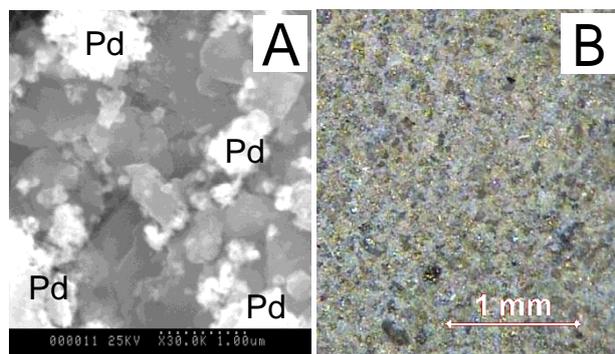


Fig. 2

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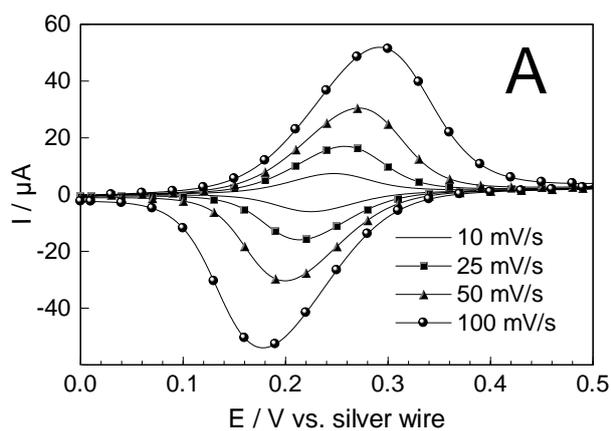
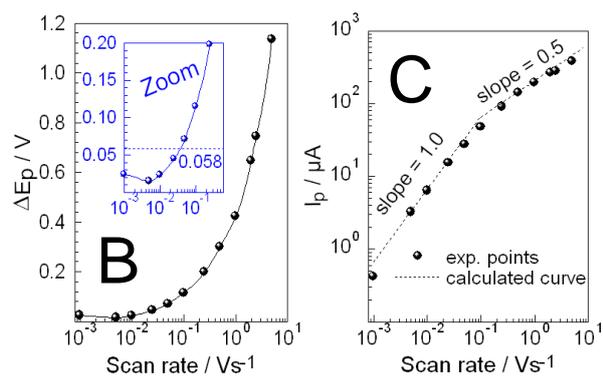


Fig. 3

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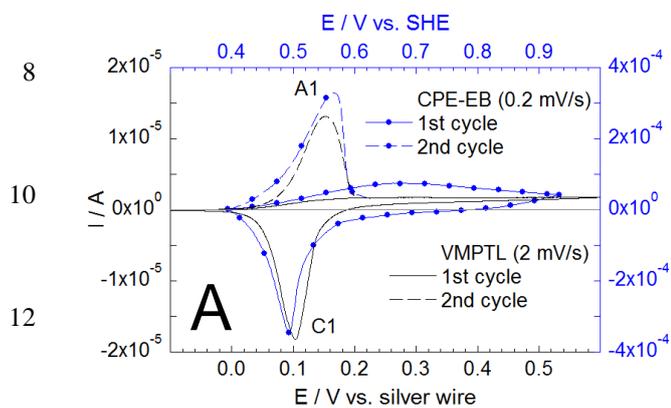
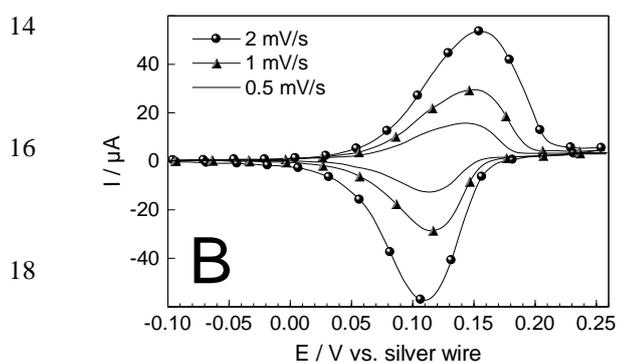


Fig. 4



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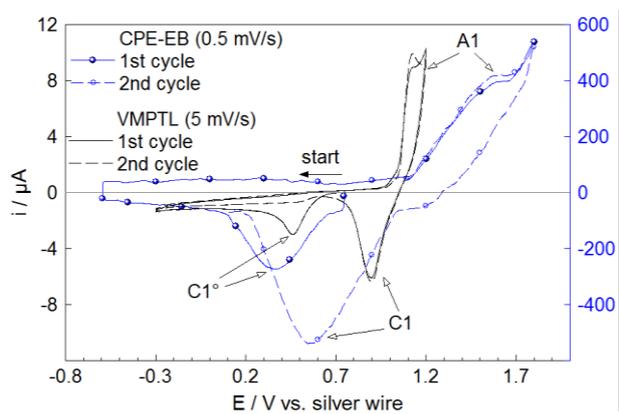


Fig. 5

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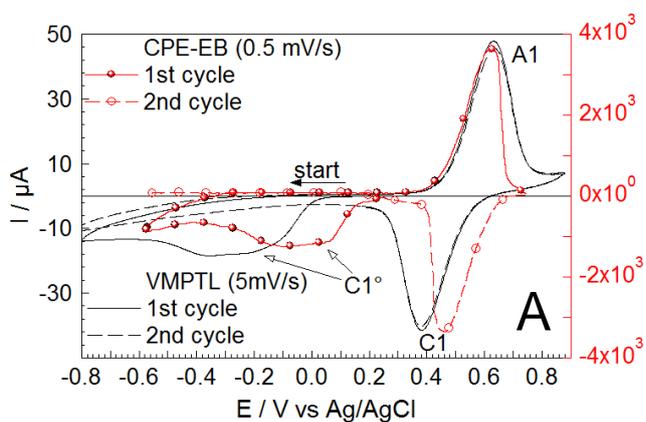
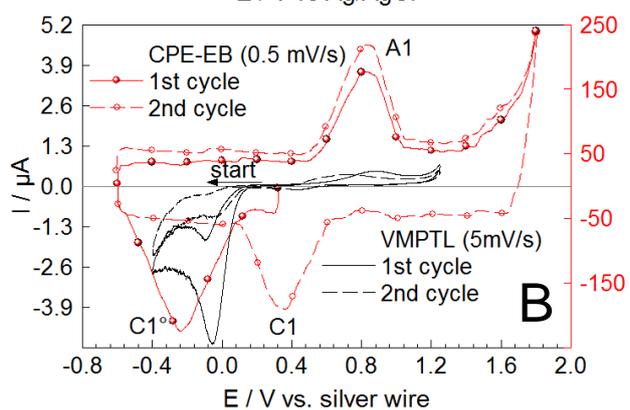
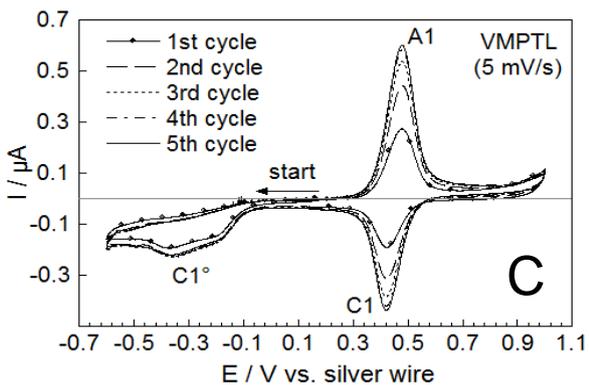


Fig. 6



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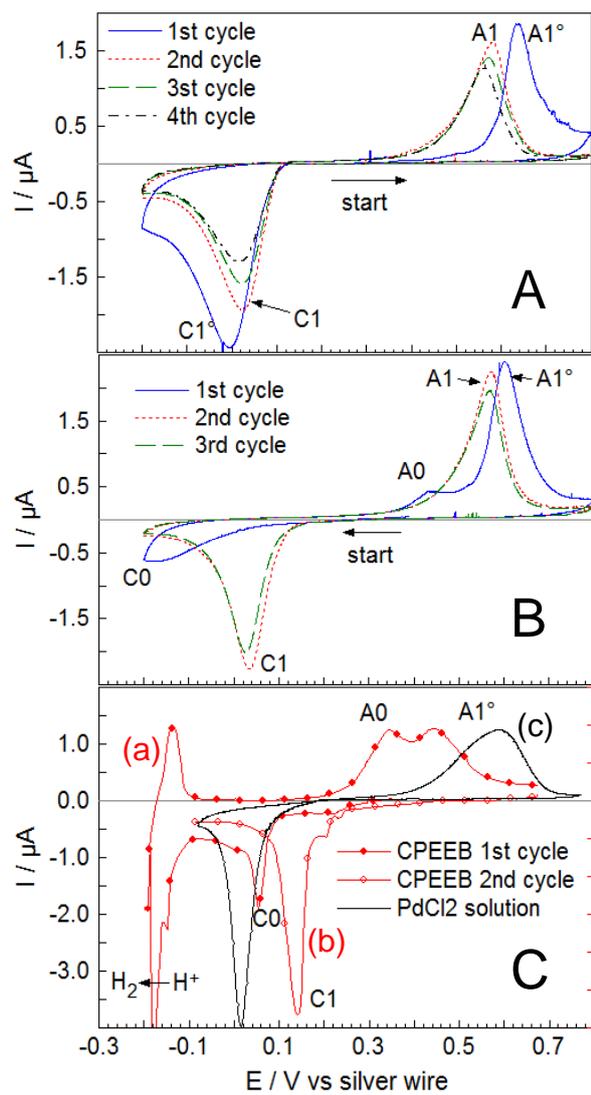


Fig. 7

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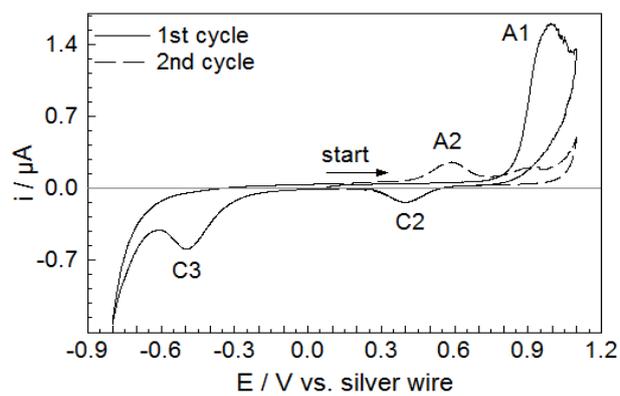


Fig. 8

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