



Short communication

## Study of hydrogen redox reactions on platinum nanoparticles in concentrated HBr solutions

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## ABSTRACT

Platinum nanoparticles are used as catalysts in most proton-exchange-membrane fuel-cells (PEMFC). A major issue with their use is the problem of catalyst poisoning by the adsorption of anions. In hydrogen–bromine fuel cells and electrolyzers, bromides and bromine species migrate across the membrane and poison the hydrogen–electrode catalyst, thereby reducing the electrode activity. The adsorption of bromide ions is thus a critical factor which must be studied. In this work, the adsorption of bromide ions and the hydrogen redox reactions were studied, for the first time, on XC72-supported platinum nanoparticles in concentrated HBr solutions with the use of rotating-disk-electrode and cyclic-voltammetry techniques. It was found that in 3 M HBr, the charge related to Pt–H desorption decreased by 30% relative to the charge obtained in 0.5 M sulfuric acid, and only a small part of the adsorbed bromide is released at zero volts. In addition, the HOR/HER exchange-current density decreases as a result of bromide adsorption.

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### 1. Introduction

Hydrogen–tribromide (HBr<sub>3</sub>) fuel cells and electrolyzers are promising candidates for the storage of electrical energy. These cells consist of a bromine electrode and a hydrogen electrode with a proton-conducting membrane between them. It is advantageous to use, if possible, a single electrochemical unit for both modes – fuel-cell and electrolyzer – making the system more economically attractive.

The hydrogen-oxidation catalyst with the highest activity is platinum (and some of its alloys) and it is used in most hydrogen–oxygen proton-exchange-membrane (PEM) fuel cells. The platinum-group metals are known for their underpotential deposition (UPD) of hydrogen which is associated with their activity in the hydrogen oxidation reaction (HOR) and hydrogen reduction reaction (HRR). In HBr fuel cells and electrolyzers, the membrane does not completely prevent the crossover of bromides or bromine species. Therefore, these species tend to poison the hydrogen-electrode catalyst. Catalyst poisoning by the adsorption of anions (such as halides, sulfates and others) is a well known phenomenon [1,2] that decreases the activity of these nanoparticle catalysts and degrades the fuel-cell performance. The adsorption of bromides on platinum-group metals is a complex process, not well understood, 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 [3]. Previous publications [3–6] reported that the bromide coverage on platinum ( $\theta_{Br}$ ) varies from 0.42 to 0.66, where in dilute aqueous bromide solution, the saturation value of  $\theta_{Br}$  is 0.42–0.44. The surface structure of bromide adsorbed on Pt(1 1 1) from concentrated bromide solution is a (3X3) overlayer, which corresponds to  $\theta_{Br} = 0.44$ .

Several studies [7,8] have been applied to the measurement of the effect of bromide-ion adsorption on the electrocatalyst surface by measuring, with the use cyclic voltammetry, the amount of hydrogen adsorbed on the electrode surface. The addition of sub-millimolar concentrations of bromides (and tribromides) to acid solutions (HClO<sub>4</sub> or H<sub>2</sub>SO<sub>4</sub>) changed the voltammograms of polycrystalline platinum: (a) both Pt–O adsorption and desorption waves are reduced and (b) the peak of strongly adsorbed hydrogen decreases and that of weakly adsorbed hydrogen increases.

At higher concentrations of Br<sup>−</sup>/Br<sub>3</sub><sup>−</sup> (up to more than 1 mM), additional peaks were measured and assigned to the following redox couples: Br<sup>−</sup>/Br<sub>3</sub><sup>−</sup> and BrO<sup>−</sup>/Br<sub>2</sub> [8]. The rotating ring-disk-electrode technique with a Pt(1 1 1) single crystal in the disk position was used by Gasteiger et al. [9] to establish both the bromide adsorption isotherm and its electrosorption valency. In 0.1 M HClO<sub>4</sub>, 0.8 × 10<sup>−4</sup> M Br<sup>−</sup>, bromide adsorption begins at about −0.15 V (SCE) and reaches a coverage of 0.42 (160 μC cm<sup>−2</sup>) at 0.5 V. The electrosorption valency is essentially unity (the adsorbed bromine species has practically zero charge, so it is covalently bound to the platinum). At the negative potential limit, no bromide

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is adsorbed on the Pt(1 1 1) disk, so that a saturated monolayer of  $H_{\text{ads}}$  is expected to exist, similar to that on Pt(1 1 1) in bromide-free electrolyte. This means that the adsorption/desorption processes of bromide on platinum at low bromide concentrations appear to be reversible, so that at 0 V (on the SHE scale), bromide coverage ( $\theta_{\text{Br}^-}$ ) is zero. However, most publications focus on platinum at low bromide concentrations (generally in the millimolar range), whereas for practical applications such as fuel cells and electrolyzers, adsorption at higher concentrations (3–7 M) is most important. In this work, the adsorption of bromide and the hydrogen redox reactions were studied on platinum nanoparticles in concentrated HBr solutions with the use of rotating-disk-electrode (RDE) and cyclic-voltammetry techniques.

## 2. Experimental

Cyclic-voltammetry and rotating-disc-electrode tests were performed in a three-compartment glass cell, with an Ag/AgCl/3 M KCl (Metrohm) reference electrode in a Luggin capillary compartment and a Pt-wire counter electrode. All potentials, however, are reported in terms of the standard-hydrogen-electrode (SHE) scale. The working electrode was a 5-mm diameter glassy-carbon-disc rotating electrode (Pine Instruments, USA) covered by catalytic ink containing commercial 50% (w/w) Pt/XC72-supported catalyst (E-TEK) with platinum loading of  $\sim 10 \mu\text{g(Pt)}$ .

In the cyclic-voltammetry measurements, the holder for the working electrode was a 1 cm  $\times$  4 cm glassy-carbon rectangular bar. The catalyst ink (commercial E-TEK carbon-supported platinum or 'JM' unsupported platinum catalysts) was applied to the lower part of this rectangle. The platinum loading was  $\sim 15 \mu\text{g}$ .

All electrochemical experiments were carried out with the use of an Eco Chemie (Netherlands) AUTOLAB potentiostat at room temperature ( $23 \pm 2^\circ\text{C}$ ).

The electrochemically active surface area (ECSA) was measured in a quiescent 0.5 M  $\text{H}_2\text{SO}_4$  solution. Nitrogen was bubbled through the solution for 15 min before the measurements and passed over the solution during the scan. The electrode was cycled between 0 and 1.2 V at a sweep rate of  $20 \text{ mV s}^{-1}$  for a total of five scans. The voltammograms were reproducible from the second scan on. The electrochemical surface area of platinum was determined from the coulometric charge in the hydrogen-desorption region, under the assumption of  $210 \mu\text{C cm}^{-2}$  of hydrogen adsorbed [10]. All values of ECSA are normalized to the mass of platinum [ $\text{m}^2 \text{g}^{-1}(\text{Pt})$ ].

## 3. Results and discussion

50%Pt supported on XC72 commercial catalyst was investigated with the use of a rotating disk electrode and cyclic voltammetry technique in order to determine the effect of bromide-ion adsorption on the electrocatalyst surface. Fig. 1 describes  $I/V$  curves for 0.5 M sulfuric acid with the addition of 1 mM HBr and 100 mM HBr, and for concentrated 3 M HBr (without sulfuric acid). The well-known characteristic voltammogram of polycrystalline platinum in 0.5 M sulfuric acid over the range of 0–1.2 V has changed as reported by others [2,8,11] for low bromide concentration: the peak of strongly adsorbed hydrogen decreases and that of weakly adsorbed hydrogen increases. Hydrogen adsorption on platinum is weakened by the presence of bromide, as indicated by a cathodic shift of the Pt–H peak.

In the range of sweep potentials which was chosen in the present work, the addition of 1 mM HBr to 0.5 M sulfuric acid, causes both Pt–O adsorption and desorption waves to disappear, indicating that over this range of potentials, the formation of oxide is completely depressed by the adsorption of bromide (Fig. 1A). At higher bromide concentrations, the scan range has been narrowed in order

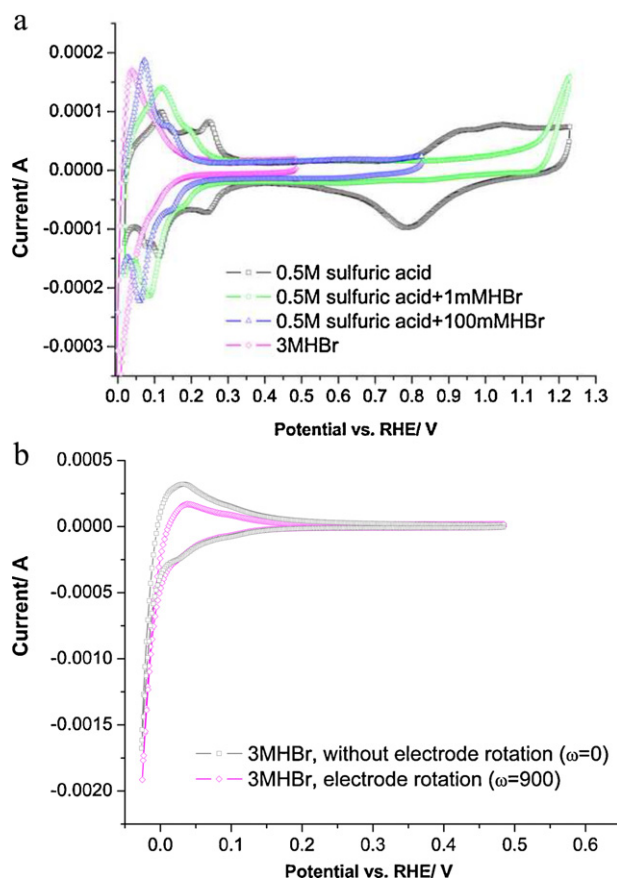


Fig. 1. Voltammograms for 50% carbon-supported Pt with platinum loading of  $9 \mu\text{g(Pt)}$  in (A) different concentrations of HBr in the supporting electrolyte (0.5 M  $\text{H}_2\text{SO}_4$ ) at  $20 \text{ mV s}^{-1}$  scan rate and 900 rpm electrode-rotation rate and in (B) 3 M HBr with and without electrode rotation.

to avoid the evolution of bromine. The height of the more negative Pt–H peak (weakly bonded) increased and the more positive peak (strongly bonded) became smaller until a single peak with a lower charge is observed. An important fact that had to be considered is that by increasing the HBr concentration (lowering pH) we are causing a shift in the Pt–H and Pt–OH peaks to higher potentials. Therefore it is important to execute the above measurements with a rotating electrode, otherwise, as a result of applying a potential more negative than the OCV, intense hydrogen evolution will interfere with the calculation of ECSA from the anodic oxidation of Pt–H. This artefact may be caused by the accumulation of  $\text{H}_2$  near the working electrode during the measurement, thus increasing the total charge, and leading to false higher active electrochemical surface area (Fig. 1B). Another way to avoid this problem is to bubble nitrogen or other inert gas near the electrode [12].

Since the adsorption/desorption of bromide on a platinum surface takes place over the same potential range as the  $H_{\text{upd}}$  desorption/adsorption, calculation of the electrochemical surface area (ECSA) with the use of charge displacement associated with these reactions [13] is complicated. Therefore, in solutions containing HBr, only the charge  $Q(H_{\text{region}})$  (and not the ECSA) in the oxidation region of  $H_{\text{upd}}$  (0.01–0.4 V) was determined (Table 1). The ECSA was determined in 0.5 M sulfuric acid, from the charge associated with  $H_{\text{upd}}$  desorption with the use of a theoretical charge of  $210 \mu\text{C cm}^{-2}$  for a polycrystalline platinum surface and found to be  $45 \text{ m}^2 \text{g}^{-1}$  of Pt. According to the ratio between  $Q(H_{\text{region}})$  and  $Q(H_{\text{upd}})$ , we can get an indication of the reversibility of the bromide adsorption, on the assumption that the initial coverage of Pt–H in this region in sulfuric acid is one monolayer, i.e.  $\theta = 1$  (Table 1). It can be seen that

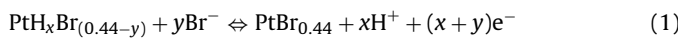
**Table 1**

The charge in the oxidation region of  $H_{\text{upd}}$  and surface coverage in this region at different concentrations of HBr in the supporting electrolyte (0.5 M  $H_2SO_4$ ).

Solution	$Q(H_{\text{region}})$ [C]	$\theta(H_{\text{region}})$
0.5 M sulfuric acid (fresh)	$8.37E-04$	1.00
0.5 M sulfuric acid + 1 mM HBr	$8.02E-04$	0.96
0.5 M sulfuric acid + 100 mM HBr	$7.10E-04$	0.85
3 M HBr	$5.76E-04$	0.69

even at HBr concentrations as low as 1 mM there is not complete desorption of bromides from the platinum surface. In the case of full desorption,  $\theta$  would be expected to be greater than 1, as a result of the charge associated with bromide desorption plus the charge of one monolayer of adsorbed  $H^+$  (as in the case of bromide-free electrolyte).

On the assumption that the maximum coverage for bromide on platinum is 0.44, the following reaction over the potential range 0–0.5 V can be written [13]:



where the values of  $x$  and  $y$  vary with potential. In the case of a fully reversible reaction, the values should be  $x=1$  and  $y=0.44$ , hence the total capacity from 0 V to 0.5 V is expected to be more than  $300 \mu C cm^{-2}$  ( $210 \mu C cm^{-2} \times 1.44$ ).

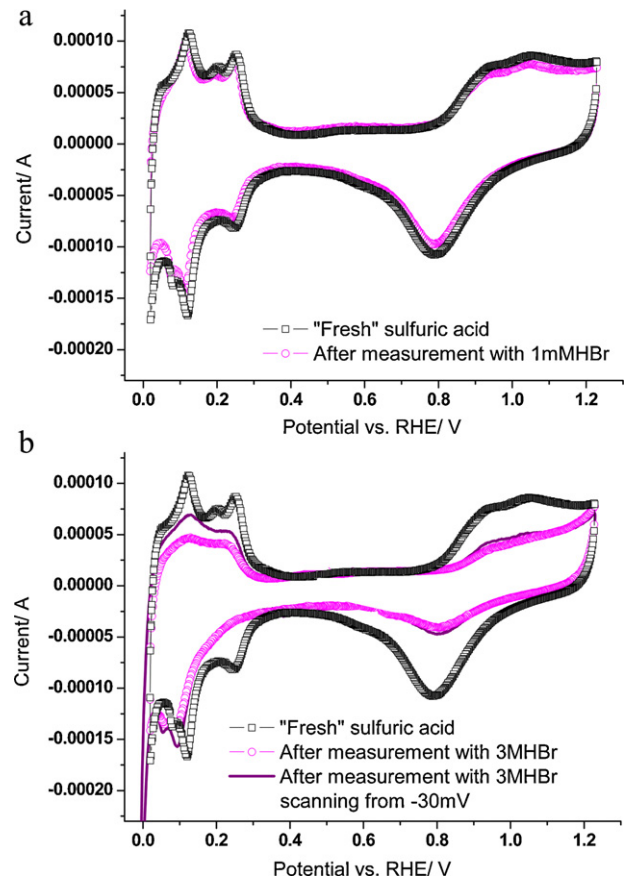
When 3 M HBr was used, the charge in the Pt–H desorption region dropped by 30% relative to the charge obtained in pure 0.5 M sulfuric acid.

In order to find if bromide can be further desorbed from the electrode, CV scans of 3 M HBr were run down to  $-60$  mV vs. RHE. However, these scans (not shown here) did not reveal higher charge, indicating that there is still bromide adsorbed on the platinum surface, even at negative potentials (tested until  $-60$  mV vs. RHE). As  $\theta$  is only 0.69, it is clear that some of the Pt–H and Pt–Br sites are not reversible. Since we are dealing with polycrystalline platinum, one face may still contain adsorbed bromide (i.e. there is no Pt–H adsorption), while on the other surface, the bromides have desorbed and the contribution is also from Pt–H oxidation.

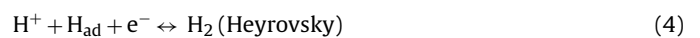
Bromides (and halides in general) adsorb more strongly on Pt(1 0 0) than on Pt(1 1 1). Since the work function and the potential of zero charge of Pt(1 0 0) are lower than those of Pt(1 1 1), bromides are still adsorbed on the (1 0 0) surface even over the HER range while the desorption of bromides from (1 1 1) may be completed earlier. For this reason, it is difficult to separate the contributions of Pt–H oxidation and Pt–Br reduction to  $Q(H_{\text{region}})$  in the range 0–0.5 V.

Returning the electrode to 0.5 M sulfuric acid after testing at low bromide concentration (1 mM HBr), shows no difference in the shape of the voltammogram obtained over the same scan range of 0–1.2 V vs. RHE (Fig. 2A). These results indicate that bromide adsorption at low concentration (up to 1 mM) is reversible. This is not the case for higher concentrations of bromide, for example 3 M HBr. The charge related to  $H_{\text{region}}$  was further reduced by nearly 40% when measured in 0.5 M sulfuric acid after being tested in 3 M HBr, indicating severe poisoning of the catalyst (a reduction by more than 50% of the initial ECSA value). Some of the bromide can be desorbed by scanning the potential to more negative values, for example, to  $-30$  mV vs. RHE in 0.5 M  $H_2SO_4$  (Fig. 2B), indicating that bromide poisoning is partially reversible. The charge addition is seen mainly in the cathodic Pt–H peaks (weakly bonded). There is also a small increase in the Pt–O oxidation/reduction peaks, supporting the fact that there was a change in the amount of adsorbed bromide.

Several steps were suggested for the hydrogen-evolution reaction (HER) in acidic solutions [14]:



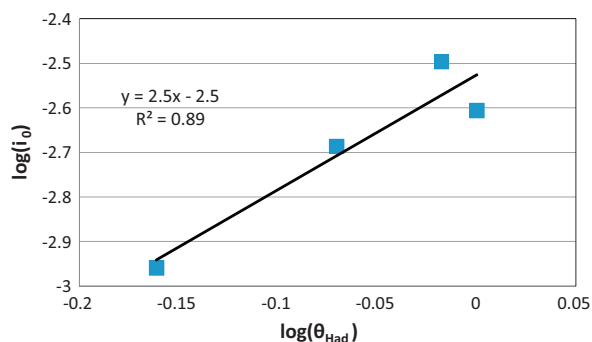
**Fig. 2.** Voltammograms for 50% carbon-supported Pt with platinum loading of  $9 \mu g(Pt)$  in 0.5 M  $H_2SO_4$  with  $20 \text{ mV s}^{-1}$  scan rate and 900 rpm electrode-rotation rate. (A) After measurement with 1 mM HBr and (B) after measurement with 3 M HBr.



Cyclic-voltammetry micropolarization measurements (with an RDE system) were made in order to estimate the HER resistance ( $R_r$ ) and the exchange-current density,  $i_0$ . The polarization curves for HER were determined in 0.5 M sulfuric acid and in solutions containing HBr, by scanning over a narrow range of potentials ( $\pm 50$  mV) around the standard potential of the reaction. The value of  $R_r$  was found from the slope of the  $V/i$  curve and  $i_0$  was calculated from the linear section of the Butler–Volmer equation, at low overpotential ( $\eta$ ) [15]:

$$\eta = \frac{RT}{F \cdot i_0} \cdot i = R_r \cdot i \quad (5)$$

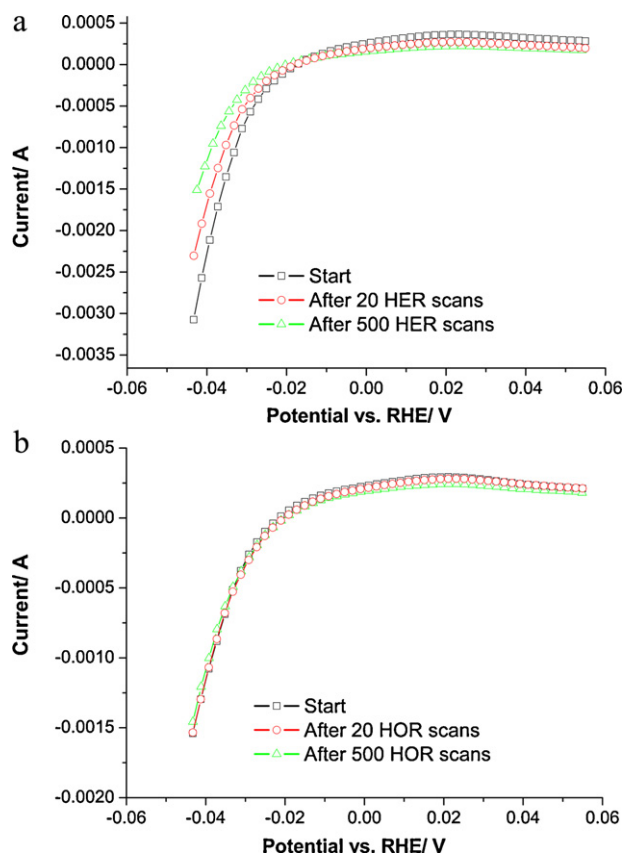
On the assumption that the reversibly-adsorbed species are mainly H atoms, the charge  $Q(H_{\text{region}})$  relative to the charge measured in 0.5 M sulfuric acid, can be assigned to  $\theta_H$ . Thus, in order to realize which of the HER mechanisms above is dominant, we draw a graph of  $\log i_0$  vs.  $\log \theta_H$ . Although a very limited number of measurements were taken, a linear relation can be seen with a slope of about 2 (Fig. 3). Other measurements with platinum wire [16,17] gave a similar value of the slope. Hence, it can be concluded with some certainty that the HER in HBr-containing solutions proceeds via the Tafel–Volmer mechanism, requiring two adjacent Pt–H sites for  $H_2$  evolution, while the recombination of two  $H_{\text{ad}}$  species is the rate-determining step. Such a mechanism is very sensitive to poisoning as the concentration of two adjacent sites in the poisoned state is lower than their concentration on a bromide-free surface.



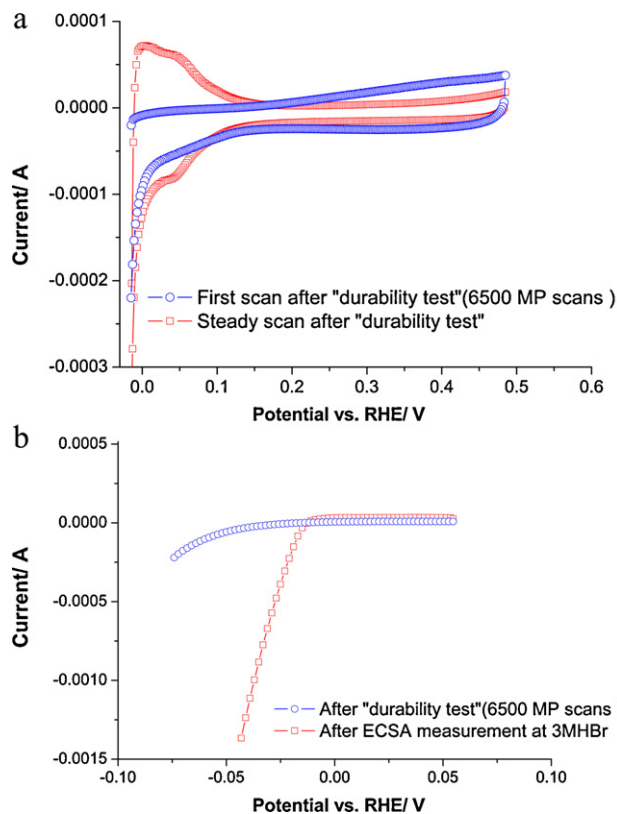
**Fig. 3.** Logarithmic value of the exchange-current density for HER vs. the logarithmic value of the reversible coverage in the oxidation region of  $H_{\text{upd}}$ .

The “imprecise” results depicted in Fig. 3 are typical to poisoning effects of catalysts which are not too reproducible, however in our opinion it is important to present it in order to give some indications for the reaction mechanism at high bromide concentrations. Moreover, at low bromide concentrations desorption of bromide is partially reversible, it takes place in parallel to H adsorption. Therefore the exchange current density, measured for this solution, is higher than expected and causing deviation from linearity. By deleting of this second point from the graph (the one of the solution containing 1 mM HBr) a better linear fitting ( $R^2 = 0.95$ ) is obtained.

In order to further examine the mechanism of bromide poisoning, the HER resistance was measured in durability tests in 3 M HBr and as a function of the potential-cycling limits, demonstrating their stability following 500 potential sweeps, simulating



**Fig. 4.** Polarization curves for the (A) HER and (B) HOR potential range after 20 and 500 cycles for 50% carbon-supported Pt with platinum loading of  $8 \mu\text{g(Pt)}$  in 3 M HBr with a  $20 \text{ mV s}^{-1}$  scan rate.



**Fig. 5.** (A) ECSA measurement and (B) micro-polarization measurement at  $20 \text{ mV s}^{-1}$  scan rate for unsupported commercial Pt catalyst in 3 M HBr after 6500 cycles before and after activation by scanning to 0.5 V.

charge–discharge cycles in the hydrogen-tribromide regenerative fuel cell (HTBFC).

Fig. 4 presents the polarization curves for the HER after 20 and 500 cycles over the HOR potential range (from 0 to 50 mV), and over the HER potential range (from  $-50 \text{ mV}$  to 0 V), typical of a fuel cell and electrolyzer working separately.

It was found out that long-term cycling of the platinum electrode over the HER range in 3 M HBr resulted in a 50% increase in the resistance of the hydrogen-evolution reaction, while the resistance did not change during cycling over the HOR range.

Apparently, during prolonged hydrogen-evolution cycles over a platinum electrode contaminated with adsorbed bromide, the decrease in the activity of the electrode may also occur by the formation of inactive adsorbed hydrogen. This phenomenon has been reported in the past for gold [18] and may be attributed to a hydrogen-embrittlement process (entry of hydrogen into the outer layer of the metal or the formation of hydride).

The inactive  $H_{\text{ad}}$  can be oxidized at higher potential and this is indicated by the appearance of an anodic shoulder at 0.5 V in Fig. 5A for a commercial unsupported platinum catalyst (JM) after 6500 cycles over the whole potential range of HER plus HOR (from  $-50 \text{ mV}$  to 50 mV). This occurrence was confirmed by the increase in the Pt–H peak in post-activation sweeps and also by the decrease in the resistance of the hydrogen-evolution reaction afterwards (Fig. 5B).

#### 4. Conclusions

Most publications on platinum at low bromide concentrations have found that the adsorption/desorption processes of  $\text{Br}^-$  on Pt appear to be reversible. Thus at 0 V (or slightly negative potentials) bromide coverage ( $\theta_{\text{Br}^-}$ ) is zero. However, in 3 M HBr the charge



related to Pt–H desorption dropped by 30% relative to the charge obtained in 0.5 M sulfuric acid. Moreover, after the electrode was washed following the test in 3 M HBr and returned to 0.5 M sulfuric acid, a further decrease in the Pt–H desorption charge was found. The resulting charge was less than 50% of the initial value in sulfuric acid. Only a small part of the adsorbed bromide was released by shifting the potential to  $-30$  mV (vs. RHE), indicating that bromide poisoning is only partially reversible at this potential. On prolonged cycling of 50%Pt supported on XC72 at  $\pm 50$  mV vs. the theoretical OCV in 3 M HBr solution, the platinum catalyst was found to lose activity. Cycling only over the HOR range (0–0.05 V) is less harmful than cycling over the HER range which resulted in an increase in the reaction resistance of hydrogen evolution. Apparently, another mechanism is affecting platinum activity over the long term of cycling, besides the adsorption of bromides, probably the formation of inactive hydrogen which blocks the electrode and can be released only at a higher potential.

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