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Platinum oxide film formation–reduction: an in-situ mass measurement study *

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Abstract

The growth and reduction of oxide films at Pt was studied using the quartz crystal microbalance technique. The compact α -oxide was shown to be anhydrous in nature (either PtO or PtO₂). When the potential was extended into the hydrogen adsorption region, the electrode mass was seen to decrease, but then stabilized once the hydrogen evolution reaction commenced. These results, as well as the effect of the addition of chloride and ferrous ions on the mass measurements, have been interpreted in terms of ion adsorption–desorption processes. The mass change during the reduction of thin hydrous β -oxide films was also monitored and yielded a mass-to-charge ratio consistent with a Pt(OH)₂ film composition. Other mass data indicated that Pt dissolution can occur with repeated β -oxide growth–reduction cycles and that some Pt may redeposit, given sufficient time at negative potentials.

INTRODUCTION

Despite the great interest in and many applications of Pt electrodes over the years, full agreement does not yet exist as to the identity of the thin compact oxide (α -Pt oxide) formed at potentials positive of ca. 0.8 V vs. the reversible hydrogen electrode (RHE). PtO [1–7], Pt(OH)₂ [8], PtO₂ [9–11] and Pt(OH)₄ [12,13] have all been suggested as possible forms of the α -oxide film.

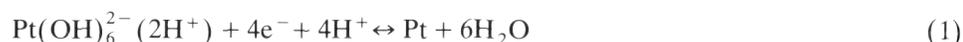
Even less is known about the thicker Pt oxide (β -oxide film) which can be formed under more rigorous oxidizing conditions, e.g. after long times at greater than ca. 1.8 V [14] or, more commonly, by rapid potential cycling between critical limits [15–21]. In one of the earliest studies of β -oxide films [22], the yellow-orange

* Dedicated to Professor Brian E. Conway on the occasion of his 65th birthday and in recognition of his contribution to electrochemistry.

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surface compound was suggested to be $\text{Pt}(\text{OH})_2\text{SO}_4\text{Pt}(\text{OH})_4\text{PtO}_2$. More recently, relatively thick β -oxide films have been shown by X-ray diffraction studies to be amorphous in nature [23], while X-ray photoelectron spectroscopy studies have indicated this film material to be $\text{Pt}(\text{OH})_4$ [13], $\text{PtO}_x[\text{SO}_4]_y$ when grown in sulfuric acid solutions [6], $\text{PtO}(\text{OH})_2$ when formed in basic media [24] and even PtO_3 [25].

It is also of interest that, based on the reported 90 mV pH dependence of the β -oxide reduction peak, Burke and coworkers [15–18] have suggested that $\text{Pt}(\text{OH})_6^{2-}$ is the oxide product. However, because of its charged nature, it is clear that counter-ions would be required to maintain electroneutrality in a phase oxide film of this kind. In sulfuric acid only protons can serve in this role, so that a 60 mV pH dependence would result and the film would be equivalent to $\text{Pt}(\text{OH})_4$, i.e.



These discrepancies concerning the nature of the β -oxide film, in particular, indicate the need for other, preferably in-situ, methods of establishing the identity/composition of the β -oxide film. Our recent work with hydrous Ir oxide films [26] has shown that the quartz crystal microbalance (QCMB) technique can be usefully applied to the study of these kinds of oxide films. Therefore in the present work the QCMB method has been used to shed some further light on the nature of the α - and β -Pt oxide films. In addition to establishing the identity of these oxides, it was anticipated that this approach could be used to assist in understanding the origin of the anomalously greater charges passed during β -oxide film reduction at constant potential compared with those in a sweep experiment, as reported in an earlier publication [27].

EXPERIMENTAL

Equipment

Standard three-electrode circuitry was employed in all this work, using either an EG & G PARC 173 potentiostat combined with the PARC 175 function generator or the PARC 273 potentiostat system. The frequency counter was a Philips PM6654C high resolution counter-timer and a Pierce-type oscillator [28] was employed. Both the electrochemical and frequency data were plotted on BBC SE 780 x-y recorders.

Cell and electrodes

The working electrodes consisted of AT cut quartz crystals 2.5 cm in diameter (Valpey-Fisher), first sputter-coated with an undercoat of titanium to a thickness of ca. 12.5 nm followed by platinum to ca. 100 nm. Electrical contact was made to each side of the crystal with Au wires, using conducting silver epoxy. The frequency-to-mass conversion factor was $57 \text{ Hz } \mu\text{g}^{-1} \text{ cm}^{-2}$.

A two-compartment glass cell was used in all this work, with the quartz crystal sandwiched between two rubber O-rings at the base of the main compartment (the exposed Pt surface area was 0.5 cm^2). The counter-electrode was a large area Pt gauze (99.999%, Johnson-Matthey), located in the same compartment as the working electrode, while the reference electrode was a reference hydrogen electrode, to which all potentials are referred in this work.

Solutions and general experimental conditions

All Pt oxide growth–reduction experiments were carried out in 0.1–0.5 M sulfuric acid solutions using triple-distilled water. Deoxygenation was accomplished by the passage of argon through or above the cell solution at all times. All experiments were carried out at room temperature.

β -Pt oxide films were formed by rapidly scanning the potential at 5 V/s between 0.5 and 2.82 V, with the film thickness being controlled by the total scanning time. Prior to β -oxide film reduction (usually at 20 or 50 mV/s), the potential was held at ca. 1.3 V for several minutes so that oxygen generated during excursions to high potentials could be removed from the solution.

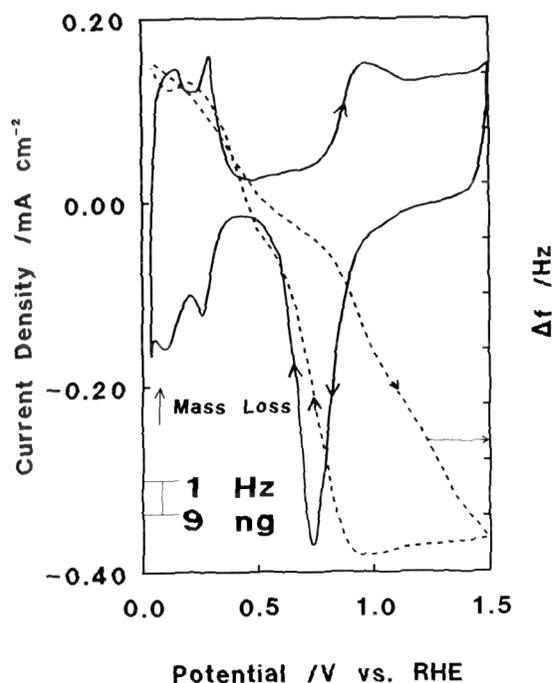
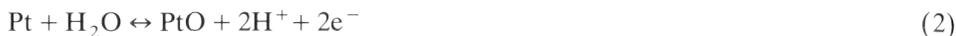


Fig. 1. CV (—) and associated frequency change (-----) of a Pt-coated quartz crystal in 0.1 M H_2SO_4 ; scanning rate, 50 mV/s.

RESULTS AND DISCUSSION

 α -Pt oxide films

Figure 1 (solid curve) shows a typical cyclic voltammogram (CV) of a Pt-coated quartz crystal in 0.1 M sulfuric acid, as well as the associated mass changes (broken curve) measured during this experiment. Like previous QCM work with Au electrodes [29,30], but in contrast with the only prior study of Pt [29], a mass increase is seen, as expected, during Pt oxide formation, while oxide reduction is marked by mass loss. From the integrated charge density during α -oxide reduction and the associated change in frequency over the potential range of the cathodic peak, a ratio of 8 ± 0.5 g/mol of electrons passed is typically obtained. It is of interest that, of the following suggested reactions for α -oxide formation–reduction, a ratio of 8 g/mol electrons would be predicted for the formation of an anhydrous Pt oxide film



while a ratio of 16 g/mol electrons would be predicted for the hydrated forms



Therefore, while the present results cannot distinguish between the Pt(II) and Pt(IV) forms of the α -oxide, they do provide in-situ support of the assumed anhydrous nature of the α -oxide film.

In the potential range of the hydrogen adsorption–desorption reaction, it is notable that as the potential is made negative and hydrogen atoms begin to adsorb, the electrode mass decreases approximately linearly; the opposite occurs during hydrogen atom desorption in the positive sweep. In fact, for the case in Fig. 1 the electrode mass decreases by ca. 5 g/mol electrons when the potential is scanned from 0.4 to 0 V. As the adsorption of one monolayer of hydrogen atoms would be expected to yield a mass gain of ca. 1 g/mol electrons, it appears that other surface processes, such as the desorption of water or bisulfate ions, may be occurring as the potential is made more negative. Extension of the potential to ca. -0.2 V does not result in a further loss of mass. Instead, the electrode mass reaches a steady state during the hydrogen evolution reaction (HER), probably reflecting the stabilization of the electrode surface by one monolayer of adsorbed hydrogen. In the brief earlier QCM study of Pt electrodes [29], it is of interest that a large mass gain was seen as the potential was extended to 0 V. However, not only was this mass gain much larger than that predicted for hydrogen atom adsorption, but the mass changes seen during Pt oxide formation–reduction were the reverse of those seen with Au or with Pt in the present work.

QCM experiments involving α -oxide growth with time at constant potential were also carried out in the present investigation. Fig. 2 shows a plot of the frequency change monitored as a function of charge passed during the reduction of Pt oxide films which were formed with time (up to ca. 30 min) at constant potentials between 1.2 and 1.6 V. It can be seen that the relationship between mass and charge remains essentially constant, yielding values between 7 and 8 g/mol electrons. Values less than 8 probably indicate that, in the conversion of the metal to monolayer levels of oxide, desorption of anions and/or solvent is also occurring. The constant slope and the fact that the plot in Fig. 2 intercepts the origin indicates that the measured mass changes are associated primarily with the removal of the α -oxide film during its reduction. The linear relationship observed between charge and mass in Fig. 2 and during both the positive and negative scans in Fig. 1 also indicates that the same α -oxide product is being formed at all potentials. Therefore suggestions that the initial film consists of PtOH species (17 g/mol electrons) and there is subsequent loss of a proton to form PtO (-1 g/mol electrons) [3,4,11,31] are not supported by the present results.

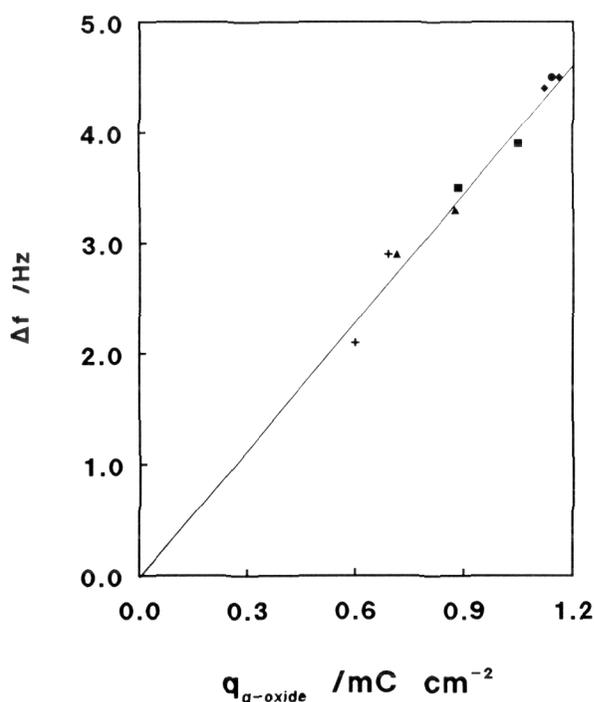


Fig. 2. Frequency change during reduction of α -Pt oxide films as a function of measured charge density. Films were formed by holding at the following E_+ values: +1.2 V; ▲ 1.3 V; ■ 1.4 V; ◆ 1.5 V; ● 1.6 V.

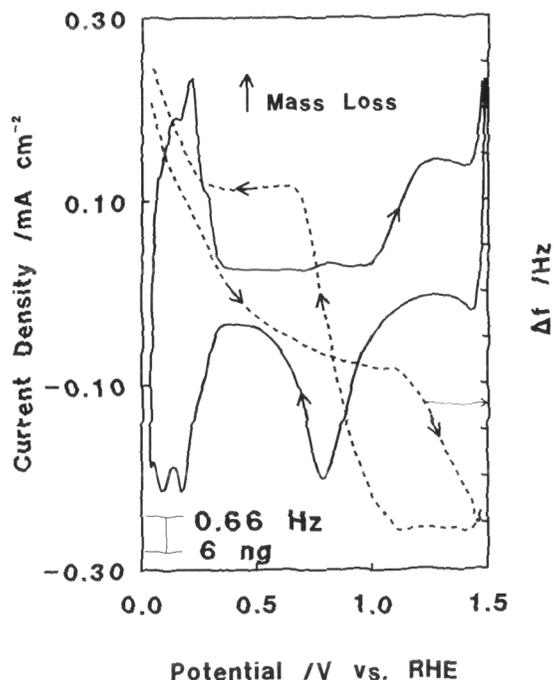


Fig. 3. CV (—) and associated frequency change (-----) of a Pt-coated quartz crystal in 0.1 M H_2SO_4 + 3 mM NaCl; scanning rate, 50 mV/s.

When chloride is added to the sulfuric acid medium, it is known [32] that its adsorption inhibits oxide film formation. Figure 3 (solid curve) shows a typical CV response for Pt in 0.1 M sulfuric acid + 3 mM NaCl. As expected, the onset of α -oxide film formation is delayed to ca. 1.0 V (compared with ca. 0.8 V in Fig. 1). The concurrent frequency measurement (broken curve) shows a gradual decrease (increase in mass) in the positive sweep from 0 V through to ca. 1.1 V, suggestive of chloride adsorption, and then a more marked increase in mass up to 1.5 V. Based on the charge passed during Pt oxide formation to 1.4 V, the mass change in the range of potential is ca. 8.5–9 g/mol electrons. The somewhat higher ratio than observed without chloride present indicates that, in addition to α -oxide formation, further chloride adsorption must be occurring. This is consistent with the results of earlier electrochemical studies [32], which have suggested that both Cl^- are Cl^- are coadsorbed in competition with OH and O species of the developing oxide film at Pt.

During film reduction (Fig. 3), it is interesting that a comparatively large frequency change (mass loss) is seen, yielding a ratio of ca. 11.5 g/mol electrons. This suggests that the surface rearrangement resulting from α -oxide reduction brings about a significant extent of chloride desorption, at least transiently. It can

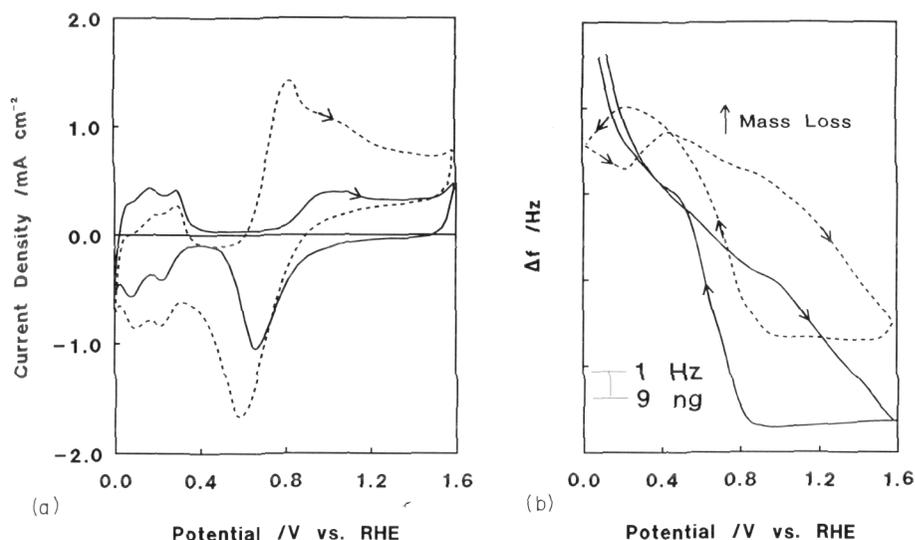


Fig. 4. (a) CV and (b) associated frequency change in 0.1 M sulfuric acid (—) and immediately after the addition of 30 mM FeSO₄ (---); scanning rate, 100 mV/s.

be seen that chloride is re-adsorbed as the sweep continues into the hydrogen atom adsorption range of potential and is scanned positively again.

Another set of experiments was carried out in sulfuric acid solutions to which some Fe²⁺ had been added. It is known that the electrochemistry of the Fe^{2+/3+} redox process obscures the α -oxide growth–reduction features substantially (Fig. 4(a)), leaving some question as to the precise impact of the Fe^{2+/3+} process on Pt oxide formation as well as on the degree of adsorption of these cations. Fig. 4(b) (broken curve) shows that this latter process occurs more or less as usual in the presence of Fe²⁺, with only a ca. 10% diminution of the mass gain/loss observed. This small change in mass may be indicative of some Fe^{2+/3+} adsorption, as has been suggested previously [33].

However, in the double-layer and hydrogen adsorption–desorption region of potential, more apparent differences in the mass changes are seen. It appears that as the potential is made negative of ca. 0.2 V the electrode mass increases, while it decreases again as the potential is extended positively of this value. As 0.2 V is very close to the potential of zero charge (pzc) of Pt in this medium [34], it is probable that the adsorption of Fe²⁺ is being detected at potentials negative of the pzc by this technique.

The above results indicate that the QCM technique can be used to monitor the formation–reduction of thin metal oxide films. In addition, it appears that it can yield useful insights into the ion adsorption–desorption processes which occur at the bare electrode surface, at oxide films and even during reactions such as the HER.

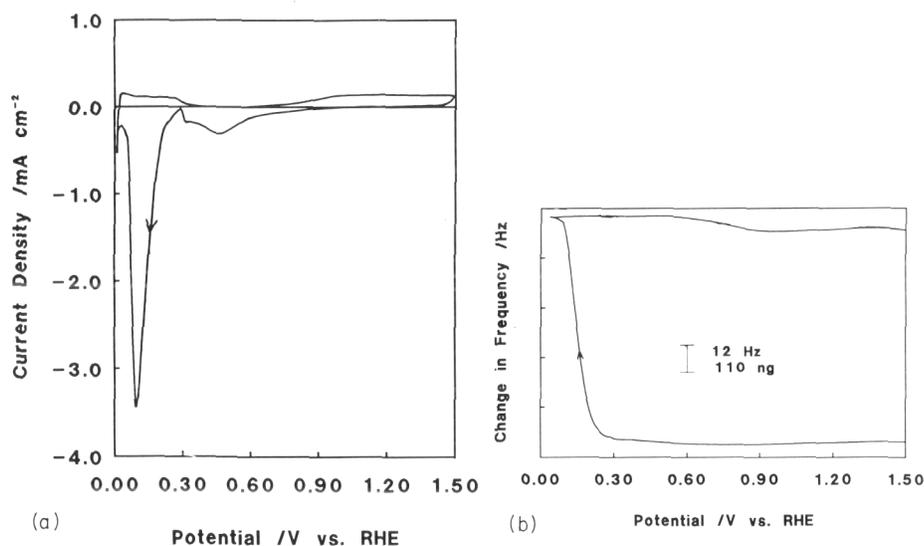


Fig. 5. (a) CV and (b) associated frequency change during α - and β -oxide reduction (20 mV/s) after 7 min of oxide growth at 5 V/s between 0.5 and 2.82 V in 0.5 M H_2SO_4 .

β -Pt oxide films

Mass measurement during potentiodynamic film reduction

Figure 5(a) shows a typical CV obtained during the negative sweep immediately after 7 min of β -oxide growth at 5 V/s between 0.5 and 2.82 V. After solution deoxygenation at 1.3 V for 2 min, the α -oxide film present beneath the overlying β -oxide film [14,35] is seen to reduce first at ca. 0.4 V, after which the large cathodic peak due to β -oxide reduction is observed. Figure 5(b) shows the associated mass change as the α - and β -oxide films are reduced. β -oxide films involving charge densities greater than ca. 30 mC/cm² were not studied in the present work because of the increasing risk of electrode roughening and dissolution (see below) with film thickness and hence the danger of damaging the Pt-coated crystal.

Figure 6 shows that the mass change measured during β -oxide reduction is directly proportional to the charge density of films grown for various lengths of time. The approximate linearity of this plot suggests that the β -oxide film properties are constant over this range of film thickness. The slope of the plot yields a ratio of 12–12.5 g/mol electrons. If the β -oxide film is assumed to be in the Pt(IV) oxidation state, this result does not concur with the ratios of 8 and 17 g/mol electrons predicted for reactions (3) and (5) respectively, i.e. for either PtO_2 or $\text{Pt}(\text{OH})_4$ formation–reduction. If these β -oxide films contain HSO_4^- ions [6,17], e.g. $\text{Pt}(\text{OH})_3\text{HSO}_4$, then the mass change measured should have been even higher, i.e. 37 g/mol electrons. The comparatively low mass change of ca. 12 g/mol

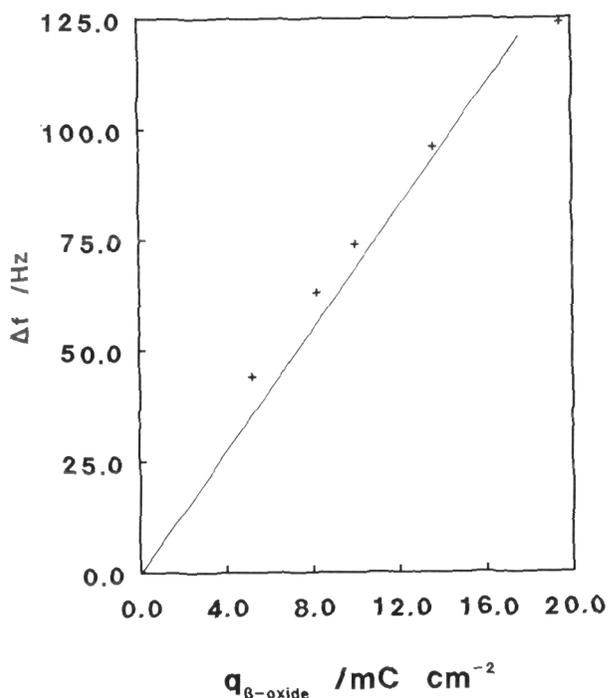


Fig. 6. Measured frequency change during reduction of β -oxide films formed at 5 V/s between 0.5 and 2.82 V in 0.5 M H_2SO_4 solutions for times ranging from 1 to 10 min.

electrons measured in the present work is consistent with the following form of β -oxide, for which a 12.5 g/mol electrons ratio would be predicted:



It is feasible that thicker β -oxide films, such as those formed in the work of Burke and coworkers [15–21], would be different in structure and could contain sulfate or bisulfate ions, particularly when two forms of β -oxide are thought to be present. Also, films formed by potential pulsing methods, using different upper potential growth limits and in solutions of different concentration or pH may lead to a different β -oxide structure or composition. Further investigations of these possibilities are presently under way.

Potentiostatic versus potentiodynamic β -oxide reduction

In earlier work [27], it was reported that when β -oxide films are reduced by sweeping to the foot of the reduction peak, e.g. 0.35 V, and the potential is then held fixed for periods of up to 10 min, followed by potentiodynamic reduction of the remaining β -oxide film, the total cathodic charge passed was significantly greater than when the films were reduced in a single uninterrupted potential

sweep. It was argued [27] that either not all the β -oxide film was being reduced using the potential sweep reduction method, while potential holding enabled complete film reduction, or that another electrochemical reaction was occurring during potential holding, resulting in the passage of additional cathodic charge. As solutions were always rigorously treated to remove dissolved oxygen, it was suggested [27] that dissolved Pt produced during β -oxide growth could be redeposited on the electrode in the potential holding phase. These suppositions have been examined in the present study using the in-situ mass measurement technique.

Two sets of experiments were carried out, one in which the potential was held at 0.340 V and another in which it was held at 0.390 V (see Fig. 5(a) for reference) for 5 min β -oxide films. When using the potential hold-sweep mode of reduction, the measured mass change per mole of electrons fell to ca. 10 (compared with 12 with sweep reduction (Fig. 6)). It is important to note that if the notion of incomplete film reduction during sweep reduction were correct, then the measured mass change should have been lower, rather than higher, than the mass change in the hold-sweep reduction mode. In fact, the lower mass change measured in the latter case supports the notion that dissolved Pt is deposited with time of potential holding, such that the observed net mass change during oxide reduction is diminished. This explanation is also consistent with the observed gradual loss of mass of the Pt-coated crystals which are subjected to repeated β -oxide growth-reduction cycles, indicative of Pt dissolution in these experiments.

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