

# Crossover-Tolerant Coated Platinum Catalysts in Hydrogen/Bromine Redox Flow Battery

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## **Abstract:**

The hydrogen-bromine redox flow battery's ( $\text{H}_2\text{-Br}_2$  RFB) advantages of high energy capacity, high round-trip conversion efficiency and low cost, make it an optimal candidate for large-scale energy storage systems. The crossover of bromide species through the membrane degrades the performance of the  $\text{H}_2\text{-Br}_2$  RFB by poisoning the catalyst responsible for the hydrogen evolution and oxidation reactions. Herein we propose the new concept of a selective catalyst coating layer that mitigates the effect of bromide crossover. The polymerization of dopamine on the catalyst surface yields a nanoscale conformal polydopamine layer which acts as a semi-permeable barrier to block bromide species. The  $\text{H}_2\text{-Br}_2$  RFB with the coated catalyst shows a low capacity fading of 6% at  $300 \text{ mA cm}^{-2}$  after exposure to 4.5 M charged electrolyte for 2 hours. Even the beginning of life polarization curves show the benefit of catalyst coating with a high peak power of  $\sim 550 \text{ mW cm}^{-2}$ . Hence, the catalyst coating opens a way to solve the crossover issue in  $\text{H}_2\text{-Br}_2$  RFB technology.

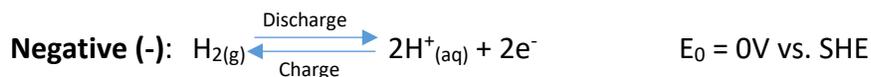
**Keywords:** electrochemical energy storage, redox-flow battery, electrocatalysis, catalyst, nanoparticle, bromine

## 1. Introduction

The large interest in renewable energy sources (e.g. solar and wind) during recent years has raised the demand for large-scale, low-cost and durable electrical energy storage (EES) solutions. Although the technology was previously known, Redox Flow Batteries (RFBs) have recently garnered attention as a highly promising choice for EES due to certain advantages over other EES solutions. RFBs are electrochemical energy conversion devices, which exploit redox processes of species in a fluid solution form, stored in external tanks and flowed into the RFB. High scalability and flexibility, independent sizing of power and energy, high efficiency, long durability and fast responsiveness allow for wide ranges of operational powers and discharge times, which along with a reduced environmental impact makes RFBs ideal for assisting EES from renewable sources.[1–3]

The hydrogen-bromine RFB (H<sub>2</sub>-Br<sub>2</sub> RFB) is one of the most interesting candidates for grid scale EES.[4] H<sub>2</sub>-Br<sub>2</sub> RFB technology displays several unique features such as the high volumetric energy densities of bromine catholyte (> 200 Wh L<sup>-1</sup>), the high abundance and low cost of bromine and a high stability of more than 10,000 hours without significant degradation.[5–9]

The reactions in the H<sub>2</sub>-Br<sub>2</sub> RFB are:



During charge the hydro-bromic acid decomposes to  $H_2$ , via the hydrogen evolution reaction (HER), and to  $Br_2$  on a carbonaceous electrode.  $H_2$  can be compressed and stored for use during the discharge cycle. During discharge,  $H_2$  oxidizes to  $H^+$ , the hydrogen oxidation reaction (HOR), on a catalyst which is currently composed of precious group metals (PGMs). This  $H^+$  combines with bromide species once it has crossed the proton conducting membrane to form the hydro-bromic acid.

The  $H_2$ - $Br_2$  RFB lifetime is mainly limited by the deactivation of the PGM catalyst in the negative electrode.[8,10] The adsorption of bromine and bromide species on the catalyst surface is one of the main reasons for the poisoning of the PGM catalyst and the degradation of the performance in the  $H_2$ - $Br_2$  RFB. The effect of halogen chemisorption on the adsorption of hydrogen, oxygen and methanol on smooth platinum electrodes has been investigated already in the early 1970's.[11] The chemisorption decreases the Pt-H bonding energy and the total amount of adsorption. Early studies have shown the impact of bromide chemisorption on the hydrogen binding energy of Pt single crystals, without decrease of the H coverage.[12] More recent studies show the decrease in the Pt/C electrochemical surface area (ECSA) related to Pt-H desorption by 30% in HBr electrolyte, with major irreversible bromide chemisorption.[13] After washing, Pt can recover only 50% of its initial ECSA. The adsorption of bromides on platinum-group metals is a complex process, which is affected by several factors, including the metal itself and its crystal facets, the concentrations of the bromide species, the type of dosing (from bromine gas or in bromide solution), the pH and the temperature.[11]

The main focus of the research in this field dealing with the bromine/bromide crossover and catalyst poisoning was directed at the ability of the membrane to be more selective for bromides

without harming its proton conductivity. Membrane-electrode assemblies (MEAs) of H<sub>2</sub>/Br<sub>2</sub> RFBs are based on perfluoro-sulfonic acid (PFSA) membranes such as Nafion®. PFSA membranes should selectively transport protons while blocking H<sub>2</sub> and bromine/bromides species. Reducing Nafion concentration in membranes decreases the conductivity and the permeability of the membrane.[14] Membrane conductivity limits system efficiency at high current density, and the bromine/bromide crossover limits efficiency at low current density. The performance and the efficiency of the cell are more sensitive to membrane thickness and pretreatment procedure than the equivalent weight and the reinforcement of the membrane. After more than 3000h of operating a cell with pretreated membrane, the bromine crossover decreased moderately, but remained higher than the crossover of the as-received membrane.[9] Tucker *et al.* illustrates the competition between adsorbed hydrogen and bromide ions on the Pt surface by testing the electrode potential response to hydrogen shortage and Br<sub>2</sub>/HBr contamination. Bromide reversibly adsorbs at the hydrogen electrode when its potential exceeds a critical value, resulting in a peak limiting cell current.[15][16] Other types of membranes such as nanoporous proton conducting membranes (NP-PCM) made of polyvinylidene fluoride (PVDF) and silica are even more prone to Br<sub>2</sub>/HBr crossover with a high liquid flux across the NP-PCM membrane.[17]

Since no membrane can completely block crossover, the investigation of poisoning/corrosion tolerant catalysts is of major importance. Pt-rich alloys show a better tolerance to bromide poisoning.[9] Rhodium sulfide catalysts demonstrates high tolerance but low initial catalytic activity.[18][19] Other ternary sulfides of earth abundant transition metals and Ru (Co<sub>0.3</sub>Ru<sub>0.7</sub>S<sub>2</sub>) show interesting HER activity in HBr but are inactive towards HOR.[20] Therefore, the main path

towards crossover tolerance goes through the investigation of Pt-rich catalysts, as shown with the successful development of a bromide tolerant Pt-Ir-N<sub>x</sub>/C catalysts.[21]

In a recent study we have shown that a nanoscale polydopamine coating on a Pt catalyst can effectively protect the catalyst surface from corrosion in 3M HBr, allowing the catalyst to maintain its activity (when measured via a rotating disc electrode).[22] The catalytic activity of the polydopamine coated Pt remains high, even after dipping the catalyst in concentrated HBr for hours, with an almost unchanged hydrogen diffusion constant. Herein, we implement the use of polydopamine coated Pt in a H<sub>2</sub>-Br<sub>2</sub> RFB in an effort to prevent Pt poisoning during the unavoidable bromine crossover. Upon H<sub>2</sub> pressure release, charged electrolyte rapidly crosses through the nanoporous proton conducting membranes (NP-PCM). The H<sub>2</sub>-Br<sub>2</sub> RFB with polydopamine coated Pt catalyst shows a low capacity fading of 6% at 300 mA cm<sup>-2</sup> after exposure to 4.5 M charged electrolyte for 2 hours. Even the beginning of life polarization curves shows the benefit of catalyst coating with a high peak power of ~550 mW cm<sup>-2</sup>.

## **2. Experimental**

### *2.1 Catalyst synthesis*

The Pt catalyst polydopamine coating has been described in a recent publication.[22] The polymer coating was conducted on a standard Pt black catalyst (Premetek). The dopamine was polymerized in an aqueous dispersion of the catalyst (5 mg/mL) from dopamine hydrochloride (Sigma Aldrich, 99%) in tris-HCl pH 7.5 buffer solution (10 mmol/L - Tris-HCl Trizma base, Sigma

Aldrich) under magnetic stirring in a glass vial for 20 minutes at 25°C. At the end of the reaction, the residual dopamine was washed from the sample three times with absolute ethanol and deionized water by sequential centrifugation/dispersion procedures. Afterwards, the catalyst was dried in a vacuum oven at 80°C for 4 hours. After the polydopamine coating, we performed thermal annealing of the sample at 150°C for 60 minutes under N<sub>2</sub>. The structure was investigated by Transmission Electron Microscopy (TEM) on a JEOL 1400 (LaB<sub>6</sub>) operating at 200 kV.

## *2.2 Preparation of catalyst inks and fabrication of MEAs*

Both electrodes were supported on SGL 29AA carbon paper. All the wet layers were coated via a Doctor Blade coater. The bromine electrode contains one layer of PVDF (Kynar 2801, Arkema), carbon black Vulcan (XC72R, Cabot), Pt catalyst powder ( $\sim 0.01 \text{ mg cm}^{-2}$ ) and a pore former (Propylene Carbonate, Sigma-Aldrich). The hydrogen electrode was made from two layers of carbon black and PVDF. The catalytic ink was a dispersion of the coated Pt catalyst, carbon black and high surface area graphite (HSAG 300, Timcal) in water, 2-propanol, TBAOH (tetrabutyl ammonium hydroxide in Methanol 1M, Sigma-Aldrich) and 5% Nafion solution mixture. It was mixed overnight before thin coating. After drying and Nafion curing for 1 hour at 145°C, the electrode was washed for 1 hour at 80°C in 0.5M H<sub>2</sub>SO<sub>4</sub> and for 1 hour at 80°C in water and was then dried at 100°C. The top layer of the electrode was applied via spraying with 5% Nafion solution mixture (50% in Ethanol). After drying under ambient conditions and Nafion curing (1 hour at 145°C), the electrode was ready for the MEA. 7 cm<sup>2</sup> electrodes in Teflon frames were hot pressed (100°C for 45 seconds) to the membrane (NP-PCM,  $\sim 200\mu\text{m}$ ). [23,24] The Teflon frames

(100 $\mu\text{m}$  for the bromine electrode and 200 $\mu\text{m}$  for hydrogen electrode) are to keep the electrode's thickness and for sealing the cell. The MEA was located between two graphite plates which were tightened between two copper current collectors. The flow channels of the solution side are interdigitated and the gas side is single serpentine.

### *2.3 RFB operation*

Cells were operated with dry hydrogen and 20ml recycled 4.5M HBr solution (12ml min<sup>-1</sup>) at 40°C. Hydrogen pressure was controlled by a needle valve on the cell exhaust line. Polarization curves and cycling tests were obtained using a Biologic Science Instruments BCS-815 battery cycler.

The initial step of each cell was a deep charging to 60% SOC. After AC measurement, micro and macro polarization tests were operated. After discharge and another AC measurement, voltage limits were obtained and the cell started its cycling. After more than 100 cycles, and in order to test the catalyst in strict conditions, the hydrogen flow was stopped for 30 min and for 2 hours. Following every hydrogen stop, a polarization test made to compare the ability of the coated and un-coated catalyst to recover after hydrogen stoppage.

### *2.4 Electrochemical, structural and chemical diagnostics*

The electrochemical surface area (ECSA) of new electrodes was measured via cyclic voltammetry (CV) and was compared to the ECSA of the electrodes after soaking for 2 hours in hydrobromic acid (HBr 4.5M). The electrolyte of all the measurements was perchloric acid (HClO<sub>4</sub>, 0.1M). After a purge of Ar for 10 minutes, the voltammogram was collected at scan rate of 20 mV/sec, from 0V to 0.8V vs. standard hydrogen reference electrode and with a platinum wire as a counter electrode. All the data was collected on the impedance channel of the potentiostat (Bio-Logic

VMP3). The potentials were corrected for ohmic loss by measuring impedance before every polarization curve (iR free measurement). The ECSA was calculated from the  $H_{UPD}$  between 0.015-0.25V.

The used electrodes were investigated by High Resolution Scanning Electron Microscopy (HR-SEM) FEI, Magellan 400L in order to compare the exposure of both electrodes to bromine species. Samples of new and used electrodes were investigated with X-ray Photoelectron Spectroscopy (XPS) in order to better understand the surface structure of the first nanometric layers of the electrodes that are closest to the membrane and determine the electrode performance in the cell. The XPS analysis was carried out using Kratos Axis HS spectrometer (England) equipped with a monochromatic Al K $\alpha$  X-ray source (photon energy 1486.6 eV).

The quantity of platinum on both electrodes was measured by X-ray fluorescence (XRF) using a XGT 7200 from Horiba to compare new and used electrodes. The tested point diameter was 10  $\mu\text{m}$  and the pixel width was 6  $\mu\text{m}$ .

### **3. Results and discussion**

In this work, we focus on a catalyst coating to mitigate Pt catalyst deactivation. The catalyst coating is adopted from our previous work where the polydopamine nanoscale film on Pt catalyst shows high selectivity to hydrogen species and blocks bromide species.[22] Impeding bromide chemisorption improves the durability of Pt catalyst in 3M HBr.

Herein, the polydopamine coated Pt serves as hydrogen catalyst in a  $H_2$ - $Br_2$  RFB. The overall design of the cell is described in the experimental section. The use of a PVDF thick membrane is primordial to achieve a low cost and long lifetime EES.

The negative electrode is coated with a Pt loading of  $0.95 \pm 0.1 \text{ mg cm}^{-2}$ . The  $\text{H}_2\text{-Br}_2$  RFB is run at  $40^\circ\text{C}$  with an initial HBr concentration of 4.5 M. At beginning of life, the standard Pt catalyst layer shows an OCV of 0.95 V, close to the thermodynamic potential of the cell. The polarization curve shows a peak power of  $480 \text{ mW cm}^{-2}$  with a potential of 0.8 V at  $300 \text{ mA cm}^{-2}$  (Fig. 1). These values match the needs for EES.

Compared to standard Pt, the coated Pt electrode displays an increase of 14% in peak power density and 2.5% in voltage at  $300 \text{ mA cm}^{-2}$  discharge. The initial micro-polarization resistors of the coated platinum cell are lower by 26 % than those of the plan platinum cell ( $0.45 \text{ }\Omega\cdot\text{cm}^2$  vs.  $0.61 \text{ }\Omega\cdot\text{cm}^2$ ). We did not expect the higher peak power measured for the coated Pt electrode since we expect the ECSA to be reduced by the coating (as will be confirmed below). At this stage, the main explanation for the higher peak power observed for the coated catalyst would be the bromine crossover taking place even at this very early stage, which we call beginning of life. In fact, the initial micro-polarization occurs several hours after the cell assembly and exposure to the electrolyte.

Those resistors grow during the operation of the cells at a similar rate. The lower impedance of the cell is related to the interface between the Pt catalyst and the electrolyte. In our previous study, we have shown that a Pt catalyst undergoes chemisorption processes which account for the large variations of impedance. On the contrary, coated Pt catalysts have a lower impedance and are stable over time, even in a bromide environment.[22]

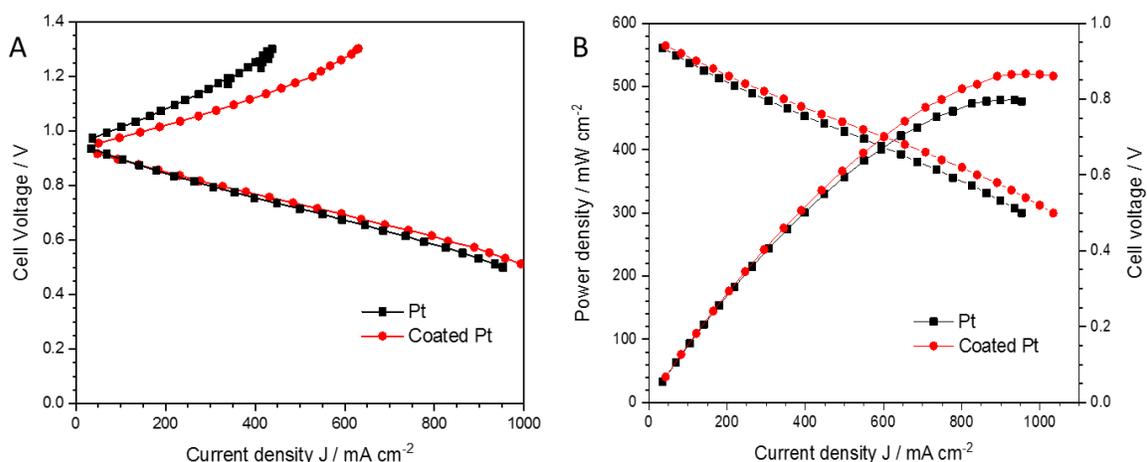


Figure 1: Initial Polarization curves of H<sub>2</sub>-Br<sub>2</sub> RFB with GDE made of Pt (black squares) or coated Pt (red dots): (A) charge/discharge; (B) discharge and power density.

Long-term galvanostatic cycling of the RFB is compared for the two catalyst layers (Fig. 2). The capacity shows a constant fading and the initial capacity can be fully restored (and even improved) with a fresh electrolyte. The sharp steps in the galvanostatic cycling correspond to the refilling of a fresh electrolyte. This phenomenon is inherent to the testing procedure used in the laboratory, where the electrolyte container is not fully sealed. The charge capacity of both cells is almost similar (at approx. 1100 mAh for a 7 cm<sup>2</sup> cell), but the operational voltage window of the coated catalyst layer is narrower by 0.1 V than the pristine Pt catalyst layer. Narrowing the operational voltage window can certainly enable a better durability of the coated catalyst, since platinum poisoning occurs mainly at high overpotential on the negative electrode.[22] The coated Pt cell reaches better efficiencies, with an overall energy efficiency (EE) of 72% (coulombic efficiency CE:89%, voltage efficiency VE:81%) compared to the plain Pt cell (EE:68%, CE:90%,

VE:76%). The enhancement in peak power density and overall EE is related to the decrease of the impedance with polydopamine Pt catalyst coating. This result may appear rather counter-intuitive, since a polymeric layer should increase the contact resistance at the catalyst surface, but it's consistent with the formation of a stable interface with high hydrogen diffusion constants.

The polarization curves after cycling show the main discrepancy between the coated Pt catalyst and the pristine Pt catalyst (Fig. 2 C-D). While the pristine Pt catalyst displays a significant decrease of the peak power density (25% loss at cycle 51), the coated Pt catalysts does not suffer from any capacity loss, even after 90 cycles. The peak power density slightly increases with the addition of a fresh electrolyte. This striking result reflects the deactivation of the Pt catalyst at work in the gas diffusion electrode. As pointed in the introduction, the proton conducting membrane is not fully selective and bromine crossover occurs during the cell operation.

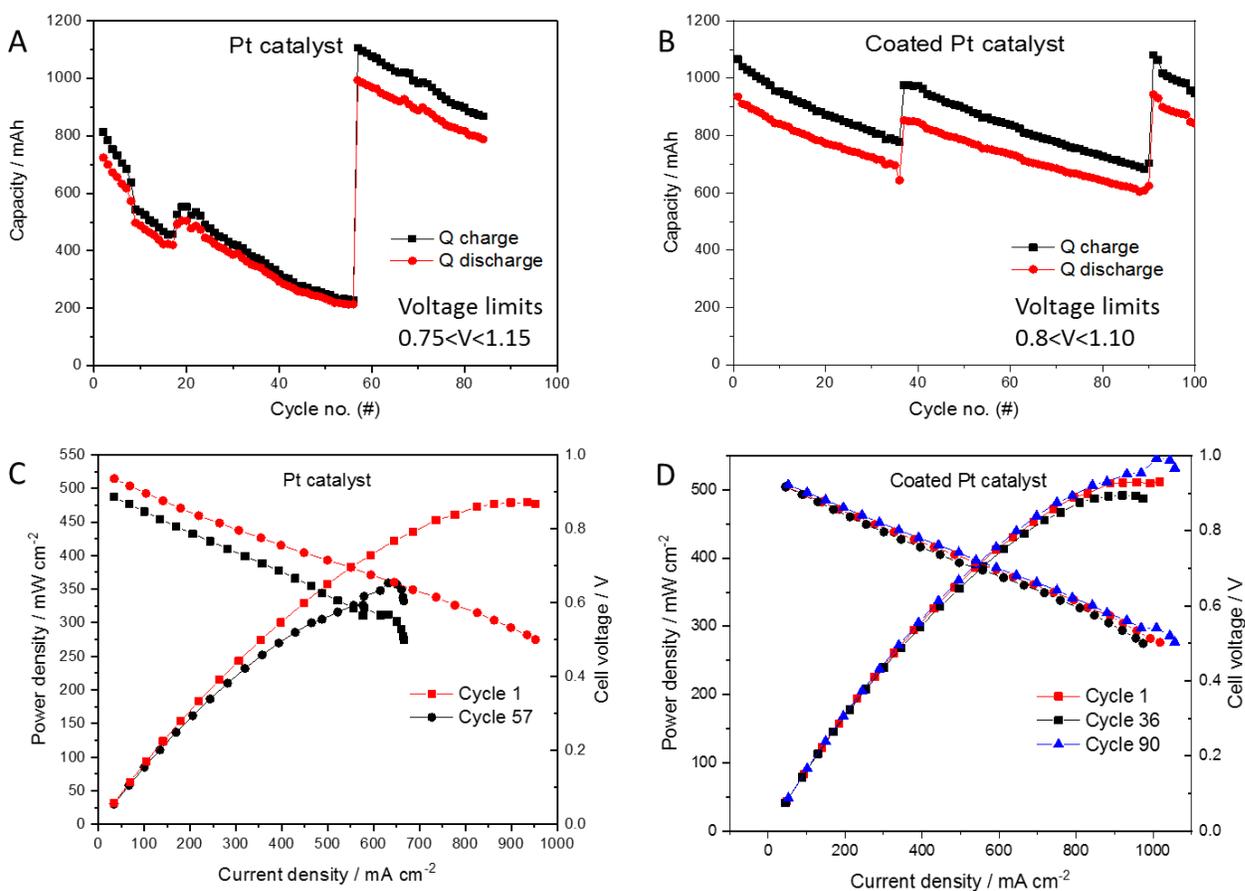


Figure 2: Cycling of H<sub>2</sub>-Br<sub>2</sub> RFB with gas diffusion electrode (GDE) made of (A) platinum catalyst and (B) polydopamine coated platinum catalyst. Polarization curves after addition of fresh electrolyte for Pt GDE (C) and coated Pt GDE H<sub>2</sub>-Br<sub>2</sub> RFB (D)

After a few days of stable operation, the catalyst layer faced its first significant challenge when the hydrogen flow was stopped for 30 minutes on the anode. The hydrogen shortage is a practical accelerated stress test to force the bromine crossover through the membrane. The OCV rapidly drops to less than 10 mV and the Pt catalyst layer is flooded with charged electrolyte (4.5 M solution). The orange color of the Br<sub>3</sub><sup>-</sup> ions was easily observed even in the hydrogen pipes.

	Peak Power Density [mW/cm <sup>2</sup> ]			
	New	After (#) cycles	30 min. H <sub>2</sub> stop	2h H <sub>2</sub> stop
<b>Pt</b>	479	(#57) 359	377	230
<b>Coated Pt</b>	520	(#90) 546	368	270
	Cell voltage at 300 mA/cm <sup>2</sup> [mV]			
	New	After (#) cycles	30 min. H <sub>2</sub> stop	2h H <sub>2</sub> stop
<b>Pt</b>	798	(#57) 730	777	732
<b>Coated Pt</b>	807	(#90) 818	794	768

Table 1: Power density peak and cell voltage comparison of the two cells after hydrogen shortage

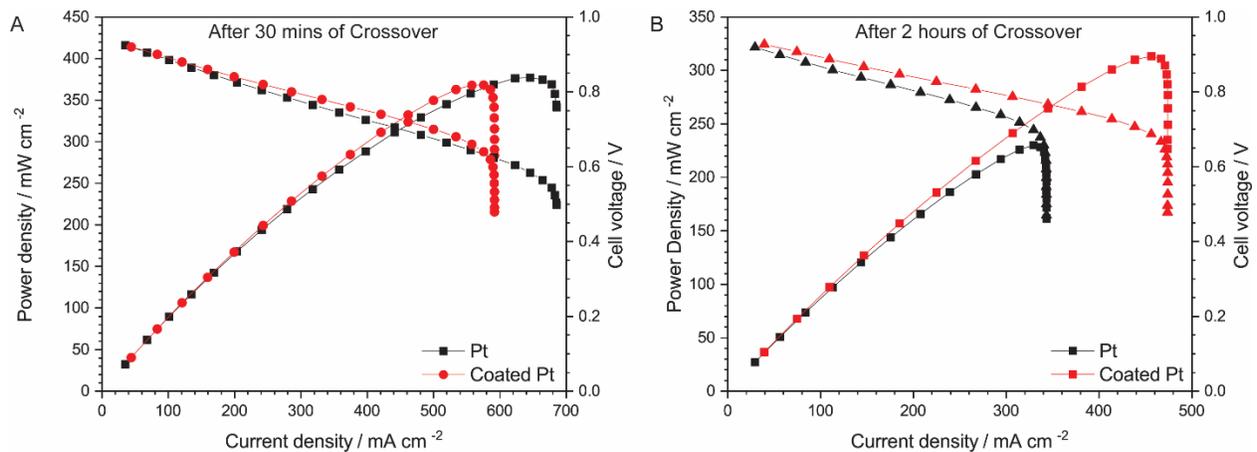


Figure 3: Polarization curves of H<sub>2</sub>-Br<sub>2</sub> RFB with GDE made of Pt (black squares) or coated Pt (red dots) (A); after 30 minutes of hydrogen shortage and (B); after 2 hours of hydrogen shortage.

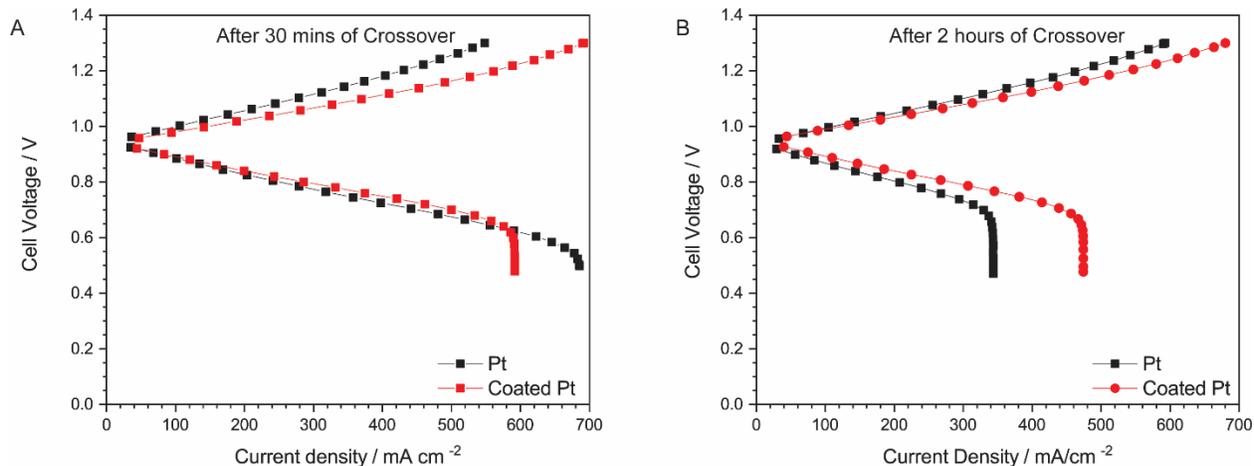


Figure 4: Charge/discharge polarization curves of H<sub>2</sub>-Br<sub>2</sub> RFB with GDE made of Pt (black squares) or coated Pt (red dots) (A); after 30 minutes of hydrogen shortage, (B); and after 2 hours of hydrogen shortage.

After restarting and stabilizing the hydrogen flow and the OCV, a polarization test was conducted. As shown in fig. 3A, 4A and table 1, both cells performances decrease but the voltage of the coated platinum cell at 300mA/cm<sup>2</sup> is still 2.2% higher than the uncoated Pt cell. The coated Pt cell still has better efficiencies (CE:90%, EE:71%, VE:79%) compared to the uncoated Pt cell (CE:90%, EE:69%, VE:77%).

After three days of continuous operation of the cells in charge/discharge mode, they face an even greater challenge: hydrogen flow stoppage for 2 hours. As in the first hydrogen stop, the OCV drops to few millivolts after 12 minutes. During this long break, the OCV reaches almost 0V which means that there is no hydrogen left in the negative electrode to protect the catalyst from

chemisorption of bromine species which floods the membrane and the negative electrode. The hydrogen electrode is totally flooded with a 4.5 M charged solution. This accelerated stress test is the most extreme case of catalyst deactivation. When the hydrogen flow restarts, the orange colored electrolyte is drawn out of the exhaust line. The recovery from this case is longer than before. After cycling at low discharge current ( $100 \text{ mA cm}^{-2}$ ) overnight, we run a polarization test. The comparison is shown in fig. 3B, 4B and table 1. The difference between the cells now is more significant. The power density peak of the cell with the coated Pt catalyst is 17.4 % higher than the pristine Pt catalyst and the cell voltage at  $300 \text{ mA cm}^{-2}$  is 4.9 % higher. The coated platinum cell has better voltage efficiency (79%) than the platinum cell (74%). Even after 2 hours hydrogen shortage, the coated Pt cell's impedance is significantly lower than the uncoated Pt cell ( $0.57 \text{ } \Omega \cdot \text{cm}^2$  vs.  $0.75 \text{ } \Omega \cdot \text{cm}^2$ ).

The electrochemical surface area (ECSA) of the gas diffusion electrodes is calculated from the hydrogen desorption charge on the cyclic voltammetry (CV) measurements in 0.1 M  $\text{HClO}_4$  before and after soaking for 2 hours in 4.5 M HBr (Fig. 5). The results are summarized in table 2. Pristine Pt black shows the typical adsorption/desorption hydrogen features corresponding to the crystallographic facets of Pt ( $\{110\}$  and  $\{200\}$ ). These features disappear after soaking in HBr. On the coated platinum electrode, the polymeric coating on the catalyst powder broadens the hydrogen adsorption/desorption region. The coated Pt electrode has a remarkably stable ECSA after soaking in HBr. The coated Pt ECSA decreases by only 5%, while the pristine Pt ECSA decreases by 30%. This immunity towards Br poisoning/corrosion is consistent with our previous measurements on rotating disc electrodes.[22]

	ECSA – new electrode (m <sup>2</sup> /g)	ECSA after 2 hours in 4.5M HBr (m <sup>2</sup> /g)
Pt electrode	22.9	15.5
Coated Pt electrode	20.5	19.4

Table 2: Electrode's ECSA comparison before and after exposure to 4.5 M HBr.

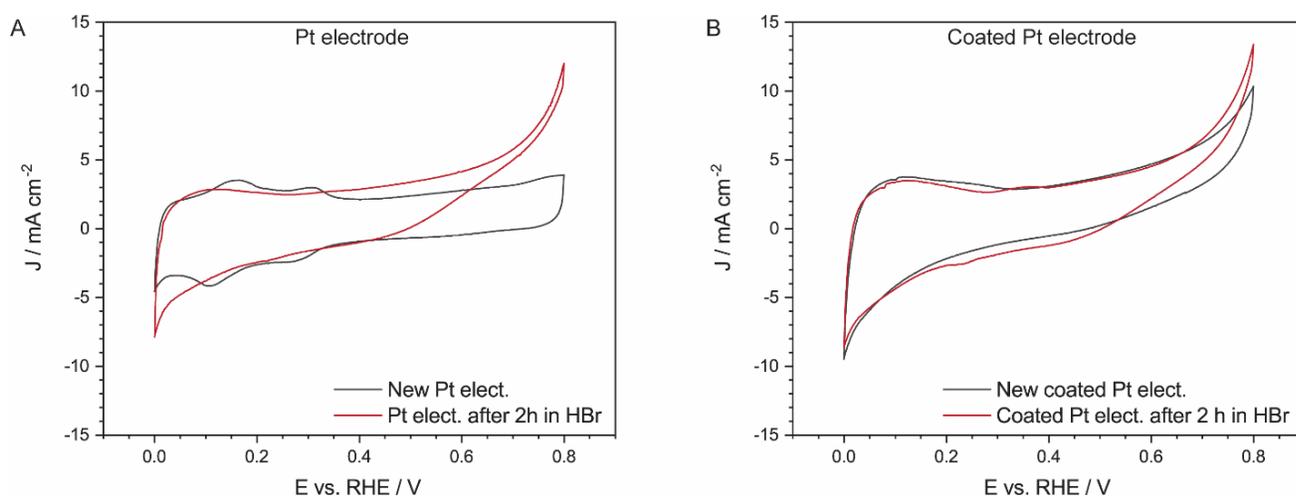


Figure 5: Cyclic Voltammetry (CV) of (A); platinum and (B); coated platinum electrodes, before (black line) and after (red line) soaking in HBr.

To further prove the bromine crossover and to assess the surface state of the catalysts after crossover, a series of post-mortem experiments were carried out on the gas diffusion electrodes (GDE). After the cells are disassembled, the used hydrogen GDEs are peeled from the membrane and observed by HR-SEM (Fig. 6). The elemental mappings from EDAX show the large amount of bromine species in both electrodes, which remain even after further cycling and proper washing of the GDEs.

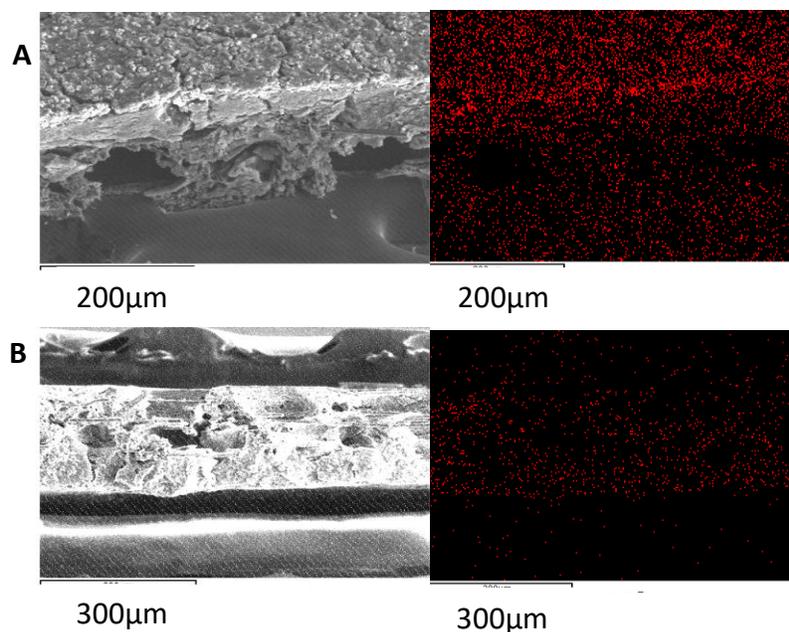


Figure 6: HR-SEM cross section images and EDS mapping of bromide for used electrodes with (A); plan platinum (B); and coated platinum.

The XRF semi-quantitatively measure the amount of platinum in the electrode before and after exposure to bromide species (as discussed above) and further operation of the RFB (Fig. 8). For beginning of life GDE, with pristine and coated Pt, the XRF spectrum reveals the same amount of Pt, consistent with the Pt loading ( $0.95 \pm 0.1 \text{ mg cm}^{-2}$ ). The post-mortem GDEs show a large discrepancy in the Pt content. The XRF spectrum of the Pt catalyst without coating does not display the Pt L lines anymore while the coated catalyst still shows the Pt L lines, albeit with a lower intensity. Further experiments are needed to quantitatively measure the Pt content in the GDEs after cell operation. In any case, the significant loss of platinum in the electrode can explain the performance fading.

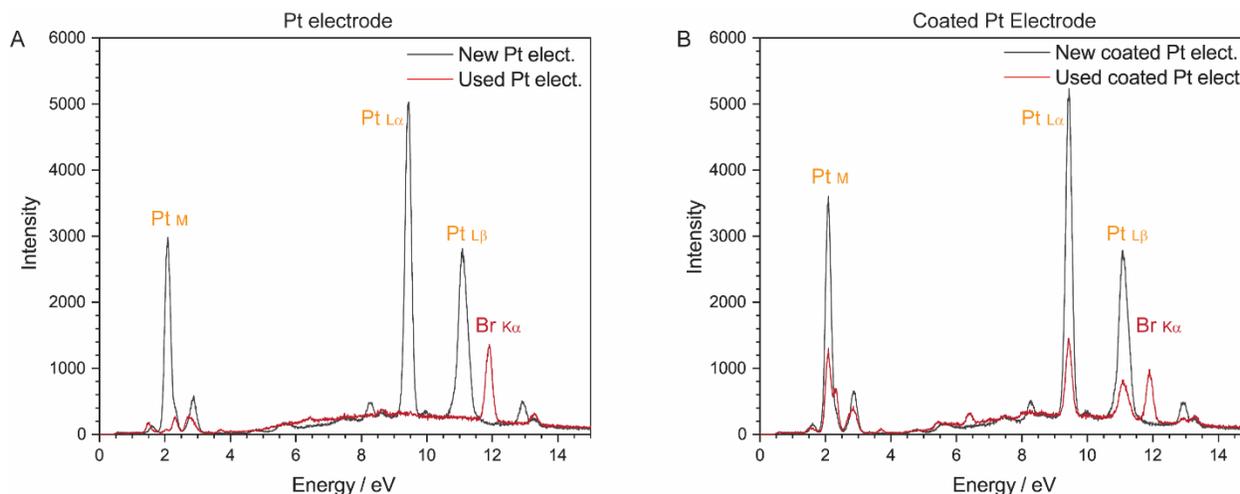


Figure 7: XRF spectra on the gas diffusion electrode after crossover and cycling for: (A) pristine platinum and, (B) coated platinum.

X-ray photoelectron spectroscopy gives a more precise knowledge on the surface state of the catalysts and reflects the chemical nature of the catalysts surface in the gas diffusion electrodes, before and after crossover and cycling of the RFB (Fig. 8). The coated and pristine Pt catalysts display a similar XPS spectrum and the Pt 4f lines can be fitted with two components corresponding to the Pt(0) and Pt(II) oxidation states. After exposure to bromide species, the XPS of the pristine Pt does not show any noticeable lines. It may indicate that exposure to bromine creates a film on the surface of the pristine Pt catalyst and/or corrodes the unprotected Pt. The formation of a surface film on the Pt catalyst surface is consistent with the decrease of the ECSA. On the other hand, the exposure to bromine does not alter the XPS spectrum of coated Pt. It proves that the polydopamine coating contributes to the Pt chemical stability even after long exposure to bromine species, in conditions where uncoated Pt catalyst undergoes deactivation following a chemisorption and corrosion process.

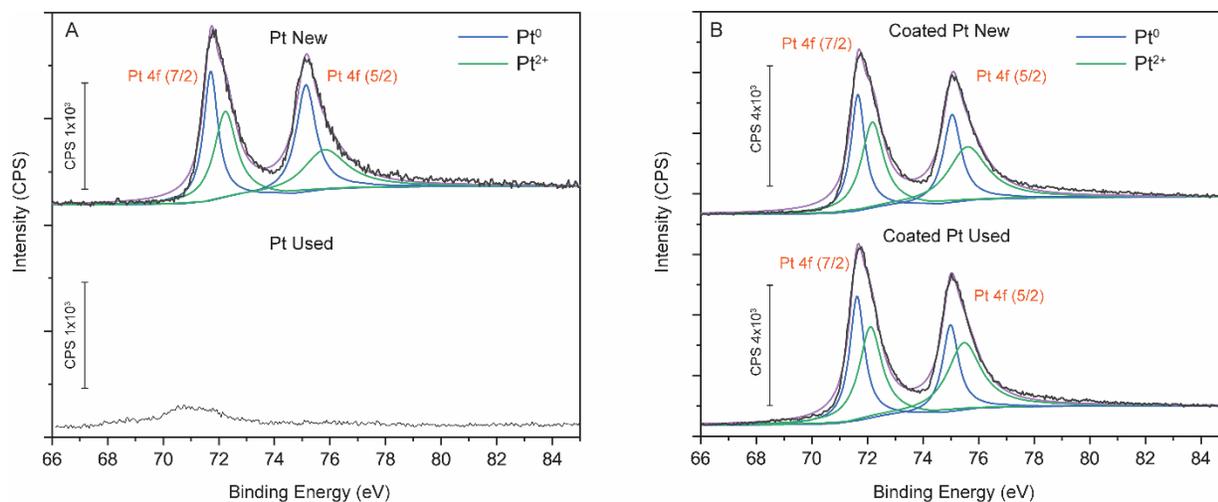


Figure 8: XPS results for (A); plan platinum (B); and coated platinum.

#### 4. Conclusions

Catalyst poisoning on the hydrogen electrode of  $H_2$ - $Br_2$  RFB is one of the critical issues that affects its performance and durability. Herein, we have synthesized a polydopamine nanoscale coating on a standard Pt catalyst. The peak power density of the polydopamine coated Pt catalyst is 14% higher than uncoated Pt, reaching  $550 \text{ mW cm}^{-2}$ , with lower values of impedance and higher energy efficiency. The voltage of the  $H_2$ - $Br_2$  RFB cell during cycling is higher for the coated catalyst at the beginning of life. After three days of cycling, the  $H_2$ - $Br_2$  RFB with a coated catalyst does not show any sign of capacity fading, compared to the 25% losses observed with the pristine Pt catalyst. After long exposure to charged electrolyte (4.5 M at  $45^\circ\text{C}$ ) on the negative electrode, the  $H_2$ - $Br_2$  RFB with a coated catalyst shows an increase in peak power density of 17 % and lower values of impedance compared to uncoated Pt catalyst. Advanced electrochemical and spectroscopic investigations of the used hydrogen gas diffusion electrodes show the stability of

the electrochemical surface area for the coated catalysts, compared to the uncoated catalyst. The polydopamine coating effectively stabilizes the surface of the catalyst and acts as an efficient barrier against bromine chemisorption and corrosion. The coated catalyst shows no sign of deactivation even during the accelerated stress test, offering a practical solution to one of the main bottlenecks in the way to energy efficient H<sub>2</sub>-Br<sub>2</sub> RFB.

**Declarations of interest:** none

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