

Cathodic corrosion: Part 1. Mechanism of corrosion via formation of metal anions in aqueous medium

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In this paper we describe an unusual electrochemical phenomenon, namely cathodic corrosion of platinum. We show that all existing models of cathodic corrosion are inconsistent with our experimental observations. Therefore, we present a new model of cathodic corrosion, which is based on the assumption that metal anions are formed at the electrode surface during the corrosion process. These anionic species function as precursors for the formation of the final product of cathodic corrosion—metal nanoparticles.

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82.45.Bb Corrosion and passivation;
82.30.-b Specific chemical reactions; reaction mechanisms.

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1. Metals and metal cations

The periodic system of elements is traditionally divided into metals and non-metals, with a small transitional group of metalloids in between. Perhaps the most characteristic difference between these two is that during chemical reactions the metals donate their electrons and become positively charged ions — cations, while the non-metals accept these extra electrons and become negatively charged ions — anions. Some metals, like the alkali, have a single electron on their valent orbital and therefore form a singly charged cation when oxidized. Others, like the transition metals, form positively charged cations in various oxidation states from +1 (Ag) up to +8 (Os). The strength with which an atom resists losing its electrons is known as electronegativity. Its value is lowest for the alkali metals, and highest for the halogens, with coinage metals in between. Except for the latter, it is relatively easy to oxidize metals, and so they mostly occur as cations (e.g., in a halogen salt). Due to the low electronegativity of metals, and the ubiquitous presence of electronegative oxygen and water, negatively charged metal ions are not known to exist under standard conditions.

This is somewhat in contrast to another property of atoms, namely electron affinity, which is defined as the amount of energy gained by an atom when one extra electron is added to it. For alkali metals, for example, filling the half-filled *s*-orbital with one extra electron means “closing” the electronic shell. Such negatively charged alkali metal

anions would have enhanced stability compared to the neutral atoms. This is indicated by the slightly higher value of electron affinity for the alkali compared to alkali earth metals [1]. At the same time, the electron affinity of oxygen and halogens is a few times higher, meaning that they are much more likely to capture the extra electron, often removing it from a neutral alkali atom. By looking at the electron affinity table we can make a remarkable observation, namely that the electron affinity of some metals like gold and platinum is *even higher* than that of oxygen! This suggests that under the right circumstances these metal atoms could also take electrons from the much more electropositive metals like the alkali, becoming negatively charged themselves. Indeed, such behavior has been observed in recent experiments, where the existence of platinide and auride salts of alkali metals was experimentally established in vacuum [2–4] and under electrochemical conditions [5,6].

Perhaps the only other system where such behavior has been known is liquid ammonia. This polar solvent is very similar to water with one crucial difference: its auto-dissociation constant is nineteen orders of magnitude less than that of water. This means that the probability of encountering a proton H^+ created via the dissociation reaction $NH_3 \leftrightarrow NH_2^- + H^+$ is extremely low. The latter is the reason why free electrons injected into liquid ammonia can exist for a very long time, being solvated by ammonia dipoles but not reacting via $2H^+ + 2e^- \rightarrow H_2(g)$. This spectacular effect can be simply observed by putting a piece of alkali metal in liquid ammonia: the persistent blue color of

the solution will reveal the presence of solvated free electrons. Applying a negative potential to an electrode in liquid ammonia will also inject free electrons into the solution, resulting in the same characteristic blue color. Clearly, such solvated electrons are metastable and thus very reactive. For example neutral gold or platinum, both having high electron affinity, will capture these electrons creating negatively charged ions in solution — Au⁻ (auride) or Pt²⁻ (platinide) [7,8]. These would be extremely unstable in water towards hydrogen reduction reaction $2\text{Au}^- + 2\text{H}^+ \rightarrow 2\text{Au}^0 + \text{H}_2$. Yet in ammonia, where the protons are extremely scarce, these anions are stable. In fact, in the early 20th century a whole class of metals in groups 13–15 of the periodic system has been shown to form thermodynamically stable negatively-charged ions, named “Zintl ions” after a German chemist E. Zintl [9].

While these results suggest that the chemistry of metals may be much richer than what is currently known, these anionic states of metals were shown to be absolutely intolerant to air or moisture [10]. This could well be the reason why they remain so obscure. Yet for a myriad of (bio-) chemical reactions the mechanism of electron transfer in aqueous medium is the pivotal question, and a solvated electron in water has been proposed as the key intermediate [11]. Obviously such electrons are short-lived as they are extremely prone to recombination with water’s protons. In this article we argue that negative charges in the form of metal anions can be formed during strong cathodic polarization of an electrode in aqueous medium, and that they have a sufficiently long lifetime to warrant their consideration as an alternative intermediate in the electron transfer process. Furthermore, we propose a mechanism in which these metal anions carry the negative charge across a water depletion layer adjacent to the cathode and, once discharged by free water, form metal nanoparticles in solution. The latter is shown to be a facile and versatile method for the electrochemical synthesis of nanoparticles [12,13].

2. Cathodic corrosion

Even before the discovery of Zintl ions in liquid ammonia, electrochemists reported a peculiar observation in aqueous electrolytes. By applying a sufficiently negative voltage to a Pb metal electrode immersed in an alkaline medium, it rapidly decomposed into what was described as “metal dust” in solution [14]. Without going into details, authors have mentioned that even such noble metals as platinum were subject to cathodic disintegration. This was a dramatic violation of the general concept of cathodic protection, which is used everywhere where a steel structure comes in contact with ground or sea water. The corrosion

process was then explained by the electro-deposition of the alkali metal onto the (platinum) electrode, formation of an alloy between the two metals, and subsequent leaching of this alloy by the electrolyte’s water [15]. The mechanical destruction of the remaining sponge-like electrode’s surface due to vigorous concomitant hydrogen gas evolution would then lead to the formation of the observed “metal dust”. The original paper from 1898 received little follow-up, perhaps because the phenomenon was viewed as an undesired side-effect in the acid battery research, and an occasional paper from Haber’s group recites the original explanation given above [16].

Starting from the 1950’s Soviet electrochemists studied this phenomenon extensively [17–25]. Cathodic corrosion was described in many different electrochemical systems, yet the explanation remained largely in line with the original one given by Haber, even though some of the reports were seemingly inconsistent with the alloying scheme [26–28]. The particular case where ammonium cation was used instead of an alkali was recently developed by Simonet *et al.* [29–31] and Ghilane *et al.* [5,6,32], who argued that an anionic metal–ammonium complex must be formed at the surface of the electrode. Very recent experiments have shown that the “metal dust” produced during Haber’s cathodic corrosion consists of metallic nanoparticles. This takes this phenomenon from the obscurity of an undesired side-effect and puts it into a new light of becoming a very attractive method for nanoparticle synthesis [12,13,33–35].

Driven by the desire to understand the process of cathodic corrosion, we have performed the following electrochemical experiments. A platinum wire electrode (marz purity, 0.13 mm diameter) was submerged in a 10 ml solution of a salt (at least *pro analysi* purity) in MilliQ water (18.2 MΩ·cm). Submerged by 1 mm (typical value), the geometrical surface area of the working electrode was ~0.4 mm², with random variations of ~10% coming from the height of the meniscus. Using glassy carbon as a counter-electrode, potential was applied via a computer-controlled home-built power amplifier providing the desired dc or ac voltage*. The counter-electrode was placed into a glass tube with an open bottom to separate the reaction products without creating a significant ohmic drop between the counter and the working electrode. This was verified by measuring the voltage between a Hg/HgO reference electrode, introduced into the electrolyte at various positions, and the working electrode. The resulting current was recorded with high-temporal resolution** and analyzed with LabVIEW software [12]. After the formation of a black suspension, the electrolyte was repeatedly centrifuged, decanted and re-dispersed in MilliQ water until the

* It is crucial to use a non-inductive voltage source, as copious gas evolution at the electrodes can potentially cause intermittent interrupts of the electrical circuit, creating high-voltage spikes and causing the undesired spark erosion of the electrode (cf. Wehnelt interrupters [36]).

** At 50 kS/s current sampling rate, we have not observed any current interrupts in our circuit due to gas sheath forming around the electrode.

conductivity of the suspension was below $1 \mu\text{S}/\text{cm}$. By controlling the initial amount of cathodically corroded metal we define the mass concentration of the nanoparticles in suspension, and thus use a known weight amount of nanoparticles for further experiments. This water-dispersed suspension of nanoparticles was drop-cast on carbon-coated grids for transmission electron microscopy (TEM) studies, on zero-background sample holders for x-ray diffraction (XRD) measurements, and on supporting electrodes (glassy carbon or gold) for electrochemical characterization. The latter is performed in a standard three-electrode glass cell, with the platinum flag as a counter electrode. In order to measure the current–voltage characteristic of only one metal–electrolyte interface — the one at the working electrode — a reversible hydrogen electrode (RHE) is used as a reference, separated by a thin capillary. This reference electrode has a constant potential in the electrolyte, and so, after subtracting this constant value, the voltage between the reference and the working electrodes gives the potential drop across the metal–electrolyte interface of interest. Recording electrochemical current while repeatedly sweeping this potential between two limiting values at a constant rate is known as cyclic voltammetry (CV) [37].

For simplicity, we performed most of the corrosion experiments in an aqueous solution of NaOH, which contains H^+ , OH^- and Na^+ ions only. First we examine the effect of cathodic polarization at constant dc bias. As expected, copious evolution of hydrogen gas is observed at the cathode. While this is clearly the dominant electrochemical process in an aqueous electrolyte, it alone cannot alter the cathode's surface (see Fig. 8 (c), (d)). Yet the observed effect

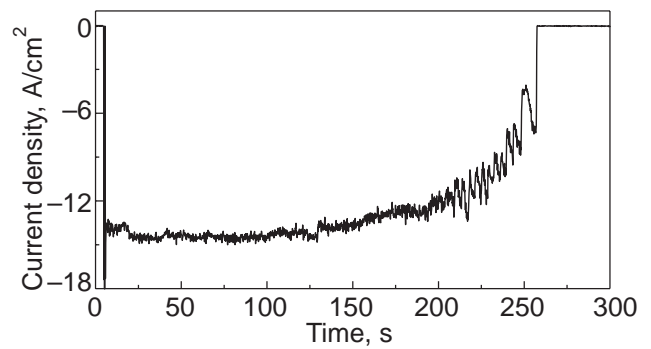


Fig. 1. Cathodic current flowing through a Pt wire as a function of time measured in a 20 M NaOH solution at -10 V applied bias. The Pt wire was 0.13 mm in diameter and submerged 1 mm into the electrolyte. The submerged part of the wire was atomized completely into a suspension of nanoparticles after 255 s . The measured current density is much lower than the one expected during spark discharge ($\sim 100 \text{ A}/\text{cm}^2$) [36,39]. Apparent oscillations are due to the intermittent hydrogen bubble formation at the electrode.

is quite dramatic: while no visible changes occur to the structure of the wire at concentrations below 1 M , at 10 M the surface of the wire blackens, and above 10 M the electrode corrodes readily and the solution turns into a suspension of nanoparticles. At the solubility limit ($\sim 20 \text{ M NaOH}$) the whole wire is corroded into the “metallic dust” of platinum nanoparticles within minutes, see Fig. 1 [38]. Scanning electron microscope (SEM) images of an annealed Pt wire before and after cathodic corrosion are shown in Fig. 2 (a), (b). Figures 2 (c)–(f) show additional high resolution SEM images of the same electrode that

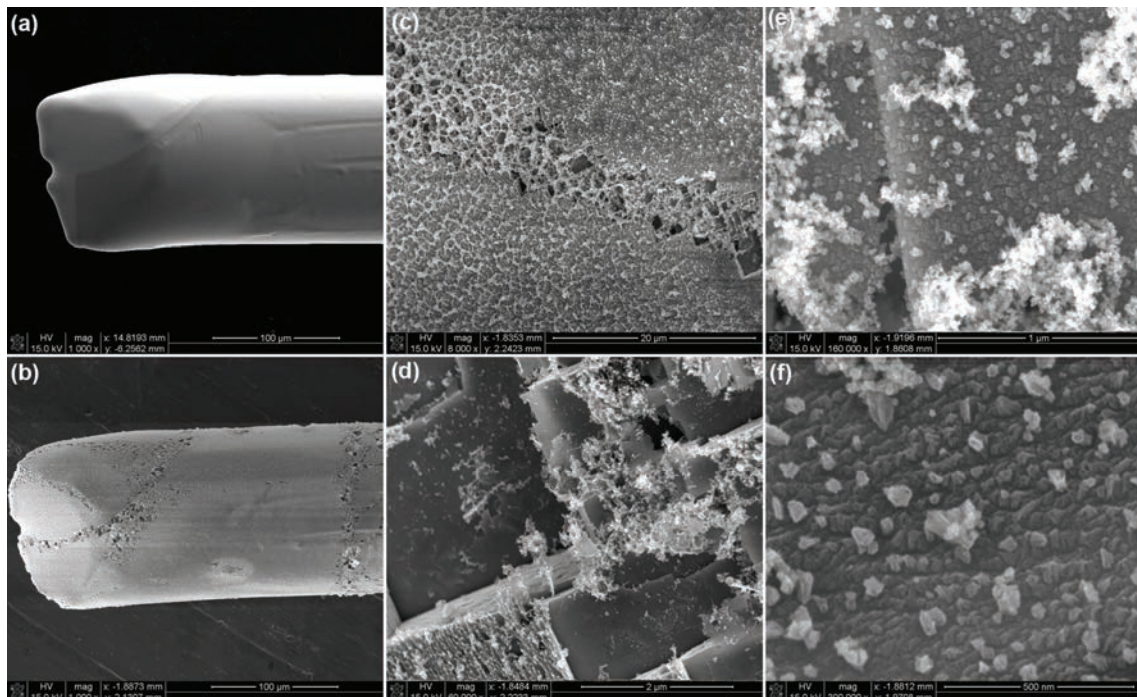


Fig. 2. SEM images of a platinum wire (a) before and (b) after cathodic corrosion in a solution containing 10 M NaOH at -10 V applied potential for 1000 s . Figures (c)–(f) show zoom-in images of the corroded electrode, revealing rough electrode surface and agglomerates of nanoparticles on it.

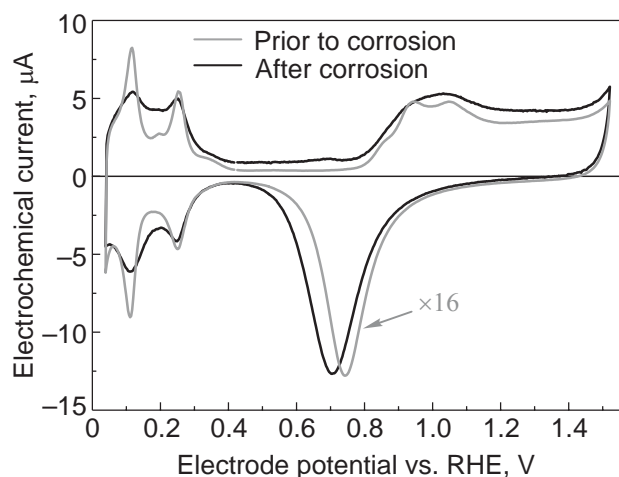


Fig. 3. (Color online) Cyclic voltammograms of the same Pt wire before (grey) and after (black) cathodic corrosion for 1000 s at -10 V in a solution containing 10 M NaOH. The voltammograms were recorded in a de-aerated solution of 0.5 M H_2SO_4 at a sweep rate of 50 mV/s. The current in the grey voltammogram that was acquired prior to corrosion is magnified 16 times. The Pt wire was 0.13 mm in diameter and submerged 1 mm into the electrolyte.

reveal the sponge-like structure of the electrode's surface formed by agglomerates of nanoparticles.

In Fig. 3 we show CVs of the same wire as in Fig. 2 recorded before and after cathodic corrosion in 0.5 M sulfuric acid. Such CVs can be used to characterize the quality of the surface. Before corrosion, using the standard method [40] we integrate the current between 0.05 and 0.45 V, corrected for the double-layer charging, to obtain the electrochemically active area of 0.6 mm^2 . This value is higher than the geometric estimate of $\sim 0.42 \text{ mm}^2$, which we attribute to the meniscus, deviations from the cylindrical shape of the submerged wire, and surface roughness. After corrosion we see that while the overall shape of the voltammogram remained the same, indicating that only platinum metal is exposed at the interface, the intensity of the signal increased more than a tenfold. This indicates that the surface had become extremely rough, which is consistent with the SEM images in Fig. 2.

The surface of the platinum electrode seems to be covered with nanoparticles after cathodic treatment. In order to detach the nanoparticles from the electrode we can either perform this cathodic treatment using dc bias in a highly concentrated 20 M solution of NaOH, or use an ac bias in a less concentrated solution. Previously we have shown that both methods lead to rapid atomization of a wire into nanoparticles [12,13,38]. Figure 4(a) shows the time evolution of the current during the corrosion of a Pt wire under ac bias, whereas Fig. 4(b) shows the current during a single ac cycle. We estimate that a layer of about 4 nm is etched within one ac cycle. The advantage of the ac bias is that detachment of nanoparticles from the electrode's surface is facilitated during the non-negative part of the ac cycle. This is illustrated in Fig. 5, which shows the time required

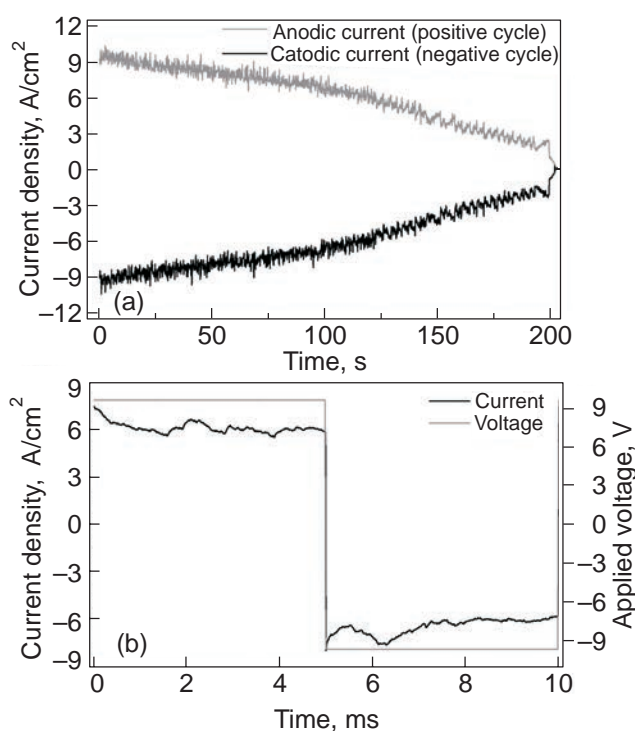


Fig. 4. (Color online) (a) Time dependence of the average ac currents flowing during (grey) anodic and (black) cathodic half-cycles of the -10 V to $+10$ V, 100 Hz, applied ac voltage in a 20 M NaOH. The Pt wire was 0.13 mm in diameter and submerged 2.5 mm into the electrolyte. (b) Current (black) and voltage (grey) during a single ac cycle.

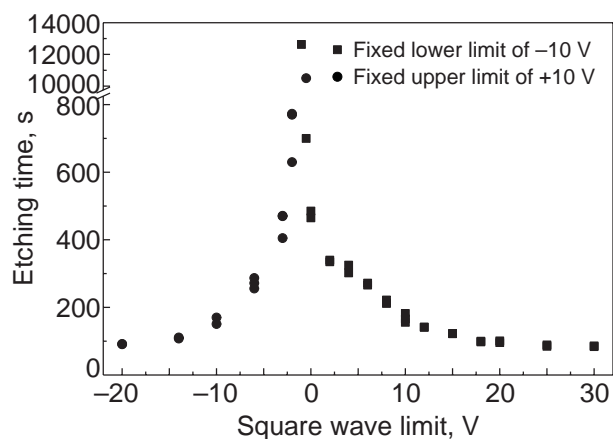


Fig. 5. Dependence of the atomization time of a Pt wire on the limits of the square wave ac voltage applied. Circles represent the measurements, in which the upper value of the square wave was fixed at $+10$ V, and the lower one systematically varied between -20 and -0.5 V. Squares represent the measurements, in which the lower value of the square wave was fixed at -10 V, and the upper one varied from -1 to 30 V. Where available, several measured values of etching time are plotted for the same ac voltage. For each point on the graph, 1 mm of a Pt wire was completely atomized, and the atomization time was recorded. The experiments were conducted in a solution containing 1 M NaOH. The frequency of the applied ac voltage was $f = 100$ Hz. A glassy carbon electrode was used as a counter-electrode.

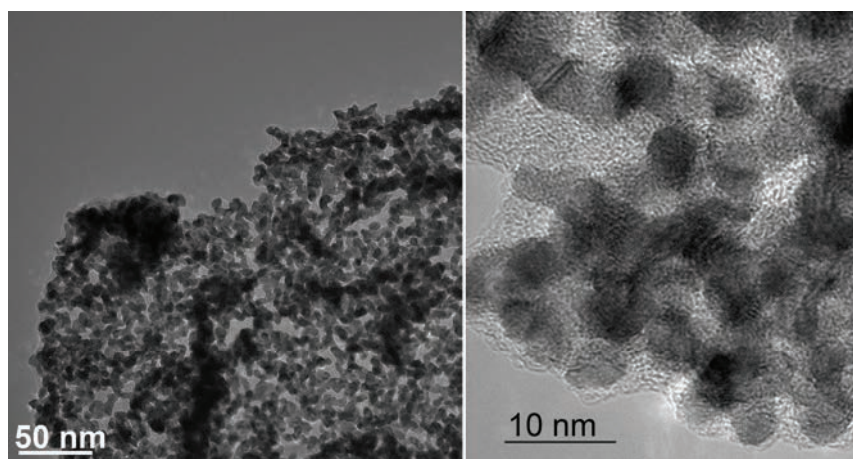


Fig. 6. TEM images of Pt nanoparticles that were formed during cathodic corrosion of a Pt wire. Although the nanoparticles agglomerate, individual particles can be distinguished.

to completely corrode a unit length of a platinum electrode as a function of the ac amplitude. The results of this measurement show that, while positive voltages are not required for corrosion, anodic voltage speeds up the dispersal of the electrode. By depositing a droplet of such suspension onto a transmission electron microscope (TEM) grid we can examine our nanoparticles at near-atomic resolution (Fig. 6). We see that the particles agglomerate upon drying, but sometimes individual ones can be found. Energy dispersive x-ray (EDX) analysis on those individual particles (not shown here) reveals their composition to be pure platinum, proving that the original electrode wire has been transformed into nanoparticles of the same composition.

With this we conclude that cathodic corrosion indeed takes place, readily affecting even a very noble metal like platinum. It results in the formation of metallic nanoparticles, which either remain at the electrode's surface, dramatically increasing its surface area, or can even detach from it under certain conditions, leading to complete disintegration of the electrode.

3. The existing models of cathodic corrosion

In the following we present experimental results that put all existing models of cathodic corrosion to the test. We convincingly show that none of those can explain all our experimental observations. Thus we introduce a new, unconventional, and rather counter-intuitive model, which nonetheless accounts for all of the results presented here and offers a broad outlook on the novel chemistry of metal anions. Our model is based on the assumption that metal anions are formed at the electrode surface during the cathodic corrosion process.

As we have shown in the previous section, if a Pt electrode is immersed into a concentrated solution of NaOH at a sufficient cathodic voltage, a corrosion process sets in. From the data of Fig. 5 we can already dismiss the anodic corrosion pathway. Therefore we are left with the three

known cathodic corrosion mechanisms. Even though Haber *et al.* once reported cathodic corrosion of platinum in pure sulfuric acid [15], already in the earliest reports it was noted that the presence of an alkali cation was necessary for the corrosion to commence. Therefore, the first mechanism, originally proposed by Haber and later developed by Kabanov [19], involves an electrochemical reduction of the alkali ion from the electrolyte onto the cathode, forming a (surface) alloy with the host metal of the electrode. Subsequently, the alkali metal is leached from this alloy by the electrolyte's water, leaving a porous structure of the host metal behind. This porous surface disintegrates into "metallic dust" in solution due to the exothermic leaching reaction and concomitant hydrogen gas evolution at the cathode. While this explanation seems to lack consistency in that at the same potential both the reduction of alkali from the solution and the oxidation of the alkali from the alloy seem to be favored, we could not dismiss it simply using a theoretical argument. Therefore we performed the following experiment.

Due to its non-metallic nature, a (tetraalkyl-)ammonium cation cannot alloy with platinum. Cathodic corrosion in a solution of tetraalkylammonium hydroxide would therefore discard the alloying mechanism. Regrettably, it is not possible to obtain aqueous solutions of a tetraalkylammonium hydroxide of concentration and conductivity comparable to the 10 M NaOH solutions used in the dc experiments in the previous section [38]. Nevertheless, after a treatment of a Pt electrode in a 2.7 M (25 weight percent) tetramethylammonium hydroxide (TMAH) solution in water at -10 V dc for 10 min we clearly observe signs of corrosion at the electrode's surface in the SEM, see Fig. 7(a) and (b). However, the corrosion is relatively weak. In analogy to our experiments in solutions with a low concentration of NaOH (2 M), this can be explained by the abundance of free water in the solution, which is readily reduced at the cathode at much milder cathodic potentials.

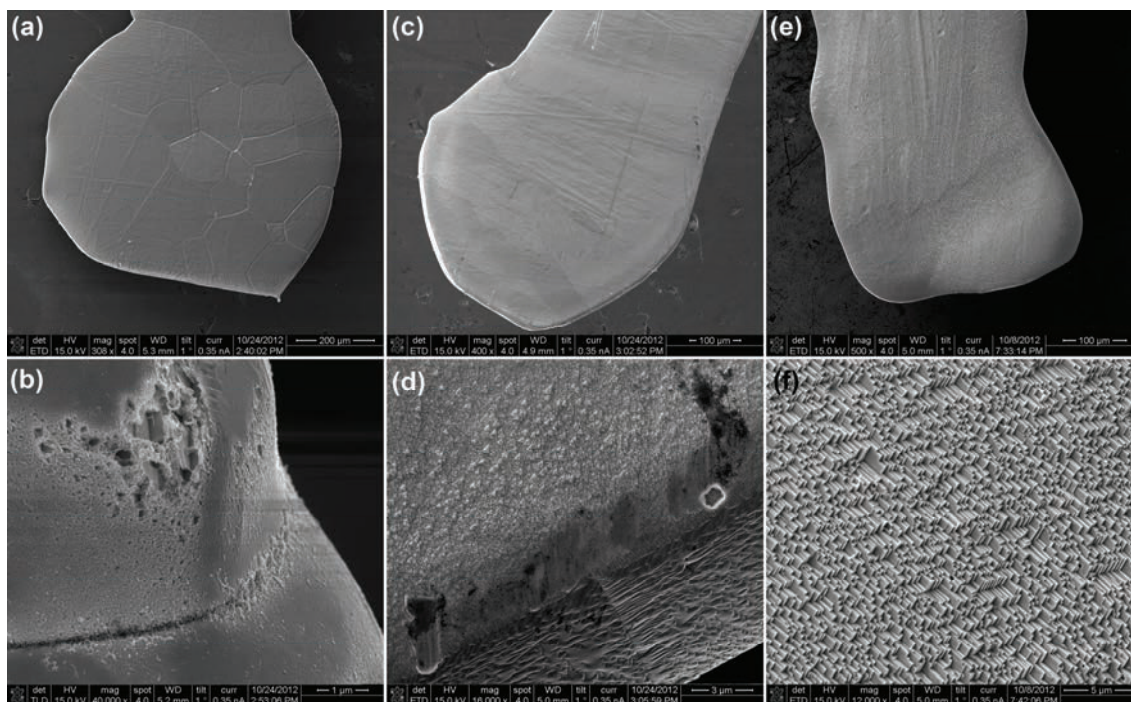


Fig. 7. SEM images of Pt electrodes that were subjected to cathodic corrosion in tetraalkylammonium hydroxide solutions. Figures (a) and (b) show a polycrystalline Pt electrode after treatment for 10 min at -10 V dc in a solution containing 2.7 M TMAH. The Pt electrode in (c) and (d) was treated with -10 to 0 V ac voltage (100 Hz block waveform) for 10 min in the same solution. Figures (e) and (f) show a third Pt electrode that was treated with -10 to +1.5 V ac voltage for 10 min in a solution of 0.5 M TEAH. In (f) certain surface termination, possibly (100), appears enhanced by corrosion. Although cathodic corrosion is visible even after application of a negative dc voltage to a Pt electrode, it becomes more apparent after an ac voltage treatment, especially if the upper limit of the ac voltage is positive.

Therefore, in order to keep our comparison fair, we employed the ac method. As has been shown previously, ac bias improves detachment of nanoparticles from the electrode and thus facilitates corrosion [13]. Figures 7(c) and (d) show a Pt electrode after an application of an ac voltage of -10 to 0 V for 10 min in this solution (2.7 M TMAH). Corrosion of the electrode surface is much more apparent than that under dc bias. Please note that we can exclude anodic oxidation of Pt as a mechanism enhancing corrosion, since the bias of the electrode is ≤ 0 V during the whole ac period. In addition, we have conducted a different experiment in a solution containing 0.5 M tetraethylammonium hydroxide (TEAH), in which we have applied an ac voltage of -10 to +1.5 V to a Pt electrode for 10 min, see Fig. 7(e) and (f). Corrosion of the electrode surface in this experiment was much more severe, leading to both macroscopic and microscopic changes to the electrode surface. Moreover, a suspension of nanoparticles formed in the solution during this experiment. One might suspect that in the case of an ac voltage of -10 to +1.5 V corrosion occurs at the anodic (positive) branch of the voltage cycle. To exclude this possibility we have carefully verified that no trace of corrosion can be seen at the applied anodic potentials up to +10 V.

Hence, we conclude that the corrosion process in solutions of TMAH and TEAH is cathodic. And since alloy

formation between tetraalkylammonium and platinum is impossible, the alloy formation and leaching mechanism is insufficient to explain observed cathodic corrosion of Pt.

Since corrosion of a Pt electrode occurs during a concomitant intensive hydrogen evolution reaction, the next mechanism under scrutiny is that of hydrogen corrosion. Although thermodynamically unfavorable in platinum [41], hydride formation and hydrogen corrosion is a well-known phenomenon in steel [42]. To rule out this mechanism, we perform the following experiment. A freshly-annealed Pt electrode is immersed into a solution containing 2 M H_2SO_4 and a -10 V dc voltage is applied to it for 10 min. At these conditions we observe vigorous hydrogen evolution at the cathode with a current density of about 2 A/cm^2 . If hydrogen would be responsible for the cathodic corrosion of the electrode, one would expect a strong effect under these conditions. However, if we compare the surface of the same Pt electrode before and after such cathodic treatment in sulfuric acid, we see almost no changes (Fig. 8(a), (b) and (c), (d)). This shows that hydrogen alone cannot account for the cathodic corrosion of platinum.

In the next step, we repeat the experiment in a solution containing 1 M Na_2SO_4 in addition to 1 M H_2SO_4 . After 10 min of cathodic treatment in this solution at a current density of 0.7 A/cm^2 , we find that the electrode surface has corroded significantly (Fig. 8(e) and (f)). Therefore we

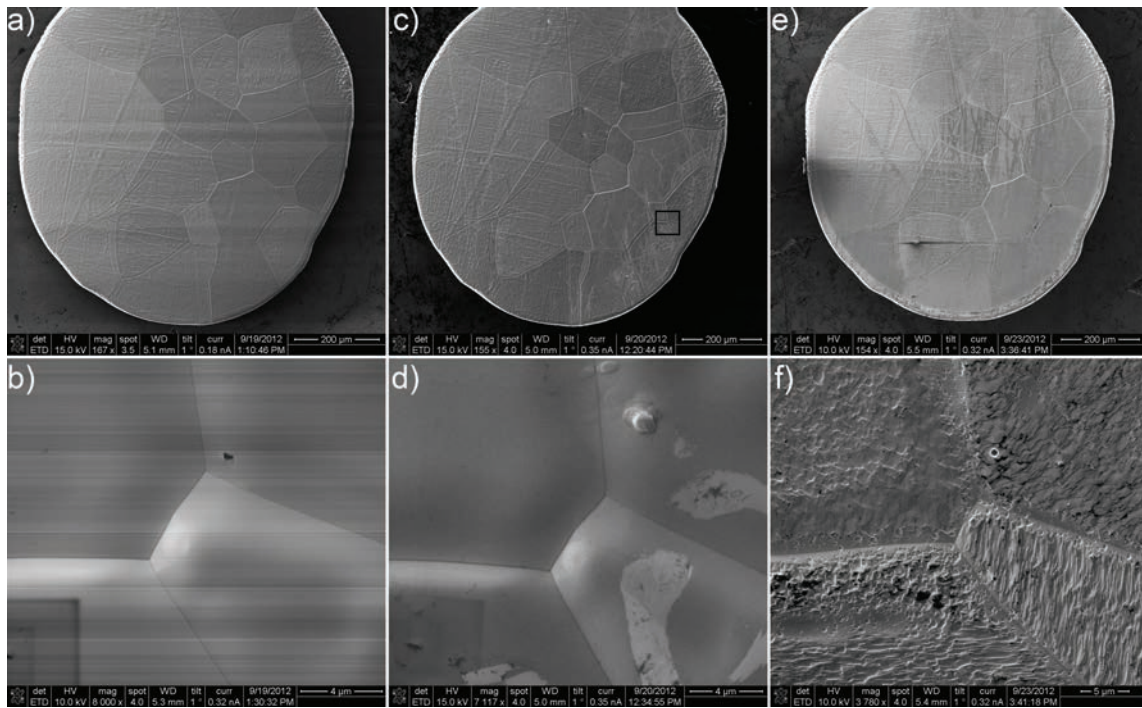


Fig. 8. SEM images of the same polycrystalline Pt electrode after flame-annealing (a), (b), subsequent cathodic polarization for 10 min at -10 V dc in a solution containing 2 M H_2SO_4 (c), (d), and in a solution containing 1 M H_2SO_4 and 1 M Na_2SO_4 (e), (f). Images (b), (d), and (f) show a zoom-in of the same area marked by a square in (c). While slight deposits in (d) are possibly due to contamination, clear morphological changes in (f) reveal the extent of cathodic corrosion in a Na^+ containing electrolyte.

conclude that cathodic corrosion does not proceed with only H^+ ions and requires the presence of strong cations (Na^+ ions).

As all other physical properties of this electrolyte (electrical, heat conductivity etc.) are almost identical to those of the previously used 2 M H_2SO_4 , this experiment also discards the possibility of physical disintegration rather than chemical corrosion. Although the current densities are rather high, they are at least an order of magnitude less than required to obtain a glow discharge in aqueous electrolytes [36,39]. Furthermore, a close examination of the electrode surface post-corrosion reveals well-defined low-index crystallographic structure on its surface. This also shows that corrosion is not of physical but of chemical nature. The latter observation also discards the rather unlikely hypothesis of hydrogen and oxygen microexplosions inside the platinum lattice [43].

As a final note we would like to mention that the corrosion process is not specific to Na^+ ions. We have also observed cathodic corrosion in solutions containing such strong cations as Li^+ , K^+ , Cs^+ , Ca^{2+} , along with the above-mentioned ammonium and tetraalkylammonium. Moreover, we confirmed experimentally that cathodic corrosion occurs in solutions of hydroxides, chlorides, sulfates, perchlorates, and nitrates quite irrespective of the anion. This, together with a hard requirement for a strong cathodic potential, removes any remaining possibility of platinum oxidation and discards the possibility of a cationic route for cathodic corrosion.

4. Our proposed mechanism of cathodic corrosion

In the previous section we have shown that the existing models of cathodic corrosion cannot account for all our experimental results. In the following we summarize the differences between the most relevant mechanism of Haber and Kabanov [19], which involves the formation of an alloy between the electrode and the alkali metal and subsequent leaching of the alkali by the electrolyte's water, and our experiments.

Firstly, we observe complete dispersion of a Pt electrode within minutes under highly cathodic dc potential in a concentrated solution of NaOH , see Fig. 1. From a thermodynamic point of view, reduction of a Na^+ ion into a Pt–Na alloy, and simultaneous oxidation plus leaching of Na from this alloy into the electrolyte are improbable. Furthermore, changing the cathodic potential should shift the equilibrium either towards the reduction or towards the oxidation of Na, in both cases slowing down the overall reaction rate. The opposite is observed experimentally, see Fig. 5. Secondly, as we mention in the previous section as well as in Part 2 of this article, cathodic corrosion of electrodes of virtually any metal and even alloys takes place in aqueous solutions with a high concentration of alkali(ne) cations. This process seems to be independent of the type of the cation. Even though phase diagrams of alloys containing alkali metals are scarce, the formation of a (surface) alloy between any metal electrode and any alkali(ne) metal from the solution is quite unlikely. Thirdly, we estimate that in

concentrated solutions, within one ac voltage cycle a layer of a metal electrode of up to 10 nm can be corroded. Even if we allow for the possibility of formation of a surface alloy, there are hardly any thermodynamic arguments for its propagation beyond the first one or two atomic surface layers. Finally, the direct observation of cathodic corrosion of a Pt electrode in pure aqueous solutions of tetraalkylammonium hydroxides excludes any possibility of alloying in the conventional sense of the word.

From the results of the previous section we conclude that the requirements for observing cathodic corrosion are: a platinum electrode at a highly cathodic potential, and an aqueous electrolyte with a high concentration of a strong irreducible cation. Based on these requirements we propose the following mechanism for the cathodic corrosion and the formation of metallic nanoparticles at the cathode.

Due to copious hydrogen evolution from the reduction of water, a layer of very high pH is created at the surface of the electrode. This layer is extremely rich in alkali cations and depleted of water, resembling a molten alkali salt. In contrast to the latter, it still contains sufficient water to remain fluid and prevent the reduction of the alkali cations. These remaining water molecules are heavily involved in solvation, and therefore do not get reduced. Thus, while this layer remains liquid, there is little reducible water in it. We propose that cathodic polarization of the electrode induces reduction of platinum metal to its anionic form at the surface. These Pt anions are stabilized by the alkali cations that are attracted to the interface, forming a complex that resembles a platinide salt or a Zintl ion [10,44]. Since the metal anion is stabilized by the alkali cations, the whole complex becomes solvated in this water-free layer, diffusing away from the cathode. Upon encountering free water, the Pt anions are oxidized by it, forming hydrogen and charge-neutral platinum atoms (or clusters). These atomic building blocks agglomerate to form metallic nanoparticles, which then precipitate.

Another, perhaps more elegant way of looking at the mechanism of nanoparticle formation during cathodic corrosion has been recently proposed [45]. A platinum electrode under cathodic polarization is extremely efficient in transferring its electrons to the protons in water. Normally this happens when either protons adsorb on its surface, or water molecules diffuse into the Helmholtz layer. However, when there are no protons and the water molecules can only be found outside the Helmholtz layer, the electron transfer from the platinum cathode to those species has to happen across this water free, Na^+ rich layer. The platinum anions therefore perform the role of the electron transfer agents, charging at the electrode's surface, diffusing through this layer while being stabilized by the Na^+ cations, and discharging upon encountering free water outside of it. After transferring the negative charge from the electrode to the water molecules, platinum becomes neutral again, agglomerating into nanoparticles. An attempt to

estimate the stability of metal anions in aqueous medium has been reported [46].

In case the alkali salt solution is not extremely concentrated, the water-free layer is not thick enough to allow these agglomerates to sufficiently separate from the electrode. Therefore they deposit back onto its surface, repeating the cathodic corrosion cycle. Only in the highly concentrated electrolytes can they diffuse far enough from the electrode not to be re-deposited. This is why in dilute solutions we observe blackening of the cathode due to the formation of nanoparticles on its surface, but do not find dispersed nanoparticles in solution. In such case applying ac voltage helps, as during the anodic half of the cycle the particles disperse, possibly due to the partial oxidation of their surface which improves solvation.

5. Conclusions

In this article we have presented our study on corrosion of platinum electrodes at cathodic potentials. Using carefully designed experiments we have shown that no existing mechanism can explain the observed process of cathodic corrosion. We have defined the two requirements which have to be fulfilled for cathodic corrosion to take place. Firstly, the electrolyte must contain a high concentration of strong irreducible cationic species, and secondly, a highly cathodic potential must be applied to the electrode. Based on these requirements, as well as on our experimental results, we have devised a new mechanism, consistent with all experimental observations, which invokes novel chemistry of metal anions in aqueous solutions.

In addition, we have shown that cathodic corrosion can lead to the formation of metallic nanoparticles. In the second part of this paper, we explore the application of cathodic corrosion as a simple and versatile method for the electrochemical synthesis of nanoparticles, and show the universality of cathodic corrosion by producing nanoparticles of various metals.

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