Recovery of Active Surface Sites of Shape-Controlled Platinum Nanoparticles Contaminated with Halide Ions and Its Effect on Surface-Structure

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The interaction of halide ions (I⁻, Br⁻, Cl⁻) with well-cleaned faceted platinum (nanocube, cuboctahedral) nanoparticles and platinum polycrystalline is investigated in 0.5 M H₂SO₄ electrolyte. Under electrochemical conditions, the Pt surface gets poisoned with halide ad-atoms and it causes the attenuation of both hydrogen adsorption/desorption in the lower potential region (0.06–0.4 V) and electrooxidation of Pt nanoparticles in the higher potential region (0.6–1.2 V). Above certain concentration (5 × 10⁻⁶ M), the strongly adsorbing I⁻ ions mask the Hupd features. On the other hand, Br⁻ and Cl⁻ ions alter the peak features in the Hupd region, those are characteristic of different Pt surface sites. On excursion to higher potentials (∼1.2 V), concurrent halogen evolution, Pt oxidation, and oxygen evolution are observed; the increase in peak intensity in the Hupd region reflects the reconstruction of the Pt surface. To remove the adsorbed halide ions from the Pt surface, an in-situ potentiostatic method is employed, which involves holding the working electrode at ~0.03 V in 0.1 M NaOH solution. The cleanliness and retention of surface-structure are confirmed from the voltammograms recorded in the test electrolyte and the recovery of oxygen reduction reaction (ORR) activity after cleaning the Br⁻ ion-contaminated Pt surface supports this conjecture.

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Manuscript submitted February 28, 2017; revised manuscript received May 31, 2017. Published June 17, 2017.

Anions specifically adsorbed on precious metal surfaces adversely impact several electrochemical reactions including oxidation/reduction, metal deposition, corrosion and dissolution. 1-4 Catalyst poisoning by the adsorbed anions (halides, sulfates and others) is a well-known phenomenon and it decreases the activity of electrocatalysts; for example, in fuel-cell, batteries and electrolysers. 7,8 Especially platinum, a material for catalyzing a variety of electrochemical reactions, is prone to get poisoned in the presence of ad-atoms/adsorbates/solution anions under electrochemical conditions. Thus, oxygen reduction reaction (ORR) in fuel cells is affected by the adsorbed species or impurities and it is highly dependent on the cleanliness and surface structure of the catalyst. 8-13 In hydrogen–bromine fuel cells, bromides and bromine species migrate across the membrane and poison the hydrogen-electrode catalyst; moreover, Pt dissolves in Br⁻ ion-containing solutions. 8

Effects of cations (Na⁺, K⁺, etc.), anions (chlorate, bi-sulfate, etc.) and impurities (halides, phosphates, ammonium, CO, SO₂, H₂S, etc.) on ORR and organic molecule oxidation reactions with platinum single crystal electrodes are well documented in the literature. 10-21 Feliu et al., Abruna et al., and others have extensively investigated the influence of halides (I⁻, Br⁻, Cl⁻) on platinum single crystal electrodes. 22-35 Most of the available surface sensitive techniques were used to elucidate adsorbate coverage and structure. Such techniques, including auger electron spectroscopy (AES), low energy electron diffraction (LEED), second harmonic generation (SHG), surface X-ray scattering (SXS), electrochemical scanning tunneling microscope (ESTM) 35,34 and electrochemical quartz crystal microbalance (EQCM), used to investigate anion adsorption have offered significant insight on the dependence of adsorption process on exposed single crystal orientations. Thus, AES/LEED studies revealed that Cl⁻ ion adsorption occurs on Pt(100) surface at lower potential than that with Pt(111) surfaces, indicating the higher susceptibility of the former to Cl⁻ ion poisoning. 3 Bagotzky et al. reported that the chemisorbed I⁻, Br⁻, Cl⁻ ions, and organic species present on smooth platinum electrode surface affect the distribution of adsorbed hydrogen and therefore the Hupd area. 36

The adsorption of halides on platinum is a complex process and it is affected by several factors including the crystal facets, concentration of the halide species, pH, potential and the temperature. 7-24 Most of these investigations were conducted under ultra-high vacuum conditions using single crystal surfaces. Inferences obtained from those studies cannot be implied directly on the bulk polycrystalline catalyst surfaces.

Recently, Devivaraprasad et al. established the adsorption of solution anions with lower potential cycling, which results in the decrease of Hupd area and the reconstruction of faceted Pt nanoparticles with higher potential cycling. 42 The relative adsorption strength of anions (F⁻ < ClO₄⁻ < HSO₄⁻ < OH⁻ or ad-OH species < Cl⁻ < Br⁻ < I⁻) decides whether the surface is regenerated in the Hupd region in H₂SO₄ or HClO₄ electrolyte during the potential excursion to 1.2 V. Or the reconstruction takes place by the exchange of ad-layer of anions with the oxygenated species; all these affects the surface structure and electrochemical surface area (ESA) and thus the electrochemical reactions simultaneously. Thus, there is a need to redeem the platinum surface devoid of impurities for long-term durability and sustained catalytic activity. Therefore, it is imperative to investigate the interaction of halide ions along with the solution anions on Pt nanoparticle surfaces and further to develop an in-situ method to recover ESA from contaminated Pt surface.

In this work, Pt-NC (platinum nanocube), Pt-CO (platinum cuboctahedral) and Pt-PC (platinum polycrystalline) morphologies are confirmed using ex-situ high resolution transmission electron microscopy (HR-TEM) and the fraction of {100}/{111} sites are estimated through the irreversible adsorption of Ge and Bi. Subsequently, these nanoparticles are subjected to voltammetric investigation in halide-free acidic electrolyte (0.5 M H₂SO₄) and that contaminated with different concentrations of halide ions (I⁻, Br⁻, Cl⁻). The investigations conducted over a wide range of halide ion concentration and potential reveal the significance of specific adsorption. The results obtained with shape-controlled Pt nanoparticle surface are compared to that reported with single crystal well-defined surfaces. Thereafter, two methods are used to clean the surface: (i) potential cycling and (ii) NaOH cleaning. The former causes reconstruction of the surface and complete recovery of the active surface is too difficult. The latter removes the adsorbed halide ions without perturbing surface structure of the shape-controlled nanoparticles. It is found that the halide ions on Pt surface effectively retards the reconstruction when cycled in the potential region of 0.06–1.2 V and the ORR. These investigations with shape-controlled nanoparticles helps bridge the gap between well-defined single crystal surfaces and the polycrystalline Pt nanoparticles. The findings in the present work have
prominent relevance to catalyst durability and activity in electrocatalytic applications.

**Experimental**

**Materials.**—Potassium tetrachloroplatinate (K₂PtCl₄), tetra-decyltrimethyl ammonium bromide (TTAB) and sodium poly-acrylate (PAA) from Alfa Aesar; bismuth (III) oxide (Bi₂O₃) and germanium (IV) oxide (GeO₂) procured from Sigma Aldrich; sodium carbonate (Na₂CO₃), sodium bisulfite (NaHSO₃), sodium borohydride (NaBH₄), potassium chloride (KCl), potassium iodide (KI) from Merck; ultrapure ethanol (EMSURE quality); potassium bromide (KBr), potassium iodide (KI) from Merck; ultrapure water. ORR voltammograms were recorded in oxygen-saturated electrolyte with a rotating disk electrode at a scan rate of 20 mV s⁻¹. The contributions from different facets, those terrace sites and the other due to the strongly adsorbed Bi and Ge voltammogram with that of the Hupd region of the shape-controlled nanoparticles is less than 100%, and therefore, particles with other morphologies also coexist with the desired nanoparticles. Moreover, an impressive electrochemical and catalytic response characteristic of well-cleaned surfaces with the shape-controlled nanoparticles is obtained (see the discussion on voltammetric analysis).

**Synthesis and Cleaning of Pt-NC, Pt-CO and Pt-PC nanoparticles.**—Pt-NCs and Pt-COs were synthesized from K₂PtCl₄ precursor, using sodium poly acrylate (PAA) and tetra-decyltrimethyl ammonium bromide (TTAB) capping agents, respectively. Pt-PC nanoparticles were synthesized through the sulfito-complex route following the conventional sodium borohydride (NaBH₄) reduction. The as-synthesized nanoparticles were centrifuged at 15,000–16,000 rpm for 30 min. and were washed repeatedly with excess of ethanol 3–4 times. The cleaned Pt nanoparticles were used for the physical and electrochemical characterizations.

**Physical characterization.**—The HR-TEM and STEM images of Pt nanoparticles were recorded using a JEOL JEM 2100 F field emission electron microscope operated at 200 kV. The Pt nanoparticles were dispersed in ethanol, drop-cast on a Cu-grid and dried under an IR lamp (to remove the solvent and moisture content) prior to recording the images.

**Electrochemical characterization.**—A measured amount of the cleaned nanoparticles (5 mg) was taken in a glass bottle and 5 mL of ultrapure water was added to it. The mixture was then ultrasonicated for 30 min. to get a fine free flowing ink. A measured volume of the catalyst ink was drop-cast on the rotating disk electrode (RDE) (loading ∼30 μg cm⁻²) and it was dried at room temperature. The electrochemical measurements were performed in a conventional three-electrode electrochemical cell. A Pt wire was used as the counter electrode and the reference electrode was Ag/AgCl (double junction with outer tube filled with saturated KCl). The potential was controlled using a WaveDriver 21 Bipotentiotstat/Galvanostat system from Pine Research Instrumentation, USA. Cyclic voltammograms (CVs) were recorded at a scan rate of 50 mV s⁻¹ in argon-saturated 0.5 M H₂SO₄ electrolyte. All the potentials were recorded vs. Ag/AgCl but are reported vs. reversible hydrogen electrode (RHE) throughout this work. The surface structure of the shape-controlled Pt nanoparticles was examined through in-situ irreversible Bi and Ge adsorption and by the ex-situ HR-TEM analysis. The fraction of {111} and {100} terrace sites were estimated by comparing the charge obtained from the irreversibly adsorbed Bi and Ge voltammogram with that of the Hupd region of the respective blank voltammograms.

A potentiostatic method was used to recover the active surface sites, which involves holding the halide ion contaminated Pt electrode in strongly adsorbing electrolyte (i.e., in 0.1 M NaOH) for ~15 min. at ~0.03 V vs. RHE. The cleanliness and recovery of the active surface were confirmed from the voltammetric features recorded in the test electrolyte (0.5 M H₂SO₄) and the same were compared with the results obtained from the working electrode cleaned with ultrapure water. ORR voltammograms were recorded in oxygen-saturated electrolyte with a rotating disk electrode (RDE) at a scan rate of 20 mV s⁻¹ with 1600 rpm with and without Br⁻ ion contamination.
On extending the upper potential above 0.8 V (upto 1.2, 1.4 and 1.6 V) the electroxidation features of Pt are observed as shown in Fig. 2 (indicated by red, blue and green lines). Also see Fig. S1 where the precious metal features are evident in Hads/des region (0.06–0.4 V), and double layer region (0.4–0.65 V).

The formation of oxide monolayer on Pt at higher potentials irreversibly roughens the ordered terrace surfaces with the intrusion of defects; thus, Pt surface reconstruction happens at a potential of 1.2 V. When the potential is increased to 1.4 V, the flat region observed is attributed to the formation of superoxides of platinum. Oxygen evolution reaction (OER) is evident at further higher potentials (1.6 V). Conway et al. documented these findings with Pt electrodes.\(^{(51)}\) Recently, Savaleva et al. established three types of potential of 1.6 V. When the potential is increased to 1.4 V, the flat region observed is attributed to the formation of superoxides of platinum.

Reactions at the oxide formation region:

\[
\begin{align*}
\text{Pt} + \text{HOH} &= \text{PtOH} + e^{-} + H^+ \quad [1] \\
\text{PtOH} &= \text{PtO} + e^{-} + H^+ \quad [2] \\
\text{PtO} + \text{HOH} &= \text{PtO}_2 + 2e^{-} + 2H^+ \quad [3]
\end{align*}
\]

Reaction at OER:

\[
2\text{HOH} = O_2 + 4e^{-} + 4H^+ \quad [4]
\]

However, anions such as halides (I\(^{-}\), Br\(^{-}\), Cl\(^{-}\)) not only adsorb irreversibly on the metal surface but also interfere in the hydrogen adsorption and Pt oxidation processes. The extent of hindrance depends on their adsorption strength, and it is in the order of I\(^{-}\) > Br\(^{-}\) > Cl\(^{-}\). Furthermore, there exists a multi-fold reduction in the ORR activity under the influence of halide ad-atoms due the active site blocking effect. Similar decrease in ORR activity is observed with the catalysts in an operando fuel cell due to the presence of Cl\(^{-}\) and Br\(^{-}\) ions.\(^{(6,14,15,18)}\)

Thus, it is imperative to investigate the influence of other ad-atoms/anions along with the solution anions on metal nanoparticles. In the following, the adsorption processes are elucidated with sequential potentiodynamic experiments carried out with different concentrations of anions and the investigation of site blocking effect of the halide ad-atoms is done with shape-controlled and polycrystalline Pt nanoparticles.

### Iodide adsorption on shape-controlled and polycrystalline Pt nanoparticles

In 0.5 M H\(_2\)SO\(_4\) electrolyte without any contamination, presumably one hydrogen atom occupies a Pt site during hydrogen adsorption. The coverage of bulkier anions (sulfate/chlorate) is much less than that of hydrogen on the Pt surface, may be due to steric/mass-transport effects. However, if the potential range is limited to 0.06–0.6 V, the number of adsorbed anions on the Pt surface increases gradually with potential cycling, resulting in the reduction of H\(_{upd}\) area (see the Fig. S2).\(^{42}\) The surface is regenerated in the H\(_{upd}\) region after potential excursion to 1.2 V (Fig. S3). Therefore, surface sites free of adsorbed species are regenerated on the reverse scan to form complete H\(_{upd}\) feature. In addition, when oxygenated species (OH) is adsorbed on Pt (at potential above ~0.7 V), an H\(^+\) is also generated which combines with SO\(_4^{2-}\) to form HSO\(_4^-\) and thus converts to H\(_2\)SO\(_4\). Perhaps, during the lower potential cycling (below 0.65 V), once hydrogen is desorbed, HSO\(_4^-\) ions may accumulate in the electrolyte; anions might adsorb any available surface sites to attain more stable state.\(^{42}\)

Reactions at H\(_{upd}\) region:

\[
\begin{align*}
\text{Pt} + H^+ \left[\text{HSO}_4^-\right] &= \text{Pt-H} + \left[\text{HSO}_4^-\right] \quad [5] \\
\text{Pt} + \left[\text{HSO}_4^-\right] &= \text{Pt-H} + \left[\text{SO}_4^{2-}\right] \quad [6]
\end{align*}
\]

These dynamic surface processes do get affected in the presence of halide ions (I\(^{-}\), Br\(^{-}\), Cl\(^{-}\)) or impurities. Fig. 3 shows the CVs recorded in 0.5 M H\(_2\)SO\(_4\) solution with different concentrations of I\(^{-}\) ions. With minute amount of I\(^{-}\) ions in the electrolyte, i.e., 5 × 10\(^{-6}\) M, the H\(_{upd}\) area decreases gradually (see Fig. S4) with potential cycling and with higher concentration of I\(^{-}\) ions the voltammetric features are significantly affected (Figs. 3a, 3b and 3c).

This observation is similar to that reported with the potentialdynamic studies conducted in 0.5 M H\(_2\)SO\(_4\) electrolyte (see Fig. S2) without ad-atoms in the lower potential range (0.06–0.6 V). It is to be noted that the decrease in H\(_{upd}\) area with cycling in pure H\(_2\)SO\(_4\) is much slower as compared to that in contaminated H\(_2\)SO\(_4\) electrolyte. This is due to the higher adsorption strength of I\(^{-}\) ions that of the solution anions, which causes a greater ionic concentration at the Pt

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**Figure 2.** CVs of Pt-NC (a), Pt-CO (b), and Pt-PC (c) nanoparticles in argon-saturated 0.5 M H\(_2\)SO\(_4\) electrolyte recorded at a scan rate of 50 mV s\(^{-1}\).

\[\text{Reaction at OER:} \quad 2\text{HOH} = O_2 + 4e^{-} + 4H^+ \quad [4]\]

- **Fig. 2 (indicated by red, blue and green lines).**
- **Initial CV up to 0.8 V**
- **CV up to 1.2 V**
- **CV up to 1.4 V**
- **CV up to 1.6 V**

On extending the upper potential above 0.8 V (upto 1.2, 1.4 and 1.6 V) the electroxidation features of Pt are observed as shown in Fig. 2 (indicated by red, blue and green lines). Also see Fig. S1 where the precious metal features are evident in Hads/des region (0.06–0.4 V), and double layer region (0.4–0.65 V).

The formation of oxide monolayer on Pt at higher potentials irreversibly roughens the ordered terrace surfaces with the intrusion of defects; thus, Pt surface reconstruction happens at a potential of 1.2 V. When the potential is increased to 1.4 V, the flat region observed is attributed to the formation of superoxides of platinum. Oxygen evolution reaction (OER) is evident at further higher potential of 1.6 V. Conway et al. documented these findings with Pt electrodes.\(^{(51)}\) Recently, Savaleva et al. established three types of surface species using near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS)\(^{(52)}\) at potentials close to the onset of Pt electrooxidation: (i) adsorbed O/OH, (ii) PtO and (iii) PtO\(_2\). The pre-adsorbed or chemisorbed (HSO\(_4^-\)) solution anions will be replaced by the formation of 2D-array of adsorbed O/OH at the onset of the electrooxidation of Pt.

Reactions at the oxide formation region:

\[
\begin{align*}
\text{Pt} + \text{HOH} &= \text{PtOH} + e^{-} + H^+ \quad [1] \\
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\[
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Further increase in the concentration of I$^-$ ions in the electrolyte leads to the complete suppression of both H$_{upd}$ and Pt oxidation/reduction features. A featureless CV with a double layer region is obtained at a concentration of $1 \times 10^{-3}$ M with Pt-NC, Pt-CO and Pt-PC nanoparticles. Only a small adsorption peak corresponding to I$^-$ ions is observed at $\sim$0.6 V even when the electrode is cycled in the potential region of 0.06–1.2 V (Pt oxidation or I$_2$ evolution features are not observed in this potential region).

Figs. 3d, 3e and 3f show the CVs of Pt-NC, Pt-CO, Pt-PC nanoparticles recorded in 0.5 M H$_2$SO$_4$ electrolyte at an I$^-$ ion concentration of $1 \times 10^{-3}$ M with upper potential limits of 1.2, 1.4 and 1.6 V. The strongly adsorbed I$^-$ ions do not allow the oxygenated species to adsorb and eventual Pt oxidation is hindered up to 1.2 V, unlike that observed in the absence of halides (Fig. 2) where the onset of the formation of oxygenated species is evident above 0.8 V.

Interestingly, when the upper potential limit is increased to 1.4 V and further to 1.6 V, the features corresponding to I$_2$ evolution (in the positive scan) from the respective Pt nanoparticles are observed.

$$[I^-] + [I^-] = [I_2]$$  \[7\]

The three peaks of different intensities observed during the anodic scan at $\sim$1.27, $\sim$1.37 and $\sim$1.47 V are due to the I$_2$ evolution from the adsorbed I$^-$ ions on ordered terraces and step sites of Pt nanoparticles concurrent with Pt oxidation; oxygen evolution occurs at a further higher potential. As the fraction of these sites varies from one shape to another, the relative intensities of I$_2$ evolution features also changes. These features are realized only when the electrode is cycled to 1.4 and 1.6 V since the I$_2$ evolution takes place beyond 1.2 V. In the reverse (cathodic) scan, concurrent Pt reduction and I$^-$ adsorption peaks are observed at potentials $\sim$1.17, $\sim$1.0 and $\sim$0.67 V corresponding to the Pt oxidation/ and I$_2$ evolution happening during forward scan (compare with Fig. 2, discussed earlier).

These peaks are clearly distinguished from the bulk OER happening at 1.8 V (see Fig. S5 (a)). Furthermore, the reconstruction of shape-controlled Pt nanoparticles can also be realized from the decrease in the peak intensity of I$_2$ evolution at 1.47 V observed due to adsorption of I$^-$ on ordered terraces (see Fig. S5 (a)). Thus, the ordered terraces converts to step sites and eventually to Pt-PC nanoparticles while cycling to higher potentials (upto 1.8 V).

Bromide adsorption on shape-controlled and polycrystalline Pt nanoparticles.—Fig. 4 shows the CVs recorded in 0.5 M H$_2$SO$_4$
solution with different concentrations of Br$^{-}$ ions. Significant differences are observed in the H upd region and oxide formation region as compared to the CVs recorded in I$^{-}$ ion contaminated electrolyte. With lower concentrations ($5 \times 10^{-6}$ M and $5 \times 10^{-5}$ M), features of the Br$^{-}$ ion adsorption appears concomitant with Hupd. This results in the suppression of Hupd features, but not to the same extent as is observed with the I$^{-}$ adsorption. On increasing the concentration above $1 \times 10^{-3}$ M, the peak features corresponding to \{100\} and \{111\} terraces at 0.32–0.37 and 0.5 V, respectively, are completely suppressed due to the replacement of sulfate anions with Br$^{-}$ ions. Moreover, it makes the voltammograms of all the surfaces exceptionally symmetrical and the H upd peaks become very sharp, indicating a coupling with Br$^{-}$ desorption.

With higher concentrations of Br$^{-}$ ions ($1 \times 10^{-2}$ M), two distinguishable peaks are observed in the H upd region. The peak feature at 0.07 V corresponds to adsorption/desorption of Br$^{-}$ ions along with hydrogen from the disordered sites or \{110\} sites at 0.32–0.37 and 0.5 V, respectively, are completely suppressed due to the replacement of sulfate anions with Br$^{-}$ ions. Moreover, it makes the voltammograms of all the surfaces exceptionally symmetrical and the H upd peaks become very sharp, indicating a coupling with Br$^{-}$ desorption.

Figure 4. CVs recorded in 0.5 M H$_2$SO$_4$+x M KBr (a) Pt-NC, (b) Pt-CO and (c) Pt-PC up to 0.8 V; CVs up to 1.2 V (dotted line for $1 \times 10^{-2}$ M and solid line for $1 \times 10^{-3}$ M), 1.4 V (dotted line for $1 \times 10^{-2}$ M KCl) and 1.6 V (solid line for $1 \times 10^{-2}$ M) with (d) Pt-NC, (e) Pt-CO and (f) Pt-PC recorded at a scan rate of 50 mV s$^{-1}$.
Figure 5. CVs recorded in 0.5 M H$_2$SO$_4$+x M KCl (a) Pt-NC, (b) Pt-CO and (c) Pt-PC upto 0.8 V; CVs upto 1.2 V (dotted line for $1 \times 10^{-2}$ M and solid line for $1 \times 10^{-3}$ M) and 1.6 V (solid line for $1 \times 10^{-2}$ M) with (d) Pt-NC, (e) Pt-CO and (f) Pt-PC recorded at a scan rate of 50 mV s$^{-1}$.

The relative intensity of the reduction feature at 0.7 V is higher than that of the peak present at 1.1 V with Pt-NC and Pt-CO nanoparticles in comparison to Pt-PC, and it reveals a higher extent of specific adsorption of Br$^-$ ions on the ordered terrace sites (Figs. 4d and 4e). This is further reinforced by the less intense peak in the H$_{upd}$ region at 0.15 V with Pt-PC nanoparticles (Fig. 4c) even at higher concentrations ($1 \times 10^{-2}$ and $1 \times 10^{-3}$ M).

Moreover, after cycling to 1.4 and 1.6 V, the step density increases (roughness). Thus, the reconstruction of shape-controlled Pt nanoparticles can be evidenced with the increase in the peak intensity at 0.07 V (peak feature at less positive potential). Therefore, the CVs of shape-controlled nanoparticles resemble the features of Pt-PC nanoparticles after cycling to 1.4 and 1.6 V (see the inset to Figs. 4d, 4e and 4f).

chloride adsorption on shape-controlled and polycrystalline Pt nanoparticles.—Fig. 5 shows the CVs recorded in 0.5 M H$_2$SO$_4$ with different concentrations of Cl$^-$ ions. Though the adsorption strength of Cl$^-$ is relatively lower than that of both Br$^-$ and I$^-$ ions, the H$_{ads}$ is significantly affected. However, the OH adsorption is observed above 0.8 V and the oxide formation at further higher potentials. Voltammetric features, with the different concentrations of Cl$^-$ ions and by varying the upper potential limits, seem to be similar to that of the Br$^-$ ion-contaminated electrolyte.

It can be observed that, with increase in concentration of Cl$^-$ ions from $5 \times 10^{-6}$ M to $1 \times 10^{-2}$ M, two distinguishable features develop in the H$_{upd}$ region at ~0.15 and ~0.23 V with shape-controlled...
Pt nanoparticles (Figs. 5a and 5b). Step wise contribution with Cl− observed at ∼0.15 V is significant with Pt-PC nanoparticles as was reported by Arruda et al.7 (Fig. 5c). With Pt-NC and Pt-CO nanoparticles, Cl− ions suppress the features corresponding to {100} terraces at 0.32–0.37 V. This confirms the irreversible adsorption of Cl− ions on Pt nanoparticles. The absence of the peak at ∼0.23 V with Pt-PC reveals that this contribution is due to adsorption of Cl− ions on the terrace sites. As long as the potential limit is less than 0.8 V, even with increased concentration of Cl− ions in the electrolyte, the sulfate ad-layer at 0.5 V is not disturbed. But, once the potential limit is increased to 1.2 V and further to 1.4 and 1.6 V, the sulfate ad-layer is replaced by Cl− ions. This is evidenced by the flat double layer observed with all the Pt nanoparticles at higher concentration of Cl− ions (1 × 10−3 M). Here, first the sulfate ad-layer is exchanged with the oxygenated species (OH), those are eventually replaced by Cl− ions. Thus, {111} terraces are less susceptible to the Cl− poisoning than {100} terraces. With higher potential cycling to 1.4 V and 1.6 V after Cl2 evolution, the concurrent Pt reduction and Cl− adsorption features are observed at ∼0.71 and ∼1.41 V, respectively, in the reverse scan. Also, the reconstruction of shape-controlled Pt nanoparticles can be observed, which is evidenced from the increase in the peak intensity at ∼0.15 V as observed in the case of Br− adsorption.

\[
\begin{align*}
\text{Pt} + [\text{Cl}]^- & \rightarrow \text{Pt}^{2+} - \text{Cl}^{\text{ad}} + e^- \quad [11] \\
\text{Pt}^{2+} - \text{Cl}^{\text{ad}} + e^- + \text{H}^+ & \rightarrow \text{Pt} - \text{H}^{\text{ad}} + [\text{Cl}] \\
[\text{Cl}]^- + [\text{Cl}]^- & \rightarrow [\text{Cl}]_2 \quad [13]
\end{align*}
\]

These dynamic surface processes with the addition of I−, Br− and Cl− ions are further realized at other concentrations as well (5 × 10−6 M, 1 × 10−5 M, 5 × 10−5 M, 1 × 10−4 M, 5 × 10−4 M, 1 × 10−3 M, 1 × 10−2 M, 2 M) as given in Fig. S8.

From the above discussion it is clearly evident that the Hupd area is drastically affected by the presence of halides (I−, Br−, Cl−). With the detailed voltammetric knowledge obtained with Pt single crystal electrodes as reported by Markovic et al. and others, there exists a significant contribution from the solution anions on Hupd, even in halide-free electrolytes such as in pure H2SO4 and HClO4.53,54 Irrespective of the electrolyte or contaminants present in the solution, anions do have a role in the Hupd region. Thus, anion with relatively higher adsorption strength can be used to remove the pre-adsorbed species and the electrocatalytic nature of Pt nanoparticles can be redeemed.

Recovery of active surface from halide ion-contaminated Pt nanoparticles in 0.5 M H2SO4 electrolyte.—Potentiostating the contaminated Pt electrode surface at 0.03 V in NaOH (strongly adsorbing) electrolyte should lead to the adsorption of OH− on the Pt surface repulsing the halide ions and other contaminants. Fig. 6 shows the chronoamperometry recorded in 0.1 M NaOH for the removal of adsorbed halide ions. Holding the shape-controlled Pt catalyst electrode in 0.1 M NaOH electrolyte for 10–15 min. at 0.03 V vs. RHE removes the halide ions and other impurities from the Pt surface. Further, excess of strongly adsorbing hydroxide species in the electrolyte allows replacement of bulkier oxyanions (HSO4−, ClO4−) and halide ions (I−, Br−, Cl−). The cleanliness of the Pt surface obtained by this method can further be confirmed from the CVs recorded in the test electrolyte (0.5 M H2SO4). This method is employed for all the halide ion contaminated surfaces and the results obtained are compared with that of the surfaces cleaned with ultrapure water.

Figs. 7a, 7b and 7c show the recovery of active surface sites of Pt-CO nanoparticles contaminated with I−, Br−, and Cl− ions respectively. Figs. 7d, 7e and 7f show the corresponding chronoamperometric voltammograms recorded in NaOH electrolyte. A sequential procedure was followed which involves recording the initial CV (gray line) before contaminating the electrolyte with the respective halide solutions (0.001 M KI, 0.01 M KBr, 0.01 M KCl) (as shown by blue lines). Thereafter, the electrolyte cell was replaced with the one containing argon-saturated 0.1 M NaOH solution in which the working electrode was subjected to the potential holding at 0.03 V for 15 min. In order to confirm the cleanliness, the electrolyte is again replaced with fresh argon-saturated H2SO4 solution. From the CVs recorded (see red and green lines in Figs. 7a, 7b and 7c), the rejuvenation of pristine Pt surface is evident and the surface obtained is devoid of any halide contamination (see Hupd area comparison Table ST2). Moreover, it should be emphasized that the clean Pt surface is achieved without the loss of surface structure, as indicated by the characteristic voltammetric features.

Especially, the most unstable features corresponding to ordered {100} terraces at 0.32–0.37 V along with the relatively stable bi-dimensional {111} terrace sites at 0.5 V are intact. It means that the recovery procedure adopted does not perturb the surface-structure. To ensure that the adsorbed halide ions are not present on the Pt surface, the working electrode was rotated at 1600 rpm for few seconds during the chronoamperometry measurement. The extent of the removal of adsorbed halide ions from the Pt surface is evident from the ex-situ STEM mapping (Fig. S9). Similar results are observed with the Pt-NC and Pt-PC nanoparticles (see the Figs. S10 and S11).

To emphasize the effectiveness of this method, the above results are compared with the voltammetric features of electrodes cleaned with ultrapure water. Figs. 8a, 8b and 8c show the surface recovery of Pt-CO nanoparticles contaminated with I−, Br−, and Cl− ad-atoms, respectively. As explained above, CVs are recorded sequentially for the cleaning procedure with NaOH electrolyte. After recording the CVs with the contaminated surfaces, the halide-contaminated electrolyte is removed and the working electrode is thoroughly washed with the ultrapure water. Then the electrolyte is replaced with fresh argon-saturated H2SO4 solution.

Contrary to the above procedure, complete recovery of active surface is not achieved, even after cycling to higher potential in the range of 0.06–1.4 or 1.6 V. With potential cycling to 1.2 V, no removal of adsorbed halides is observed, which is evident from the subdued features of both Hupd and the electroxidation of Pt nanoparticles. When the potential is increased to 1.4 V, the ad-atoms etch from the Pt surface. This is evidenced by the increase in the Pt reduction current at ∼0.8 V and by the increase in the peak feature at ∼0.125 V (see Figs. 8d, 8e and 8f). On increasing the upper potential limit to 1.6 V, the reduction current is further increased due to the formation of Pt superoxides, allowing the replacement of halide ad-atoms during oxide formation. There is a significant loss in area due to the unavoidable contribution from dissolution, and more importantly, shape-controlled Pt nanoparticles undergo reconstruction. All the characteristic features of faceted Pt nanoparticles are lost and it is evidenced by the increase in the peak
Figure 7. Recovery of Pt-CO nanoparticle surface from halide ions after holding the working electrode at $\sim 0.03$ V in 0.1 M NaOH (a) $1 \times 10^{-3}$ M KI + 0.5 M H$_2$SO$_4$ (b) $1 \times 10^{-2}$ KBr + 0.5 M H$_2$SO$_4$ (c) $1 \times 10^{-2}$ KCl + 0.5 M H$_2$SO$_4$; (d), (e), and (f) are the respective potentiostatic voltammograms.

at $\sim 0.125$ V and with loss of features at 0.32 and 0.5 V (corresponding to the loss of $\{100\}/\{111\}$ terraces). These findings are further confirmed with the ex-situ STEM and HR-TEM analysis as shown in Figs. S9 and S12. It can be observed that the Pt-CO nanoparticle morphology is retained since the surface-structure is unaltered with NaOH cleaning (Figs. S12 (a) and S12 (b)). On the other hand, with higher potential cycling Pt-CO nanoparticles are converted to polycrystalline as a consequence of reconstruction (Figs. S12 (c) and Figs. S12 (d)).

Similar results are observed with the Pt-NC and Pt-PC nanoparticles (see the Figs. S13 and S14). Therefore, the adopted surface cleaning method not only removes the contaminants effectively but also retains the surface-structure of shape-controlled Pt nanoparticles, avoiding the reconstruction and dissolution of Pt nanoparticles.

Further, the utility of the recovery procedure discussed above is applied to the ORR, which is one of the fundamental and profound electrochemical reactions. The structure-sensitivity of ORR is well-established in the literature and its kinetics is significantly affected by the anion (HSO$_4^-$, ClO$_4^-$, Br$^-$, Cl$^-$, I$^-$) adsorption and by the presence of other adsorbates or impurities in the electrolyte medium. In the present context, we have verified the in-situ cleaning procedure for ORR with Pt-CO nanoparticles contaminated with Br$^-$ ions.

Fig. 9 shows the ORR voltammograms recorded in oxygen-saturated 0.5 M H$_2$SO$_4$ electrolyte at 20 mV s$^{-1}$ with 1600 rpm before and after contamination with 0.01 M KBr solution. In the presence of Br$^-$ ions, there is a multi-fold decrement in the ORR activity as was observed with the single crystal electrodes.\textsuperscript{18} This is attributed to the active site blocking by the bromide species. ORR recorded again in fresh oxygen-saturated electrolyte with the contaminated electrode subjected to in-situ cleaning procedure is compared in Fig. 9 (red and blue lines). It is evident that the ORR activity is recovered and it is close to that observed before contamination. The characteristic ORR voltammetric features of pristine Pt are clearly evident and the surface is devoid of any contamination in fresh acidic electrolyte; however, the minimal decrease observed in the ORR activity after cleaning is attributed to the unavoidable contribution due to dissolution in the presence of excess halide ions.

Therefore, recovery method adopted could be beneficial in resolving the durability issues of Pt nanoparticles in fuel cell and flow batteries. Further, this method can be extended for the removal of other contaminants and to rejuvenate the pristine Pt surface for the durable and sustained electrocatalytic activity. However, in-situ spectroscopic methods can reveal some more fundamental evidence on the nature of halide adsorption on different Pt surfaces, which is beyond the scope of the present work.

Conclusions

Influence of halide ions (I$^-$, Br$^-$, Cl$^-$) on H$_{adls}$ and electroditation (reconstruction) of shape-controlled Pt nanoparticles (Pt-NCs and Pt-COs) and Pt-PC are investigated in 0.5 M H$_2$SO$_4$ electrolyte. The $H_{adls}$ area decreases with the addition of I$^-$ ions to the 0.5 M H$_2$SO$_4$
Figure 8. Recovery of Pt-CO nanoparticle surface from halide ions after cleaning the working electrode using ultrapure water (a) $1 \times 10^{-3}$ M KI + 0.5 M H$_2$SO$_4$ (b) $1 \times 10^{-2}$ KBr + 0.5 M H$_2$SO$_4$ (c) $1 \times 10^{-2}$ KCl + 0.5 M H$_2$SO$_4$; (d), (e), and (f) are the respective potentiodynamic voltammograms recorded up to higher potentials.

Figure 9. ORR voltammograms of Pt-CO recorded in halide-free and the contaminated 0.5 M H$_2$SO$_4$ solutions.
with ultrapure water does not recover the $H_{\text{aq}}$ area of nanoparticles completely. Importantly, the surface structure is not retained because of the potential cycling in the range of 0.06–1.4 and 0.06–1.6 V. Moreover, there is an unavoidable contribution from the dissolution of Pt nanoparticles in the presence of halide ad-atoms at extremely high potentials. The in-situ cleaning method is tested for ORR recorded with the Br$^-$ ion-contaminated Pt surface and it proves the effectiveness in recovering the contaminant-free active surface. These findings have prominent relevance in obtaining the rejuvenated platinum surfaces from the contaminated electrolytes with ad-atoms/impurities in various electrocatalytic applications.

Acknowledgments

Department of Science and Technology (DST), India, is acknowledged for financial support of the project through a grant SR/S1/PC−various electrocatalytic applications.



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