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**DEVELOPMENT OF CAVITY MICROELECTRODE DEVICES AND THEIR USES IN
VARIOUS RESEARCH FIELDS**

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Abstract

The cavity microelectrodes (CMEs) have been introduced in the 1990's and since then have been employed for the characterization of various types of materials ranging from materials used for energy storage, biological applications, catalysis characterization, or corrosion studies. This technique takes advantage of working on small amount of pure electroactive materials (few hundreds nanograms) using usual electrochemical techniques (cyclic voltammetry, electrochemical impedance spectroscopy...) and allows a rapid screening of the electrochemical behavior of new materials. The CME development and its main applications for the electrochemistry of powder materials are reviewed and discussed.

Keywords: microelectrode, powder material, cavity microelectrodes, powder microelectrode, voltammetry

1. Introduction

The study of electrochemical kinetics of soluble compounds has experienced significant growth in the 80's with the development of micro and ultra microelectrodes (UME) [1]. The large decrease of the electrode size brings about a dramatic decrease of the double layer capacitance, C_{dl} , concomitantly with a smaller ohmic drop, $R_e \cdot i$ (where R_e is the electrolyte resistance and i , the current). It results in high scan-rate cyclic voltammetry experiments that can reach few megavolts per second, allowing the study of the nanosecond time-scales [2]. Otherwise, for studying the electrochemical properties of solid-state materials, a composite electrode device, also called either carbon paste electrode or powder graphite electrode has been developed as sketched in Fig. 1. It consists of a composite film [3] containing few milligrams of powder of electroactive material, which is mixed with graphite or carbon black (10 to 15 wt%) that acts as current collector between material grain, and polytetrafluoroethylene (about 5 wt%) that acts as binder. The thin film is then pressed at high pressure onto a metal sheet or a grid as shown in Fig. 1. The dimensions of these devices are usually in the range of few millimeters in diameter and few tenth of millimeter thick. Alternatively, it can be integrated in an electrode holder as described in Ref. [4]. The large dimensions result in high double layer capacitance and a non-negligible contribution of the ohmic drop (*i.e.* a value of the cell time constant in the range of few milliseconds or larger) that does not allow using high potential sweep rates. In practice, the scan rate can hardly exceed few millivolts per second in aqueous solution and few tens microvolts per second in non-aqueous solution. Thus the duration of the experiments for performing a single cyclic voltammogram with a composite electrode can reach hours instead of few minutes or less for soluble redox species with the same electrode size, and only information on the thermodynamics of the system can be obtained. Therefore these features are significant drawbacks for screening the electrochemical

properties of new materials and strongly limit the electrochemical kinetics study of solid-state materials.

The shortening of the experiment duration or the investigation of faster electrochemical kinetics requires the miniaturization of the interfacial area where the reaction takes place, as it was done with the development of microelectrodes for the study of soluble compounds. For this purpose, three main types of electrode devices have been devised during the 90's.

The first one consisted in using a micromanipulator and an optical microscope to bring a conductor wire (for instance a graphite fiber) in contact with a material particle. This technique allows selecting both the size and the shape of the single material grain which is used as working electrode [5-9]. The reaction interface is thus the whole grain periphery (a stray electrochemical reaction can also occur on a part of the fiber used to connect the particle) and cyclic voltammetry can be performed with scan rates as high as few hundred millivolts per second. This setup was successfully used for studying the diffusion of hydrogen in spherical particles of Pd and LaNi₅ [6].

The second device is the abrasive electrode [10-15]. It is based on sub-millimetric metallic electrode polished with abrasive paper to obtain a rough surface with randomly distributed scratches. The powder material can be trapped within these scratches. Nevertheless, the ratio of the whole electrode surface to the surface of electroactive material is rather small and the reported scan rates can only reach a few hundred millivolts per second. It was shown to be a convenient tool for a rapid screening of the rechargeability of battery materials [12].

The last electrode device was pioneered by Cha through a simple way [16, 17]. It consisted of a classical microelectrode, but the tip of the metallic wire was recessed (Fig. 2) hence forming a cylindrical micro-cavity. The micro-cavity was used for entrapping materials particles. In the literature, this electrode has been referred to either a powder microelectrode or a cavity microelectrode (CME).

The aim of this paper is to give an overview of the developments of the electrochemistry for powder materials studied with the cavity microelectrode, which allows working on small amount of pure electroactive material.

2. Fabrication and characteristics of CME

2.1. Electrode fabrication

CMEs are usually fabricated by sealing a metallic micro wire (Pt, Au) in a soft glass rod (Fig. 2a). Then, the electrode is polished and a microcavity is easily achieved by chemical etching of the wire in hot *aqua regia* or by its electrochemical dissolution. The size of the microcavity is controlled by the size of the micro wire (usually in the range of 50 μm in diameter) and its depth achieved by etching (20 – 30 μm). This corresponds to a volume of about $5 \cdot 10^{-8} \text{ cm}^3$. Such a procedure allows obtaining a reproducible cavity dimension, which can be easily controlled by the etching conditions. Then, a small amount of material is placed in a mortar and is inserted into the microcavity by using the CME as a pestle (Fig. 2b). Assuming a density of 5 g cm^{-3} for the electroactive material, the maximum mass of the powder inside the cavity is about 250 ng. It should be mentioned that this amount can be smaller by using smaller CMEs and should be compared to the few mg needs for preparing a composite electrode. As a result, the effective double layer capacitance which is proportional to the electrochemical surface area and the ohmic drop within the bulk solution in front of the solution are significantly reduced. Similarly to both the abrasive and the single grain electrodes, cyclic voltammograms can be recorded at scan rate of few hundred millivolts per second and even beyond this range (*vide infra*). Cha et al. shown that it was possible to perform one thousand charge-discharge cycles in a time lapse of 26 hours for mischmetal [17] whereas the composite electrode needs several months for performing a similar experiment.

Thus, thorough investigations of the processes become possible by studying the kinetic aspect of powder material electrochemistry. The striking development of the CME must mainly be attributed to the easy making of this electrode since it implicates chemistry proceedings available in academic laboratories. Moreover, its handling is as easy as for other kinds of electrode commonly used in electrochemical experiments; it is reusable many times whatever the products which are investigated, or does not require any specific electrochemical equipment. For instance, the cavity can be emptied by sonication, and then cleaned by performing cyclic voltammetry on the oxidation and reduction waves of the solvent. All these advantages probably explain the success of this technique that resulted in over 130 published articles this last decade [16-140] in various research fields. Among them, it can be mentioned battery materials, catalysts, fuel cells, molten salts electrochemistry, biological material...

2.2. Other CMEs for specific applications

Usually the body of the CME is made of soft glass allowing experiments at low temperature to be performed. For working in molten salt at temperature lower than 400° C, Pyrex™ glass can be conveniently used. Beyond this temperature value, a new device has been devised by Chen et al. [71, 96, 112, 124]. They drilled a micro hole in a metal sheet (Pt, tungsten), the size of which is about 50-100 micrometers in both diameter and depth. In that case, the body of the electrode is the metal sheet itself, increasing the surface area on which an electrochemical reaction can occur. When no side reaction takes place on the metallic part of the electrode, this device is very similar to a CME and was also used for performing experiment at room temperature in various media [93, 114]. However, the contribution of the double layer capacitance of the non-active part of the electrode still exists, which is a limitation for performing high scan rate cyclic voltammetry.

In order to increase the electrochemical window of the solvent, a carbon cavity microelectrode was fabricated [97], the conception of which is completely different from the usual

CME, because with graphite it is not possible to achieve a micro-cavity electrode device by the aforementioned techniques. In that case, the electrode consisted of a 5 mm graphite cylinder insulated by a thick layer of cataphoretic paint (about 10 μm). Then a 45 μm in diameter micro hole was machined on the apex of the electrode by laser ablation. Cosnier et al. [97] used this device for a rapid screening of redox mediator in the investigation of enzyme wiring. For the electrochemical characterization of NiMH battery material involving charge and discharge cycles [53, 87, 101] or for the study of the electrocatalytic hydrogenation of ethylene [39], the Pt current collector of the CME can be replaced by Au in order to avoid side reactions such as the electrosorption of H-atoms [39]. More recently, Ti has also been used for evaluating the electrochemical performance of carbon blacks in H_2SO_4 solution [123].

For photoelectrochemical applications, Cachet et al. [60] have used a CME in which the internal cavity wall was in platinum. This led to an increase of the area of electrochemical interface within the cavity. It was achieved by boring the tip of the Pt wire by femto laser ablation instead of the electrochemical or chemical etching. The diameter of the micro hole was slightly smaller (40 μm) than that of the Pt wire used for making the CME (50 μm). This kind of device was also used with MnO_2 as active material for the fabrication of a pH sensor [119]. We can also mention an original approach in which a cavity is drilled on the tip of a rotating disk electrode to investigate the corrosion of iron powders [62].

Today, many micro system technologies are available [41] allowing to adapt the cavity microelectrode device to any complex application. For instance, a device that consisted of spherical-cavity microelectrode array was recently developed for biosensor applications [132].

2.3. CME configurations

When the micro-cavity is filled up, different configurations can be obtained. In the simplest case, the cavity is only filled with the electrolytic solution. In this case, the electrode behaves as a usual recessed microelectrode, and was used for instance, for generating micro bubbles of oxygen, the size of which was mastered by the size of the cavity [138]. In addition, the mouth of the cavity can be closed by a thin porous film, which transforms it into a closed electrochemical micro system because all of the active species in the micro-cavity can be oxidized or reduced during the electrochemical cycle [118].

When the cavity contains both the electrolyte phase and a powder material, it is necessary for the powder to be an electronic conductor. In the case of a poor conductivity, a mixture with a conducting powder (*e.g.* carbon black) can be used as a current collector within the cavity. Sometimes, carbon black is replaced by either Pt black [20, 22], Au powder [25], NiO powder [28], boron-doped diamond powder [95] or a conducting polymer. All these configurations were similar to what is was done with the usual composite electrode, and the CME can be described as a thin layer electrode [141-151].

The micro-cavity can also be isolated from the rest of the solution by using a thin solid polymer electrolyte, as done by Cha et al. [18, 22, 24] or Jiang et al. [64, 75] to study the surface diffusion of reaction intermediates in fuel cell electrocatalysts or by Li et al. for nitric oxide detection [81]. Cachet-Vivier et al. [119] have also used a selective membrane for improving the selectivity of a MnO₂ pH-sensor.

2.4. Exploitation of the experimental data

In addition to the analysis of current - potential curves performed at low scan rate with the usual carbon paste electrode, the CME allows kinetics study of solid-state process or at the interface between the powder material and species in solution. Figure 3a shows an example of cyclic voltammograms obtained with polyaniline powder in H₂SO₄ solution with a 25 μm in

diameter CME at 2 Vs^{-1} . The anodic and cathodic peaks are unambiguously ascribed to the emeraldine / leucoemeraldine redox system, and the stability of the system is shown by the superposition of the 20 successive cycles.

Similarly to what can be done for the analysis of CV curves of redox soluble species, the peak intensity, i_a , (determined from the base line), the peak potential, E_a , and the peak width, W_a , can be determined (Fig. 3). This allows studying the electron transfer kinetics and it was shown that scan rate as high as few hundred volts per second can be reached with this material. A detailed analysis of the results also shown that the kinetic constant, determined from these experiments, compared favorably to the results obtained on thin film deposited on microelectrode [46]. For comparison, the polyaniline powder was also investigated with a carbon paste electrode (Fig. 3b) in the same electrolyte. In order to obtain a curve free from the ohmic drop contribution, very low scan rate had to be used (0.5 mVs^{-1}). In that case, the shape of the curve was very similar to the one obtained with the CME but the duration of the experiment was 45 minutes *i.e.* 4000 times that with a CME.

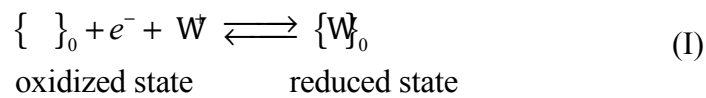
One of the main drawbacks of the technique is the filling up of the cavity with an unknown amount of material. When the experiments are performed with a carbon paste electrode, the electrode is weighted at the different steps of the preparation process and the amount of material can be determined. In the case of the CME, the procedure can be somehow more difficult because it is not possible to weight the powder inserted in the micro-cavity. However, it is possible to evaluate the included material amount indirectly. For instance, when some experiments are carried out using both CME and a carbon paste electrode, the ratio of the capacitive currents is equal to the ratio of mass of electroactive material in each device. Some material can also be dosed *post-mortem*. For example, Vivier et al. [30] studied the electrochemical behavior of bismuth oxide. After the study, they dissolved the oxide in a high purity acid solution and they used Induced Coupled Plasma spectrometry for the dosing.

Another approach has also been reported [127, 137]. It is based firstly on a making of CMEs of different sizes (both in radius and depth), secondly by performing calibration of the volumes by means of a standard powder already well characterized by cyclic voltammetry, and then by using these quantifications of specific parameters that identify the electrochemical properties of the investigated powders. This strategy allows the direct comparison of different materials for their rapid and accurate screening.

2.5. Model for the diffusion in a grain

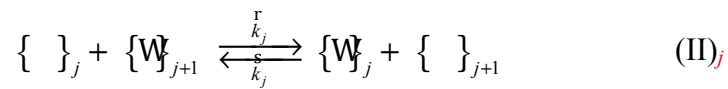
For some material such as insertion material used for energy storage, the electrochemical processes occur within the material bulk because the electroactive sites $\{ \}$ are regularly distributed through its whole volume (Fig. 4). In a film, all the electroactive sites that are located at the same distance λ of the material interface form a layer parallel to this interface. If δ is the thickness of the layer and ε the thickness of the film, the material can be described as a stack of $N = \varepsilon/\delta$ layers (Fig. 4). Thus each layer is defined by its number j where the boundary values 0 and N correspond to the interface and to the deepest layers, respectively. The site in the layer j is thus defined as $\{ \}_j$ and its distance λ_j from the interface is $\lambda_j = j \times \delta$.

The electron exchange reaction occurs at the electrolyte/material interface. It can be described by the global reaction:



where W is a counter-ion that maintains the electrical neutrality inside the material. Concerning the internal sites, the electrochemical reaction can take place when the counter-ion is present. That involves the diffusion of the species W inside the material. Two approaches have been investigated. In the first one the Fick equation [152-159] was applied to the solid-state diffusion. The second one is based on transposition of the multilayer model developed simul-

taneously by Laviron [161-163] and Savéant [160, 164] in the case of polymeric films. These two authors described the diffusion of the species W inside the material through a set of successive equilibrium reactions between two neighboring layers $j-1$ and j :



with $j = 1, \dots, N$.

The equilibrium j corresponds to the jump of the counter ion W from layer $j-1$ to j . The diffusion kinetics is linked to $\overset{i}{k}_j$ and $\overset{s}{k}_j$, and equilibria involve that the material owns both ionic and electronic conductions at sufficient level. When the material is both homogeneous and isotropic:

$$\overset{i}{k}_j = \overset{s}{k}_j \quad j= 1 \text{ to } N \quad (III)$$

The current can then be calculated assuming a Butler-Volmer relationship for describing the kinetics of the reaction (I), and by taking account of the concentrations of $\{ W \}_j$ or $\{ \ }_j$ of electroactive species inside the material.

Actually, the grain is never a rectangular parallelepiped, but rather an irregular-shaped volume. It was shown that it is possible to apply the multilayer approach at the case of a spherical material grain in order to describe the evolution of peak potential and intensity as a function of the scan rate [165]. It is noteworthy that in the case of spherical grain, zone diagram can be obtained similarly to the case of redox soluble compounds [165].

3. Application of the CME in various field of electrochemistry

3. 1. Sensors – Biological applications

Some redox materials are very expensive or can be available in small quantity, only. Among them, the biological compounds such as enzymes and their derivatives are playing an important role in the living processes and were the subject of intensive studies in order to characterize their redox activity or to detect it. Many different compounds were then investigated: dopamine [20-22, 29], ascorbic acid [33, 42], horseradish peroxidase [48, 97], α -tocopherol [55], cysteine [57], human hemoglobin [59], cholesterol [118], cytochrome C, xanthine oxidase, hypoxanthine [73], uric acid [74], glucose oxidase [21, 97, 117], reduced glutathione [84], hemoglobin and myoglobin [105]. For instance, a glucose oxidase microsensor was devised as a carbon paste microelectrode and shown a good sensitivity and selectivity upon the glucose oxidation [117, 140].

Some authors have studied the possibility of using the CME as an electrochemical sensor [29, 33, 42, 65], either as a potentiometric sensor such as for pH monitoring [119] or as amperometric sensor such as for the detection of hydrazine [35, 49]. From the comparison with usual electrode (rotating disk electrode, carbon paste electrode or millimetric electrode) a better discrimination of the signal was pointed out. For instance, the peaks of dopamine and ascorbic acid are about 300 mV apart [21] allowing a precise dosing of both compounds. A similar effect was observed with dopamine, acetaminophen and xanthine [33], and between uric acid and ascorbic acid [74].

In some case, an increase of the detection sensitivity was also reported. The reduction of nitrite has been investigated with the CME filled with carbon black and Au powder [26], leading to current densities larger by 50 to 100 fold than that for smooth carbon or Au rotating disk electrodes. These improvements were ascribed to the large interface formed by the carbon blacks inside the micro-cavity. Obviously, the sensitivity increase allows lowering the limit of detection and increases the extent of the linear current range. For instance, for dopamine, the low limit value was $20 \cdot 10^{-9} \text{ mol.L}^{-1}$ in acidic solution, and about $10^{-6} \text{ mol.L}^{-1}$ in neutral

solution [29], whereas in the case of NO_2^- , the lower detection limit was $4.4 \cdot 10^{-6} \text{ mol.L}^{-1}$ with a linear response of the sensor spreading over five orders of magnitude [25]. By changing the material inside the cavity, it is possible to improve the detection limit [51].

The interfering effect of species is the main drawback in the electroanalytical detection of biological compounds. Nevertheless, decreases of interfering effects were evidenced for ascorbic acid, uric acid, L-cystein and acetaminophen on the output of the glucose oxidase fixed on carbon black in the CME [21, 33, 42], whereas nitrate, ascorbic acid, and various ions such as Fe^{3+} , Fe^{2+} , Mg^{2+} , Cl^- , I^- , O_2 and PO_4^- did not show any noticeable interference for the dosing of NO_2^- [25]. In some cases, the use of a coating such as a Nafion membrane significantly reduced the interferences as shown with a composite gel microelectrode used for the detection of nitric oxide [82].

3. 2. Energy storage and energy production

Cha and Yang [16] underlined from the early 1990s the necessity of reducing the amount of reactants when the studies are carried out in Li/SOCl_2 and $\text{Li}/\text{SO}_2\text{Cl}_2$. These media are known for their risk of explosion when they are used as high-energy liquid cathode. Such a preoccupation led to conceive the microcavity reactor. The miniaturizing of the technique allowed making these systems more acceptable for the electrochemistry and spectroscopy laboratories, and instigated the use of CME for energy applications. Nowadays there is a strong trend towards the preparation of nanostructured materials, endowed with electrochemical properties. For this type of material, the CME is an appropriate tool for performing both a systematic screening and comprehensive studies. In the framework of Li/Li ions battery, various materials have been investigated such as $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ [27], V_2O_5 and Bi-MnO_2 [37], $\text{Li}_x\text{Mn}_2\text{O}_4$ [27,92], $\text{LiCu}_x\text{Mn}_{2-x}\text{O}_4$, [94], $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ [66], Co-doped todorokites [120] or LiFePO_4 [131] in order to study their performance. Moreover, many side studies related to improvement of Li/Li ions battery have been carried out over, for example, overcharging

protection [63, 104], increase of discharge rate capability [125], research of new electrolyte (MeCN with propylene carbonate) [133], or new carbons [135].

There is also an increasing interest to study nanometric dimensions of manganese dioxide MnO_2 in alkaline medium. Its electrochemical reactivity depends on its crystal structure, which vary with the method and the synthesis conditions [86, 115].

Concerning the nickel–metal-hydride (Ni–MH) batteries, research has focused on LaNi_5 intermetallic compound and its metal-substituted derivatives. Binary LaNi_5 suffers from severe corrosion during cycling in alkaline electrolyte, resulting in a fast decrease of the battery capacity. To overcome this problem, various derivatives have been studied to investigate the role of each substituent on the global behavior of the material [17, 28, 44, 78, 89, 101].

Other types of battery were also investigated. Among them, the Zn/Ni secondary alkaline cells were studied to evaluate new additives for improving the performance of the anodes [102, 116]. A green route for the preparation of the electrodes for lead acid batteries was also investigated. It was shown that the performances of $\text{PbO}_2/\text{PbSO}_4$ and PbSO_4/Pb obtained from PbCO_3 were as good as those prepared from PbO [36].

Electrochemical double-layer capacitors have been the subject of numerous researches during these last decades. Their main interest is their ability to provide a high power and a theoretically infinite cycle lifetimes. The materials involved must be endowed of large BET areas for which the CME is an appropriate screening tool [38]. Some of these materials were studied by mean of CME technique [99, 106, 123]. This kind of study allowed to link the pore size, the ion size and the solvent effects on the charge/discharge behavior of microporous carbons [111].

The conversion of solar radiation to electricity is a prominent challenge for energy alternative. Among photoconverter compounds, we can cite nanocrystalline SnO_2 and F-doped SnO_2 [45],

perylene-based dye-grafted nanosized SnO₂ [60], F-doped SnO₂ photosensitized with perylene substituted organotin [61], or neutral bisdithiolene nickel complexes [98].

3.3. Corrosion applications

Corrosion usually results in a heterogeneous evolution of the material and loss of its functional properties. It is thus interesting to take a sample so as to know the distribution of corrosion products or the distribution of the electrochemical reactivity over the surface. For instance, it was used to study the influence of Na₂SO₃, N₂H₄, and Cu on the localized corrosion of a low-carbon mild steel in weakly alkaline solution [47]. A striking application of the CME concerns the characterization of archaeological artifact. After the excavation, metallic objects are exposed to more aggressive conditions like polluted marine or urban atmosphere and/or acid rains that may induce the resurgence of corrosion leading to the total destruction of the material. Therefore, the protection of cultural heritage such as archaeological bronzes remains of great importance. Moreover, studying the chemical structure of corrosion layer would provide various information concerning their formation, their evolution, and is thus likely to interest archeologists and historians. Obviously, the sampling by scraping on an archaeological object is often strongly restricted. All the techniques which do not alter integrity are preferred. The CME is appropriate because the total amount of the material necessary for this kind of study is only a few tens of nanograms. In addition, it was possible to study simultaneously the electrochemical behavior of the material and the evolution of its structure with in situ Raman microspectroscopy [40, 69, 70, 77, 110] with a device in which the apex the the CME is facing up as shown in Fig. 5.

3.4. Electrocatalysis

Cha et al. [20] have focused their attention on an important aspect of electrocatalysis, the surface diffusion of reaction intermediates also known as spillover in heterogeneous catalysis. McBreen [166] observed H-atom in the interface arrangement as a double thin Pt screen electrodes pressed against a solid polymer electrolyte. For constructing industrial water electrolyzer and high power density low temperature fuel cell, powder catalysis / solid polymer electrolyte interface is usually utilized. Both catalyst particles and solid polymer electrolyte are solid phases, and the direct contact area is much smaller than the real surface area of the powder layer. The studied powder catalysts are Pt metal, Pt-black layer on metal, and Pt-black. Investigation in acetonitrile media [22] and in aqueous media of Pt/C and pure carbon black as a basis complete the first results on spillover in fuel cell [24]. The conditions of utilization and the performance of Pt/carbon packed within the microcavity electrode in a fuel cell arrangement, in the presence of CH₃OH and O₂ were also investigated [91, 130]. The CME was also used for the study of the kinetics of the electrohydrogenation of C₂H₂ on PtO₂ powder [39] and on LaNi₅ powder [32], whereas the direct oxidation of CH₃OH to CO₂ on Pt-Ru-Os-Ir [50], on Pt/C [54], or on Pt/C catalysts [67, 85], were studied by Liu et al. and Uchida et al. Direct oxidation of CH₃OH on tungsten carbide powder has also been carried out [134]. Electrochemical study of clay supported Mn(III) salen complex for O₂ activation with cytochrome P450 model [122], conversion of CHCl₃ to CH₄ on Ag nanoparticles [100, 108], and reduction of nitrophenol on tungsten carbide / Carbon nanotube [76, 87] were also reported.

3.5. Polymers and derivatives.

In the previous section, an example of cyclic voltammogram of polyaniline powder in a CME was shown as an example (Fig. 3). With this technique, it was shown that high scan rates up to 400 V s⁻¹ can be reached and a detailed investigation of the performance of this polymer was carried out [23, 38]. It was shown that the electrochemical behavior of the polyaniline

powder was similar to the one of an electrogenerated thin film [46]. In addition, a large number of cyclic voltammograms were performed (40 000 cycles) for one week, in aqueous and non-aqueous electrolytes. It was found that 85 to 90% of the initial capacity was recovered whatever the electrolyte [31, 38]. The CME was shown to be a convenient technique for studying the effects of the synthesis temperature on electrical properties of polyaniline and their electrochemical characteristics in a silver CME [129] or to synthesize and characterize Hg-polyaniline composite powder material [80] and Ag nanoparticles polyaniline powder material [107].

Hybride organic-metal polymers can also be studied as solid material in the CME. For instance, ferrocene derivatives are of interest in many fields such as homogeneous catalysis, medicine... [167-173]. Metal phosphinates are usually resistant to oxidation and hydrolysis, the phosphinate groups acting as solid bridging ligands. Their properties result from both the nature of the metal atom and the nature of the organic substituents on the phosphorus atom. This is related to the specific geometries that the ferrocenyl moiety can enforce and its redox properties. It was reported a simple and convenient method for the preparation of ferrocenylphenylphosphinic acid with a high yield, and the characterization of the metal phosphinates obtained by its reaction with zinc, cadmium and manganese salts [72].

5. Conclusions and perspectives.

This paper is intended to survey the many possibilities offered by the cavity microelectrode. The CME allows working on very small amount of powder materials in a very small reaction volume, and thus to carry out experiments in short time-scale. This represents a significant improvement when comparison is done with the usual composite electrode. In particular, it is possible to study the intrinsic properties of materials *i.e.* without the adjunction of any electronic conductor or binder. It also becomes possible to perform the screening of new kinds of

electroactive materials (nanostructured carbons, nanostructured hybrid polymers...), to investigate the cyclability of battery materials, or to develop new kind of sensors. Even though the field of investigation is already very wide, other research fields can be easily envisioned owing to its simplicity and low cost. For instance, a cavity microelectrode can be achieved by many ways which allow a design that can fit different experimental conditions and different applications.

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FIGURE CAPTIONS

Figure 1. Sketch of a composite electrode (a) and zoom on the interface formed between the powder material, the graphite, and the electrolyte (b)

Figure 2. Scheme of a cavity microelectrode (a) and zoom on the apex of the electrode (b)

Figure 3. Cyclic voltammograms obtained on Polyaniline powder in 0.5 M H₂SO₄ solution (a) with 25 μm in diameter CME (20 repetitive cycles) at 2 Vs⁻¹; and (b) with a carbon paste electrode at 0.5 mVs⁻¹ (1 cycle).

Figure 4. Multilayered-view of the active sites distribution for a film.

Figure 5. Example of experimental setup used for performing simultaneously electrochemistry and Raman spectroscopy

Figure 1

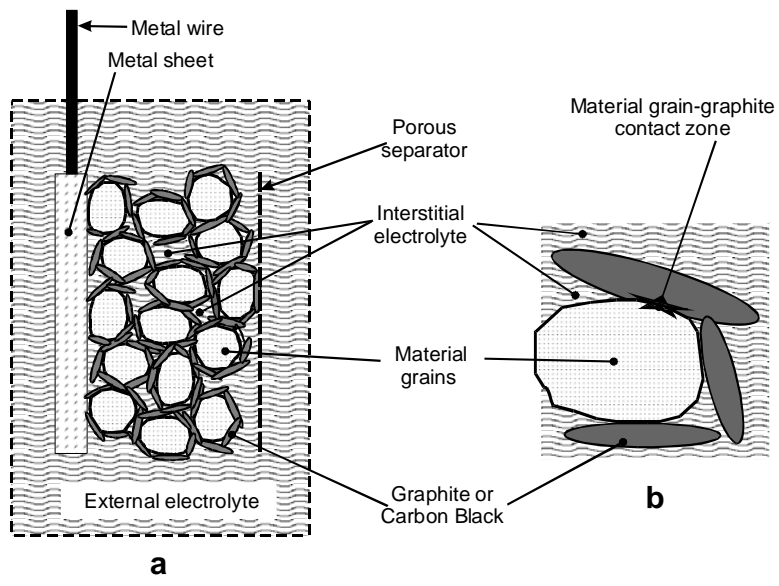


Figure 2

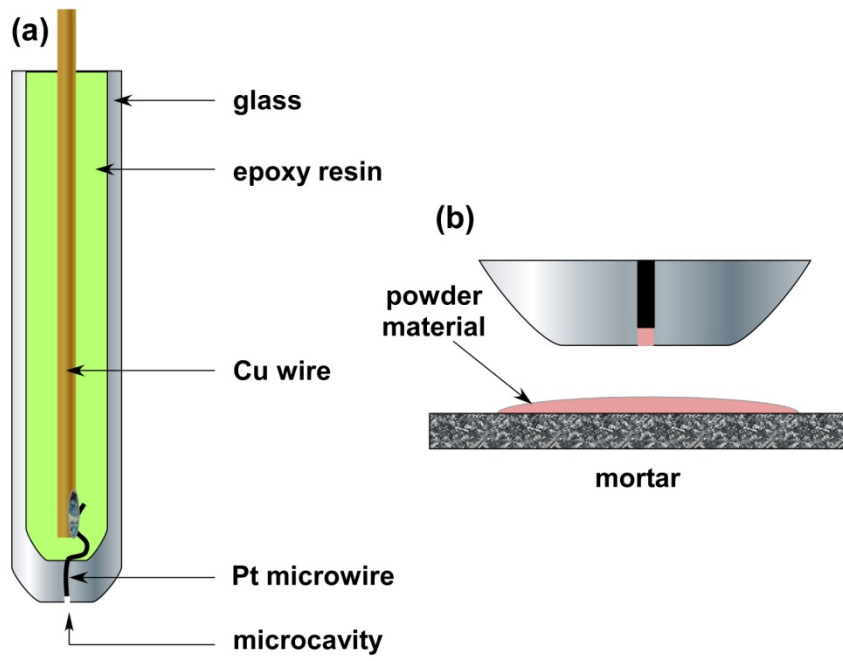


Figure 3

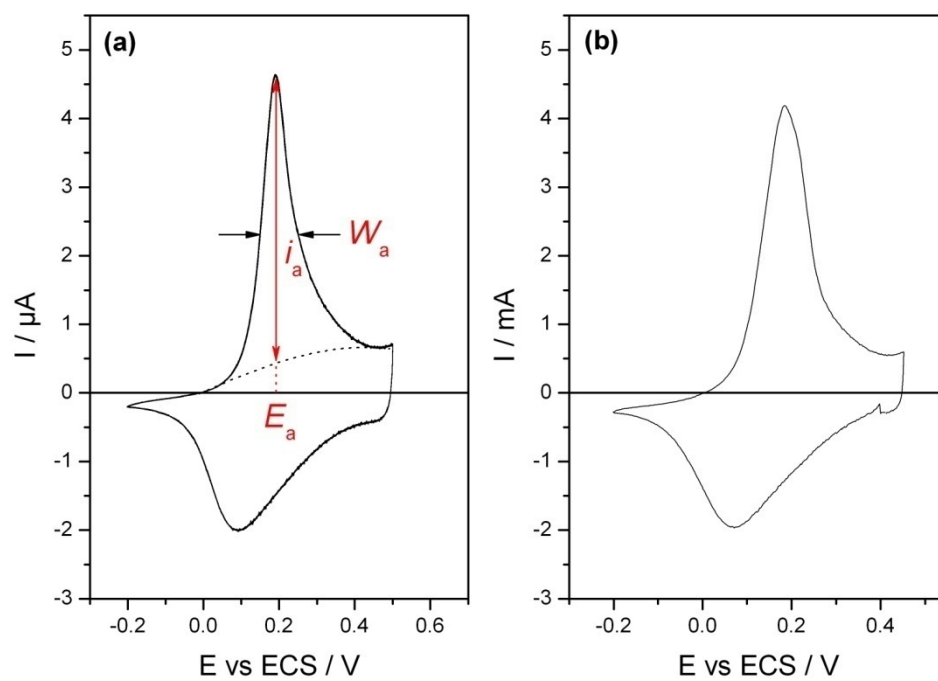


Figure 4.

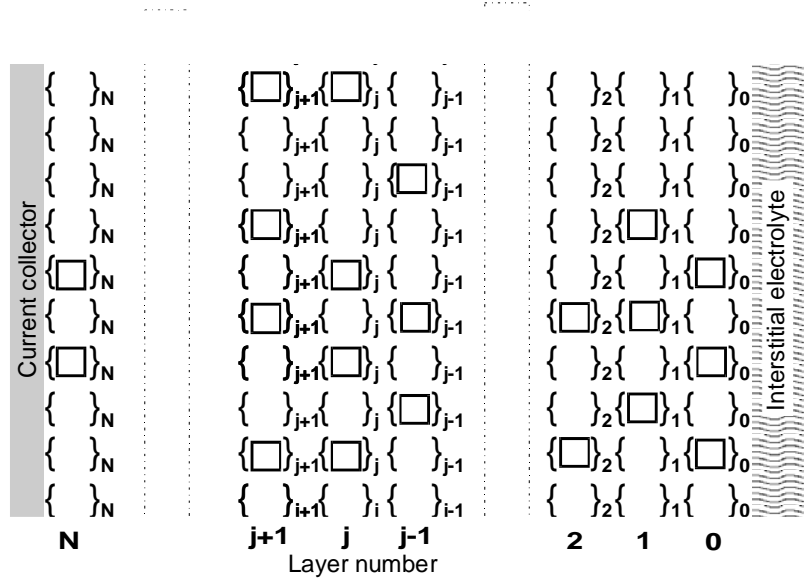


Figure 5.

