On the Stability of Pt-Based Catalysts in HBr/Br$_2$ Solution

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Dedicated to Prof. Antonio Togni on the occasion of his 65th birthday.

Stability studies on supported metal nanoparticles are essential for gaining insight into the design and optimization of high-performance materials. In this work, the dissolutions of Pt-based catalysts in HBr/Br$_2$ mixture of various concentration regimes were studied and correlated with material structural properties. The dissolution of metal nanoparticles was enhanced by adding Br$_2$ to the HBr solution. Comparing with commercial Pt/C catalyst, the well-alloyed PtIr/C catalyst was observed to exhibit high resistance towards dissolution. In addition, regulating the accessibility of the metal sites to dissolution-inducing species contributed to the marked stability of the nanoparticles in HBr/Br$_2$ solutions, as shown for the surface-modified PtIr/C catalysts with organic diamine molecules.

Keywords: bromine, hydrobromic acid, metal dissolution, stability, supported catalysts.

Introduction

Heterogeneous catalysts, consisting of metal nanoparticles (NPs) and a solid support, are widely applied in energy-related fields.$^{[1–3]}$ Precious metal-based catalysts such as Pt/C (platinum NPs supported carbon material) hold great promise for a number of catalytic transformations. Challenges associated with unstable performance and easy deactivation limit the practical application of these catalysts.$^{[4–6]}$ Deactivation tends to become more severe for supported metal-based catalysts at high temperatures as well as in an oxidizing atmosphere and in condensed corrosive solvents. An in-depth understanding of catalyst deactivation is, therefore, crucial for the rational design and optimization of (electro)catalysts with high stability.$^{[7–9]}$

During cell operations, the direct contact with liquid electrolytes and continuous potential fluctuations usually put a greater demand on the durability of electrocatalysts, because electrocatalytic properties can be critically hindered by catalyst degradation.$^{[10–16]}$ The degradation of supported metal NPs is generally reported to originate from dissolution, detachment from the support, coalescence and sintering.$^{[17–20]}$ In particular, metal NPs dissolution usually occurs through direct chemical reactions with reactants and/or electrolyte components accompanied by (electro)catalytic oxidation and reduction processes.$^{[9,11,13,21,22]}$ As well as being determined by the intrinsic structural properties of the catalyst, the intensity of the dissolution of supported metal NPs tends to vary, depending on the applied operating conditions in energy conversion and storage.
For instance, hydrogen-bromine redox flow batteries (H₂-Br₂ RFBs) involve highly reversible reactions at the anode and cathode side by flowing with H₂ gas and acid electrolyte composed of protons (H⁺) and oxidizing Br₂ species. Platinum-based catalysts still serve as the most active H₂-related electrode materials. Considerable degradation in performance often occurs due to the strong and irreversible sorption/oxidation property of Br₂ on Pt metal surface. Long-term practical durability of Pt-based catalysts is hence desirable when contacting with highly concentrated HBr/Br₂ solutions in H₂-Br₂ RFBs. In this regard, the studies on how the carbon-supported Pt-based NPs dissolve in Br₂-containing solutions and the factors that influence this can aid in optimizing and improving catalyst dissolution resistance. Up to now, however, only a few such stability studies have been published; their focus is mainly on the dipping of the Pt-based catalyst into an acidic HBr solution without Br₂ before carrying out electrical measurements.

Here, we report on the systematic evaluation of the stability of Pt/C with a regulated particle size and PtIr/ C consisting of PtIr alloy NPs in HBr/Br₂ solution with different concentration regimes. Polybromide anions (i.e., Br₅⁻) in the HBr/Br₂ solution accelerated the dissolution of metal NPs. Metal dissolution rates depend to a great extent on the size of the NPs and the surface property rather than on the concentration of Br₂ in the investigated HBr/Br₂ solutions. Sterically limited accessible sites on the PtIr/C-based catalysts after surface organic modification were responsible for the observed marked resistance towards dissolution. The findings in this work serve to provide proper guides on the design of durable (electro)catalysts, which are applied especially in HBr/Br₂ solution-involved catalytic system, such as membraneless H₂-Br₂ RFBs.

Results and Discussion

Structural and Dissolution Properties of the Pt/C Catalysts

The studies on the dissolution of carbon-supported metal NPs began with the selection of the commercial Pt/C catalyst (Alfa Aesar), the catalyst which is used most frequently in electrocatalytic transformations. Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis demonstrated that 40 wt-% of Pt was loaded on carbon. Figure 1,a is the TEM image of Pt NPs with a diameter of 1.0–2.0 nm, uniformly dispersed on the support. In order to investigate the
effect of particle size on metal dissolution, Pt/C was annealed at 350°C and 700°C in a N₂ atmosphere. Carbon-supported Pt NPs with a mean diameter of 3.5 nm and 5.0 nm were obtained on the Pt/C-350 and Pt/C-700, respectively (Figure 1,b and 1,c). When Pt/C is not heated, it is referred to as Pt/C-uncal.

Table S1 (Supporting Information) lists the concentrations of the solutions in the HBr/Br₂ series. In practical H₂-Br₂ RFBs, the concentration of Br₂ species in the electrolyte at different states of charge is around 6–8 M (m: molar L⁻¹) to meet the requirement on power density. In this regard, HBr/Br₂ solutions in our work with the concentration of 5.6 M/0.6 M, 4.8 M/0.9 M, 4.0 M/1.3 M, 3.2 M/1.7 M, 2.4 M/2.1 M represent the electrolyte compositions due to the Br⁻/Br₂ redox reactions in H₂-Br₂ RFBs. All the dissolution experiments in this work were carried out at room temperature (25.0°C). Figure 2,a presents Pt NPs dissolution profiles for the Pt/C catalysts after 16 h in HBr solution with a concentration ranging from 8.2 M to 2.4 M. The highest degree of dissolution (66%) was found for the Pt/C-uncal. in 8.2 M HBr, while that were much lower for Pt/C-350 and Pt/C-700 having larger metal particle size. With a decrease in HBr concentration, the degree of Pt dissolution also tends to decrease. In comparison, however, as shown in Figure 2,b, severe dissolution (more than 80%) of Pt NPs from Pt/C-uncal. and Pt/C-700 had taken place in HBr/Br₂ solutions after 2 h. Even when the reaction time was reduced to 40 min, the extent of Pt dissolution was still high (over 60%). All the investigated Pt/C-uncal., Pt/C-350 and Pt/C-700 exhibited almost complete Pt dissolution in HBr/Br₂ solutions when immersing for 16 h (Figure S1). The above results indicate that nanoparticle size played an important role in the dissolution of Pt NPs in acidic HBr solution, because the surface amount of low-coordinated atoms and the chemical potential for dissolution vary with the size of nanoparticles. Besides, the addition of Br₂ into the HBr solution can
significantly accelerate the dissolution of Pt NPs. As shown in Figure S2, the enhancement of Pt dissolution by adding Br₂ to the HBr solution was more remarkable for 2.4 M HBr with the highest Br₂ concentration (2.1 M).

In bromide/bromine-containing solution, polybromide complexes such as tribromide (Br₃⁻) and pentabromide (Br₅⁻) anions are formed through the Eqns. 1 and 2:

\[ \text{Br}^- + \text{Br}_2 \rightleftharpoons \text{Br}_3^- \]  
\[ \text{Br}^- + 2 \text{Br}_2 \rightleftharpoons \text{Br}_5^- \]  

The equilibrium constant for the formation of Br₃⁻ and Br₅⁻ anions are expressed by Eqns. 3 and 4. Earlier literatures have reported the \( K_3 \) value in the range of 16 to 20 L mol\(^{-1}\) (at 25.0°C),\(^{32-35}\) while that of \( K_5 \) is between 19 and 41 L² mol\(^{-2}\).\(^{33-36}\)

\[ K_3 = \frac{[\text{Br}_3^-]}{[\text{Br}^-][\text{Br}_2]} \]  
\[ K_5 = \frac{[\text{Br}_5^-]}{[\text{Br}^-][\text{Br}_2]^2} \]  

The [Br₅⁻], [Br₃⁻], [Br₂⁻] and [Br⁻] refer to the equilibrium concentration of Br₅⁻, Br₃⁻, Br₂ and Br⁻ in the HBr/Br₂ solution, respectively.

For the series of HBr/Br₂ solution employed for the dissolution of Pt/C, the equilibrium concentration of Br⁻, Br₂ and polybromide (Br₃⁻ and Br₅⁻) anions were simulated based on the initial concentration of HBr and Br₂, as well as the \( K_3 \) (16 L mol\(^{-1}\)) and \( K_5 \) (37 L² mol\(^{-2}\)).\(^{37}\) As shown in Figure S3, Br₂ was almost dissolved in the highly concentrated HBr solution by forming Br₃⁻ as the dominant species (more than 95%). Then we performed ultraviolet visible spectrometry (UV-Vis) measurements on the solution before and after Pt/C dissolution. Typically, from the spectra of 5.6 M HBr/0.6 M Br₂ (Figure S4a), the adsorption peak at 267 nm was likely assigned to the Br₃⁻ species,\(^{38,39}\) and the contributions by other polybromide anions such as Br₅⁻ and Br₇⁻ could not be ruled out. While that observed at 390 nm, with a much lower intensity, was the adsorption of Br₂.\(^{40}\) The UV-Vis analysis indicated that it is the polybromide anions formed through Br⁻/Br₂ equilibrium reactions rather than the bromide (Br⁻) that play a crucial role in enhancing the dissolution of carbon-supported Pt NPs. Furthermore, the bromoplatinic acid complex was distinguished from the two broad peaks centered at 315 and 260 nm in the UV-Vis spectra.\(^{41,42}\) This metal complex was also observable in pure HBr solution (comprising protons and Br⁻ anions) after the dissolution of Pt/C, which suggests that both Br⁻ and polybromide anions participated in the formation of Pt complexes in the HBr/Br₂ solution.

**Structural and Dissolution Properties of the PtIr/C Catalysts**

After studying the dissolution of Pt/C, PtIr alloys became the focus of the investigation on metal nanoparticle dissolution in HBr/Br₂ solutions. It has already been shown that PtIr alloyed catalysts are active in various electrocatalytic reactions.\(^{43-46}\) We obtained a PtIr/C catalyst with 40 wt-% metal loading on carbon material from TFP Hydrogen Products Ltd. This catalyst was developed to exhibit much higher activity than the commercial Pt/C towards the hydrogen evolution reaction (HER), which is the half-cell
reaction on the anode side of H₂-Br₂ RFBs. Carbon-supported PtIr NPs were characterized to be polycrystalline nature with a particle size distribution between 30 and 40 nm from the TEM images (Figure 3,a and 3,b). PtIr NPs were additionally observed to have porous nano-dendritic structures. It is worth noting that the particle size (6.6 ± 0.2 nm) of PtIr calculated based on XRD measuring is in essence not in agreement with that from TEM. It points out the PtIr nano-dendritics are formed by the aggregations of small nanoparticles during the synthesis. The bulk composition of PtIr NPs was found to have a Pt/Ir atomic ratio of 80 : 20, based on the analysis of energy-dispersive X-ray (EDX) spectra (Figure S4,c). HAADF-STEM mapping images (Figure 3,c) suggested that Pt and Ir were well-dispersed on the PtIr NPs, but they did not display the characteristic core-shell structure. The collected XRD pattern shown in Figure 3,d revealed the reflections at 39.93°, 46.42°, 67.83°, 81.57° 2θ angles, which were indexed as (111), (200), (220) and (311) planes of typical face-centered cubic (fcc) structure of Pt.[47] The absence of any phase of Ir (Ir⁰ JCDPS# 87-0715; IrO_x JCDPS# 88-0288) stands in line with the formation of a PtIr alloy phase in the resulting PtIr/C catalyst.[44,46] The lattice constant for PtIr/C was refined in the space group $Fm\overline{3}m$ to be 3.9076 Å and PtIr NPs had a nearly 100% of alloying degree,[45] as compared with that (3.9038 Å) calculated from Vegard’s law. These findings proved the formation of well-alloyed PtIr NPs on the prepared PtIr/C catalyst.

The extent of PtIr/C dissolution was evaluated under the similar conditions as for Pt/C. There was a gradual decrease in the amount of dissolved Pt from PtIr/C in the concentrated HBr as well as in the HBr/Br₂ solutions. In contrast to Pt/C, the enhancement of Pt dissolution as a result of adding Br₂ to the HBr was not as strong in the case of 2.4 M HBr/2.1 M Br₂ compared to that of 8.2 M HBr/0.3 M Br₂ (Figure 4). A similar tendency was found for Ir on PtIr/C (Figure S5). The lower degree of metal dissolution compared with Pt/C was probably a consequence of the distinct surface structure and the self-stability of PtIr nano-dendritics on PtIr/C. Furthermore, negligible metal dissolution occurred on PtIr/C when HBr was replaced by KBr in the case of 4.0 M KBr/1.3 M Br₂ (Figure S6). This confirmed that the synergy between highly concentrated H⁺ and the as-formed polybromide anions was linked to the rapid dissolution of carbon-supported Pt-based NPs.

The respective dependence of HBr and Br₂ on concentration with regard to the dissolution of PtIr NPs in a variety of HBr/Br₂ media was checked. Table S1 also shows the concentrations of HBr/Br₂ solution employed in this concentration-dependent study. The simulated concentrations of polybromide equilibria and Br₂ in these HBr/Br₂ solutions are plotted into Figure 5,a and Figure 5,c. Increasing the concentration of the initially added Br₂ could induce the formation of Br₅⁻ anions, but still maintain Br₃⁻ as the dominant species. The formation of heptabromide

![Figure 3. TEM (a), high resolution TEM (b) and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) mapping (c) images of PtIr/C. Scale bars are set as presented on the corresponding images. d) X-ray powder diffraction (XRD) pattern of PtIr/C with the standard X-ray diffraction lines of metallic Pt, Ir, and IrO_x plotted below.](image)

![Figure 4. Comparison of degree of dissolution of Pt from PtIr/C catalyst after the period of 16 h in the HBr (blue) and HBr/Br₂ mixtures (light brown).](image)
(Br$_7^-$) species at higher Br$_2$ concentrations should not be ruled out.\[^{37}\] Their exact amount, however, cannot be determined due to the lack of the equilibrium constant of Br$_7^-$ from the literature. Figure 5,b shows the rate of Pt dissolution (Ln(mmol/mg Cat./h); Ln is the natural logarithm function. There is a positive trend as a function of Ln(HBr)), showing a reaction order of ca. 4. However, a near-zero reaction order was determined from the dependence on Br$_2$ concentration (Figure 5,d). The dissolution of Ir from the Ptlr/C also exhibited similar concentration-dependent properties (Figure S7). These findings demonstrated that polybromide anions in HBr/Br$_2$ solution could easily get adsorbed on the surface of metal without transport/diffusion limitation.\[^{48}\] The dissolution of metal was supposed to be started through the dissociative reaction of adsorbed polybromide anions through the Br–Br bond cleavage on the metal sites and then eventually form the metal-bromide complexes. The representative UV-Vis spectra of the HBr/Br$_2$ solution after Ptlr/C dissolution showed a decreased intensity of the adsorption peak of polybromide species (Figure S8,a), which was most likely due to changes of the equilibrrious state of HBr/Br$_2$ solution after the formation of bromoplatinic acid and Ir-bromide complexes.

The representative XRD patterns in Figure S8,b with decreasing intensities of the diffraction peaks cor-
face-exposed Pt on PtIr NPs dissolved more easily than Ir. The observed positive shift of BEs for Ir and the high dissolution extent of Ir from PtIr/C was probably due to the disruptive effect of Pt dissolution, which might increase the amount of less stable low-coordinated surface Ir atoms.

**Structural and Dissolution Properties of the Surface Organic-Patterned PtIr/C**

Molecular patterning of the surface of metal by organics with -NH$_2$ functional groups is one of the effective strategies for enhancing the electrocatalytic properties of Pt-based electrocatalysts.$^{54-57}$ The fundamental basis of this strategy relies on the surface-engineered modifications by regulating the accessibility of metal sites to corrosive and/or poisoning adsorbates such as PO$_4^{3-}$, SO$_4^{2-}$ and crossover-obtained methanol molecule, etc. Inspired by this strategy, we fabricated several organic molecules (Figure 7), including cyclohexylamine (L1), aniline (L2), ethylenediamine (L3) and benzene-1,4-diamine (L4), onto the surface of PtIr NPs by using a facile dipping approach, followed by rinsing and drying steps (detailed in the Supporting Information). 5.6 M HBr/0.6 M Br$_2$ was selected for the evaluation of the stability of surface organic-modified catalysts, because it can induce a high degree of dissolution of PtIr/C after a certain time (Figure 4). From the dissolution in 5.6 M HBr/0.6 M Br$_2$ for 16 h, all the surface organic modified catalysts, with the exception of PtIr/C-L1, showed a marked decrease in the amount of dissolved Pt. In particular, as shown in Figure 7, 7.8% and below 1.0% of Pt dissolved from PtIr/C-L3 and PtIr/C-L4, respectively, which was significantly lower than the unmodified PtIr/C (80%). As expected, the dissolution of Ir species in PtIr/C-L3 and PtIr/C-L4 was undetectable under the given conditions.

A negligible amount of Pt and Ir dissolved from the PtIr/C catalyst during the surface organic modification, as indicated by the ICP-OES analysis of the L4 diamine-containing ethanol solution. Elemental mapping images of PtIr/C-L4 (Figure 8,a and Figure S10) illustrated that PtIr NPs had retained their geometric properties in terms of particle size, morphology or shape following surface organic modification. Due to the strong interactions between metal atoms and -NH$_2$ groups,$^{58,59}$ organic diamine molecules were still

**Figure 6.** High-resolution Pt 4f, Br 3d and Ir 4f spectra of PtIr/C materials dissolved under different HBr/Br$_2$ conditions compared to fresh PtIr/C (a). The conditions of dissolution are: b) 4.0 M HBr/2.1 M Br$_2$ 3 h; c) 4.0 M HBr/0.6 M Br$_2$ 3 h; d) 5.6 M HBr/0.6 M Br$_2$ 3 h; e) 5.6 M HBr/0.6 M Br$_2$ 48 h; f) 4.0 M HBr/0.6 M Br$_2$ 48 h; g) 4.0 M HBr/2.1 M Br$_2$ 48 h; h) 8.8 M HBr 48 h.

**Figure 7.** Dissolution of Pt from the un-modified PtIr/C and surface organic-modified PtIr/C after immersing in 5.6 M HBr/0.6 M Br$_2$ for 16 h. The molecular structures of the amines and diamines selected for the surface organic modifications of PtIr/C are presented above the dissolution column chart.

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Fourier transformation of the intensity of represents the corresponding fitting. The spectra exhibit the fitting results of PtIr/C and PtIr/C-L4. The original EXAFS spectra normalized XANES spectra at the Pt L3-edge decreased, possibly due to surface reduction of PtIr NPs by diamine molecules possessing electron-donating -NH2 groups. It was estimated from Pt L3-edge extended X-ray absorption fine structure (EXAFS) analysis (Figure 8,c, Table S3) that the first shell coordination number of both samples is about 10, which is characteristic of Pt nanoparticles. Since there is almost no difference between Pt and Ir absorbers, which have similar backscattering amplitudes and lattice parameters, it is impossible to distinguish between Pt or Ir atoms. Linear combination fitting of the Pt L3-edge X-ray absorption near edge structure (XANES) for PtIr/C (Figure S12) suggested that Pt may be present in an oxidized form, which accounts for only less than 5.5% of the total amount of Pt. Oxidized Pt species are, thus, ascribed to those species that are distributed on the surface of PtIr NPs, as shown by XPS (Figure 6). The lower amount (2.8%) of oxidized Pt after surface organic modification confirmed the formation of interactions between metal atoms and diamine molecules (L4) on PtIr NPs.

An evaluation of the accessible number of metal sites on PtIr NPs after surface organic modification by amine or diamine molecules was carried out. Pulse CO-chemisorption measurement (at 35°C) was performed, a commonly employed technology to determine the dispersion of metal NPs on metal-based catalysts. Metal dispersion was found to decrease due to surface occupation by the organic molecules through interactions between metal atoms and -NH2 groups of amine molecules. In particular, among the surface organic-modified samples, at least 85% of the surface sites on PtIr/C-L4 was lost (Figure S13). It is noteworthy that the synergy between highly concentrated H+ and polybromide anions accelerates the dissolution of metal NPs in acidic and oxidizing HBr/Br2 solutions. The marked stability of PtIr/C-L4 can, therefore, be explained by the steric limitation of accessibility of the metal surface to these dissolution enhancers, in particular, the polybromide anions.

The surface patterned molecules are beneficial for regulating the adsorption of spectator species on metal particle at the expense of blocking certain number of active sites, which is well documented in the literature in electrocatalysis field. Regarding this, we further collected the cyclic voltammograms of PtIr/C and surface organic-modified PtIr/C at a scan rate of 20 mV s⁻¹ in 0.5 m H2SO4 solution under Ar. The electrochemical surface area (ECSA), a critical parameter for electrocatalytic property, was calculated based on the hydrogen desorption charge as 0.21 μC mg⁻¹ Pt. The modification with L1, L2 and L4 organic was observed to decrease 22–25% of ECSA, while that of L3-modified PtIr/C showed 13% of loss (Figure S14). These results indicate that the surface organic-modified PtIr/C catalysts might possess the potential activities for the H2-related oxidation/evolution reactions, in particular, in the H2-Br2 RFBs. Evaluations on the performance of these catalysts in terms of electrocatalytic activity and stability are undergoing and will be covered in the following report.

**Conclusions**

In summary, the results of the present study show that the synergy between acidic H+ and polybromide anions (i.e., Br5− and Br7−) in HBr/Br2 solution contributed to the high level of dissolution of Pt-based nanoparticles from the carbon support. PtIr/C material,
which was characterized to feature well-alloyed and nanodendritic structural property, was more stable than Pt/C under similar dissolution conditions. Surface organic modification on PtIr nanoparticles by means of diamine molecules was effective in improving the dissolution resistance in acidic and oxidizing HBr/Br₂ solutions. Further studies on the electrocatalytic properties of the surface organic-modified PtIr/C catalysts are necessary to gain an in-depth understanding of the (electro)catalyst degradation mechanism and improvement of electrocatalytic efficiencies.

Notes
The content of this report does not reflect the official opinion of the European Union. Responsibility for the information in this publication lies entirely with the authors.

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Author Contribution Statement
J. A. van Bokhoven conceived the research; Q. Liu performed the dissolution experiments, analyzed the data, and wrote the manuscript; H. Meissel, S. Jones, and N. Van Dijk contributed the development of PtIr/C catalyst and providing of Pt/C catalyst; H. Meissel measured the CV curves of PtIr/C catalyst; I. Sadykov measured the XAS and processed the data fitting; P. Rzepka assisted with the XRD analysis and refined the XRD data; L. Artiglia developed XPS method and helped in analyzing the XPS data; Q. Liu, M. Ranocchiari and J. A. van Bokhoven revised the manuscript. All the authors have approved the final version of this manuscript.

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