

Cathodic Reactivity of Platinum and Palladium in Electrolytes in Superdry Conditions

THE NATURE OF THICK LAYERS ELECTROCHEMICALLY FORMED AT THE METAL/ELECTROLYTE INTERFACE

By Charles Cougnon and Jacques Simonet*

Laboratoire d'Electrochimie Moléculaire et Macromoléculaire, UMR 6510, Campus de Beaulieu, Université de Rennes, 35042 Rennes Cedex, France, *E-mail: jacques.simonet@univ-rennes1.fr

Platinum and palladium behave in an unexpected manner when cathodically polarised in the presence of electrolytes dissolved in carefully dried polar organic solvents, such as N,N-dimethylformamide. A reductive layer is formed on the metal, the thickness of which depends on the amount of electricity consumed during the course of the electrolyses. Although this reaction seems to be of a general character with most of the common electrolytes, in this paper we will focus on results obtained with a large palette of tetraalkylammonium salts and alkali metal iodides.

The reaction of the electropositive alkali metals with a large number of more electronegative main group 'meta-metals' (such as Pb, Si or Ge) to form the so-called Zintl phases (1–3) was discovered by Eduard Zintl at the beginning of the twentieth century. Zintl phases are electronically positioned between intermetallics and insulating compounds and are semiconductors. They form compounds where the heavier metal forms clusters in polyanionic units, surrounded by the lighter alkali metal cations – and have a large range of structures. Such materials may possess covalent, metallic and ionic bonding (4, 5).

The synthesis of Zintl phases (6, 7) generally involves heating up a mixture of the elements in closed tantalum or niobium containers. Another method is the reduction of post-transition metals (or more commonly of a salt of these metals) in the presence of sodium (Na) in liquid ammonia. Thus, Zintl was able to follow the reduction by potentiometric titration of Na ions (8). These experiments allowed the composition of the generated phase to be specified. On the other hand, by an electrochemical technique, cathodically-polarised post-transition metals, such as lead, could be used as working electrodes, into which the non-electroactive cations, such as potassium (K), could be inserted, as shown next (9, 10):



Until now, platinum (Pt) and palladium (Pd) were considered to be totally inactive towards the alkali metals and also electrochemically inert. The latter property has allowed Pt and Pd to be widely used as cathode materials. However, their weak hydrogen overvoltage obviously reduces the usable cathodic range (in non-aqueous solvents without careful prior-drying treatment, the usable cathodic range is limited to about –2.0 V vs. a saturated calomel electrode (SCE)). If the residual moisture in the polar aprotic solvent is drastically reduced (for example by an *in situ* solid non-electroactive drier, such as neutral alumina) down to 50 ppm, hydrogen evolution almost vanishes. What are the electrode reactions then? This field seems to be totally unexplored and the aim of the present work, devoted only to Pt and Pd, is to demonstrate that it is of importance.

Earlier observations of the cathodic behaviour of Pt in an electrolyte of dry N,N-dimethylformamide (DMF) in the presence of tetraalkylammonium tetrafluoroborate, R₄NBF₄, were the first to show the electrochemical construction of a thick layer on the Pt surface comprising both R₄N⁺ cations and the salt itself (11). The slow degradation of these layers by air led to the restoration of the Pt metal surface. However, the surface had

undergone tremendous structural changes (such as formation of dendrites, channels and/or grain boundaries) together with the visible emergence of the absorbed salt from the Pt bulk.

This paper describes results obtained for Pd and Pt cathodes in the presence of a wide range of tetraalkylammonium salts, R_4NX , as well as alkali halides (iodides because of their greater solubility) (12, 13). Experiments allowed us to determine the nature of the layers formed. Methods such as coulometry, the electrochemical quartz crystal microbalance technique, chronopotentiometry, SEM analysis and impedance spectroscopy were used. Until now the rather poor chemical stability of the layers did not allow X-ray characterisation of their structure.

Experimental Procedure

Salts and Solvent

In most of the experiments, electrolyte concentration was 0.1 M. Potassium, lithium (Li), Na and caesium iodides were used and the tetraalkylammonium salts were of > 99.7% purity (puriss grade). All salts were used without further purification after being thoroughly dried under vacuum at 100°C for 48 hours. The DMF was checked (by the Karl Fischer method) to ascertain it contained less than 50 ppm of water, having been stored over neutral alumina, previously activated under vacuum at 300°C for 4 hours. All experiments were performed in a carefully dried argon atmosphere. Electrolyte solutions were maintained in the electrochemical cell over activated alumina.

Electrochemical Instrumentation and Procedures

Cyclic voltammetric investigations were carried out in a standard three-electrode cell using a μ AUTOLAB potentiostat connected to a computer equipped with standard electrochemical system software. For analytical purposes the working electrode was a disk of Pt or Pd (area $8 \times 10^{-3} \text{ cm}^2$) and the counter electrode was a glassy carbon rod. All potentials given here refer to the aqueous SCE. However, the SCE was not used as the reference electrode in the cell (due to possible water diffusion). As reference electrode, the Ag/AgI/0.1 M

INBu₄ system (in DMF) was used, and potentials were corrected afterwards.

Prior to the experiments the Pt and Pd working electrodes were carefully polished with silicon carbide paper of successively smaller particle size (18 to 5 μm), then by diamond powder (6 and 3 μm). Finally, the working electrode was rinsed with ethanol and acetone and dried. Between each scan the electrode surface was repolished with diamond powder (3 μm).

For macroelectrolysis investigations, Pt sheets (99.99% purity, area 1 cm^2 , thickness 0.05 mm) and Pd sheets (99.95% purity, area 1 cm^2 , thickness 0.1 mm) were used. They were used once only for SEM analysis without further treatment.

Chronocoulometric Investigations on a Thin Metallic Layer

Coulometric experiments were carried out on Pt and Pd film electrodes prepared, respectively, by depositing the metals from solutions of 10 g l^{-1} H_2PtCl_6 in 0.1 M HCl and 10 g l^{-1} PdCl_2 in 0.1 M HCl onto polished gold disks ($2 \times 10^{-3} \text{ cm}^2$). The plating was carried out in a galvanostatic mode (current $10^{-2} \text{ A cm}^{-2}$). All the experiments were performed with gold substrates but with different thicknesses of deposited metal. The gold substrate could be a gold microelectrode, polished before each deposition, or (for EQCM experiments) a larger electrode of gold-coated quartz crystals.

Electrochemical Quartz Crystal Microbalance (EQCM) Instrumentation

Simultaneous voltammetric and mass balance experiments were carried out with an oscillator module quartz crystal analyser connected to a potentiostat. This device was computer controlled. In the experiments, 9 MHz AT-cut gold-coated quartz crystals were plated electrochemically with a thin film of Pt or Pd. Plating was achieved by the chronocoulometric procedure. The deposited mass was checked by the EQCM. The EQCM measurements were performed in a Teflon cell equipped with a glassy carbon counter electrode, a reference electrode and the Pt- or Pd-plated quartz crystal working electrode. The apparent area of the quartz crystal was about 0.2 cm^2 .

Electrolyte, 0.1 M	E_{pc} , V	I_{pc} , μA	$\log I_{pc}/\log v^{(a)}$	E_{pa} , V	I_{pa} , μA	I_{pa}/I_{pc}	$E_{pc} - E_{pa}$, V
LiI	-3.07	28	0.54	-2.20	19.0	0.68	0.87
NaI	-2.07	16.8	0.39	-1.13	14.0	0.83	0.94
KI	-2.12	15	0.45	-0.82	8.0	0.53	1.30
CsI	-2.22	8.2	0.42	-0.78	8.2	1.00	1.44
Bu ₄ NI	-2.84	13	0.52	-0.77	2.3	0.18	1.51
Bu ₄ NBF ₄	-2.87	17	0.45	-0.72	3.0	0.17	2.15
Bu ₄ NClO ₄	-2.82	28	0.56	-0.70	4.5	0.16	2.12

Voltammetric data are relative to a stationary palladium electrode of area $8 \times 10^{-3} \text{ cm}^2$. Potentials are referred to the SCE. The sweep rate, $v = dV/dt$ is 200 mV s^{-1} .
^(a) The slope for sweep rates from 0.02 to 5 V s^{-1}

Microgravimetric data, reported in terms of mass change, were calculated using the Sauerbrey equation, which links the resonant frequency and mass change. For most cases it was found that the mass discharge of the Pt (or Pd) film at 0 V was not completely reversible and thus, a small excess of mass remained at the start of each experiment. However, the amount of extra mass gained during the charge process remained the same. These experiments suggested that the EQCM technique was an accurate method for quantifying the charge/discharge process as there was no noticeable loss of mass (for example, occurring by mechanical degradation of the layer in the course of the charge process).

Scanning Electron Microscopy Experiments

Surfaces treated electrochemically (samples were rinsed using an alcohol/acetone mixture in an ultrasound bath for 2 h) were analysed by a scanning electron microscope.

Results

Voltammetric Data

All the monovalent cations (Li^+ , Na^+ , K^+ , Cs^+ as well as R_nN^+ – regardless of the *n*-alkyl chain length) when associated to anions (halides, tetrafluoroborate or perchlorate) displayed, at the Pt and Pd microelectrodes, an irreversible cathodic

peak (or wave in the case of ammonium ions) of current, I_{pc} , which is always associated with an anodic step peak of current, I_{pa} . The anodic step peak corresponds to the oxidation of the material(s) formed while held at the level of the cathodic step (Tables I and II).

A Pd microcathode, with only CsI (0.1 M) in dry DMF (carefully maintained over neutral alumina *in situ*) displayed an irreversible step, I_{pc} , at -2.22 V . Holding the potential at this level (-2.22 V) allowed the sharp anodic peak to increase, at $E_{pa} = -0.78 \text{ V}$ (Figure 1). In all cases, whatever the cathode material and electrolyte, the cathodic currents

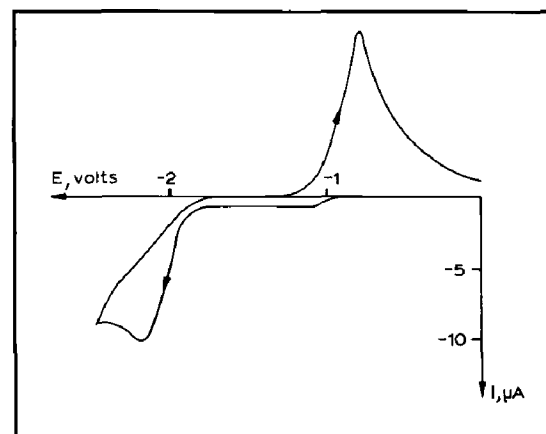


Fig. 1 Typical voltammetric behaviour of a 0.1 M CsI/DMF solution in contact with a stationary palladium microcathode (sweep rate: 200 mV s^{-1})

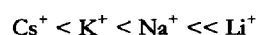
Table II				
Potentials (E_{pc} and E_{pa}) and Peak Currents (I_{pc}) Obtained from Cyclic Voltammetry at a Platinum Cathode Relative to 0.1 M Salt Alkali Halide Salts and to Tetra- <i>n</i> -butylammonium Salt Solutions in Dry DMF				
Electrolyte, 0.1 M	E_{pc} , V	$I_{pc}^{(a)}$, μA	E_{pa} , V	$E_{pc} - E_{pa}$, V
LiI	-2.84	-5	-2.42	0.42
NaI	-2.07	-10	-1.72	0.35
KI	-2.17	-6.4	-1.62	0.55
CsI	-2.18	-5.4	-1.77	0.41
Bu ₄ NI	-2.89	-11	-1.27	1.62
Bu ₄ NBF ₄	-2.91	-12.5	-1.09	1.82
Bu ₄ NClO ₄	-2.84	-25	-0.99	1.85

Voltammetric data are relative to a stationary platinum cathode of area $8 \times 10^{-3} \text{ cm}^2$.

Potentials are referred to the SCE. The sweep rate, v , is 0.2 V s^{-1} .

^(a) The relationship I_{pc} vs. $v^{1/2}$ was found to be linear in all cases in the range 0.02 to 5 V s^{-1} (correlation coefficient is always ≥ 0.99)

were found to vary linearly with the square root of the scan rate up to 5 V s^{-1} indicating a diffusion-controlled current. The small currents observed for these cathodic steps suggest that the limiting diffusion corresponds to ion insertion into the metallic bulk. It is also important to stress that such cathodic peaks do not diminish when alumina is progressively added to the voltammetric cell, and cannot be due to moisture reduction. Their limit current was found to depend on both the concentration of the salt and on the nature of the cation. Thus, in the presence of alkali iodides, the currents follow the order:



Surprisingly, tetraalkylammonium cations displayed quite large peak currents (I_{pc} values in Tables I and II).

To find out what role any residual water played, the system was dosed with water in amounts over 200–500 ppm. The specific redox system disappeared and was replaced by a cathodic wall (strong cathodic current) corresponding to water reduction.

SEM Analysis and Microelectrolyses

Potentiostatic macroelectrolyses were performed on as-received polycrystalline Pt and Pd sheets (see Figure 2(a) for as-received Pd sheet).

Fixed potentials were set very close to the corresponding peak potentials or at the beginning of the plateau region for 'wave-shaped' steps. The amount of electricity involved was somewhat larger than 20 C cm^{-2} . In all cases a chemical transformation of the metal surfaces was observed after the sheets had been removed from the electrolysis cells and carefully rinsed in DMF. The samples were exposed to air to see the change of structure caused by oxidation.

Using SEM analysis, particularly with tetraalkylammonium salts, black zones were observed to decrease progressively, while white (or light grey) areas became progressively more dominant, with time (see Figure 2(b)). The latter areas correspond to pure metal. The black zones were shown (by a suitable probe) to contain elements such as carbon and iodine (when Bu₄NI was the electrolyte, Figure 2(c)). Additionally, crystals of electrolyte were found to emerge from the disappearing black zones. This process has been explained by air oxidation of the cathodic layer at the metal surface.

After a long time in air (sometimes longer than one day) the metal structure would change dramatically, see Figure 3(a), which shows very regular fractals for Pd with angles very close to 45° and 90° . This Pd surface corresponds to pure metal after the total oxidation of the electrochemically-built layer.

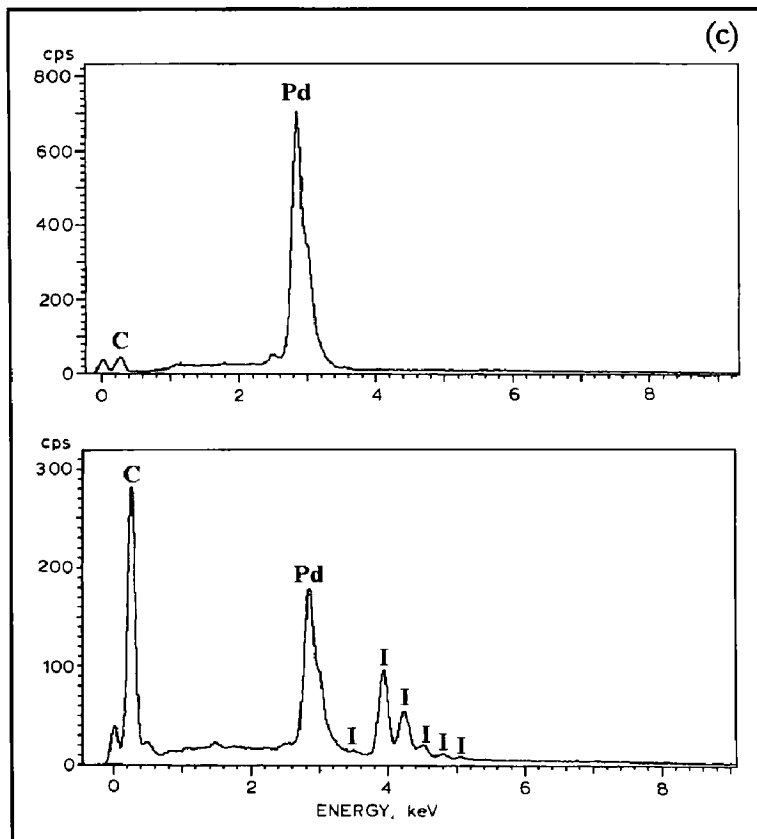
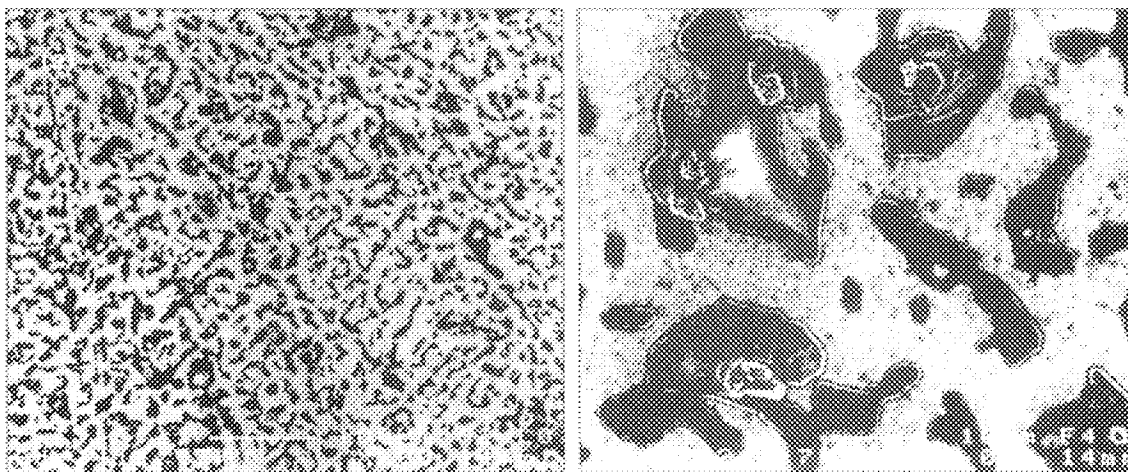


Fig. 2 SEMs of palladium sheet at two magnifications:

(a) as-received
 (b) cathodically treated in 0.1 M Bu_4NI in DMF by potentiostatic electrolysis. Potential: $-2.6 V$, amount of electricity: $130 C cm^{-2}$.
 (c) Probe of image (b) (treated palladium). The white zones (top scan) shows only palladium metal while the dark grey zones (lower scan) also exhibit the presence of carbon and iodine. Note the emergence of Bu_4NI pure crystals through the dark zones

Alkali metal iodides may also cause specific and dramatic changes to the Pd and Pt cathode surfaces, see Figures 4 and 5, respectively.

Coulometric Data

The voltammetric results and the instability of the electrochemically-formed layer strongly suggest that a charge/discharge process is taking place. This assumption can be checked by coulom-

etry since a large part of the electricity stored during the cathodic processes should be able to be anodically restored. However, the charge/discharge phenomenon was not found to be totally reversible since the solvent could not be made totally anhydrous and free of acidic impurities – some hydrogen evolution occurred (in yields of 65 to 75% depending on the salt used).

It has been suggested that the electric charge

Explore Litigation Insights

Docket Alarm provides insights to develop a more informed litigation strategy and the peace of mind of knowing you're on top of things.

Real-Time Litigation Alerts



Keep your litigation team up-to-date with **real-time alerts** and advanced team management tools built for the enterprise, all while greatly reducing PACER spend.

Our comprehensive service means we can handle Federal, State, and Administrative courts across the country.

Advanced Docket Research



With over 230 million records, Docket Alarm's cloud-native docket research platform finds what other services can't. Coverage includes Federal, State, plus PTAB, TTAB, ITC and NLRB decisions, all in one place.

Identify arguments that have been successful in the past with full text, pinpoint searching. Link to case law cited within any court document via Fastcase.

Analytics At Your Fingertips



Learn what happened the last time a particular judge, opposing counsel or company faced cases similar to yours.

Advanced out-of-the-box PTAB and TTAB analytics are always at your fingertips.

API

Docket Alarm offers a powerful API (application programming interface) to developers that want to integrate case filings into their apps.

LAW FIRMS

Build custom dashboards for your attorneys and clients with live data direct from the court.

Automate many repetitive legal tasks like conflict checks, document management, and marketing.

FINANCIAL INSTITUTIONS

Litigation and bankruptcy checks for companies and debtors.

E-DISCOVERY AND LEGAL VENDORS

Sync your system to PACER to automate legal marketing.