



Impact of SO₂ poisoning of platinum nanoparticles modified glassy carbon electrode on oxygen reduction

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ABSTRACT

An extraordinary recovery characteristic of Pt-nanoparticles from SO₂ poisoning is introduced in this study. Platinum nanoparticles (nano-Pt) modified glassy carbon electrode (nano-Pt/GC) has been compared with polycrystalline platinum (poly-Pt) electrode towards SO₂ poisoning. Two procedures of recovery of the poisoned electrodes were achieved by cycling the potential in the narrow potential range (NPR, 0–0.8 V vs. Ag/AgCl/KCl (sat.)) and wide potential range (WPR, –0.2 to 1.3 V). The extent of recovery was marked using oxygen reduction reaction (ORR) as a probing reaction. SO₂ poisoning of the electrodes changed the mechanism of the oxygen reduction from the direct reduction to water to the stepwise reduction involving the formation of H₂O₂ as an intermediate, as indicated by the rotating ring-disk voltammetry. Using the WPR recovery procedure, it was found that two potential cycles were enough to recover 100% of the activity of the ORR on the nano-Pt/GC electrode. At the poly-Pt electrode, however, four potential cycles of the WPR caused only 79% in the current recovery, while the peak potential of the ORR was 130 mV negatively shifted as compared with the fresh poly-Pt electrode. Interestingly, the NPR procedure at the nano-Pt/GC electrode was even more efficient in the recovery than the WPR procedure at the poly-Pt electrode.

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1. Introduction

Oxygen reduction reaction (ORR) has been extensively studied because of its potential importance for electrochemical science and technology. During fuel cell operation the polarization at the cathode (oxygen reduction) is highly significant compared with the polarization at the anode and thus much interest has been directed to the study of the factors affecting the cathodic reaction including the adsorption of several poisoning species. Among poisoning species SO₂ has the most deleterious effect on the ORR. Adsorption of SO₂ or sulfur species on Pt is irreversible under electrochemical or ultra high vacuum environments because of the formation of strong covalent bond [1–5]. Trace amounts of adsorbed SO₂ are reported to deteriorate the performance of platinum towards oxygen reduction [6–16] either by decreasing the active area or by changing the mechanism of the oxygen reduction from 4e pathway to 2e pathway forming H₂O₂ [8,11], which deteriorate the Nafion membrane in the fuel cell.

The optimum conditions required for an efficient SO₂-tolerant electrode in fuel cell are using high humidity, high temperature

and excursions to high potential. However, applying high anodic potential leads to dissolution of Pt and the corrosion of carbon substrate in addition to competing reactions as water oxidation [17]. In the present study the resistance of platinum nanoparticles modified glassy carbon electrode (nano-Pt/GC) and polycrystalline Pt electrode (poly-Pt) against SO₂ poisoning and their in situ electrochemical recovery are compared. The recovery of the poisoned electrodes was attempted by cycling the potential in the potential range of the oxygen reduction and between the onset potentials of the hydrogen and oxygen evolutions. This method of recovery is selected in the present work as it has been reported that applying a constant potential as much as 1.6 V vs. NHE does not completely recover a sulfur poisoned platinum electrode, and that potential cycling is essential for the complete recovery of the poisoned platinum electrodes [18]. The approach is accessed using voltammetric measurements where the ORR is utilized as a probing reaction for the extent of poisoning and recovery of both electrodes.

2. Experimental

All chemicals used are of analytical grade. Platinum nanoparticles (nano-Pt) modified glassy carbon electrode (nano-Pt/GC) was prepared from acidic bath of 0.1 M H₂SO₄ containing 1 mM H₂PtCl₆ by applying bi-potential steps from the open circuit poten-

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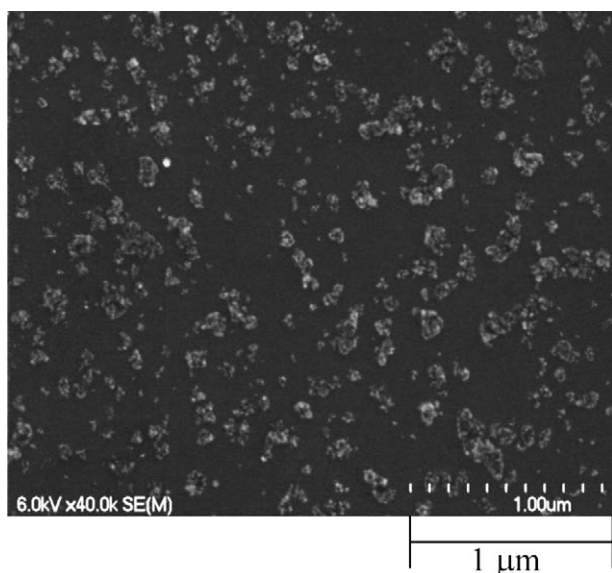


Fig. 1. SEM image for nano-Pt/GC electrode showing the Pt nanoparticles distribution on the GC electrode.

tial to -1.5 V (0.1 s) and then to -0.3 V (1 s) vs. Ag/AgCl/KCl (sat.). Holding the potential at -1.5 V was to initiate the nucleation at a high rate followed by stepping the potential to -0.3 V to continue the growth of the platinum nanoparticles. The counter and the reference electrodes were, respectively, a spiral Pt wire and a Ag/AgCl/KCl (sat.). Prior to the electrodeposition of nano-Pt, the glassy carbon (GC) substrate was polished first with no. 2000 emery paper, then with aqueous slurries of successively finer alumina powder (particle size down to 0.06 μ m) with the help of a polishing microcloth. The bare GC electrode was then sonicated for 10 min in milli-Q water. The nano-Pt with an average particles size of 40 nm was found to be uniformly distributed on the GC substrate as estimated from the scanning electron microscopy image (cf. Fig. 1). Polycrystalline platinum was prepared in the same manner as the GC electrode followed by electrochemical pretreatment between the onset potentials of the hydrogen and oxygen evolution until the characteristic voltammetric behavior of clean Pt electrode was obtained. A commercially available nano-Pt catalyst (46%, particle size 3 nm, abbreviated as nano-Pt_{comm}), purchased from Tanaka Metal Industry Corp., supported on glassy carbon electrode (nano-Pt_{comm}/GC) is used for the sake of comparison with the electrochemically deposited nano-Pt. The ink of nano-Pt_{comm} was prepared according to the literature [11] by mixing (0.4 ml isopropanol (Kanto, Japan) + 2 mg Pt catalyst + 8 μ L Nafion (Aldrich, Germany)) thoroughly by sonication for 30 min in an ultrasonic bath. Prior to casting of this ink, the glassy carbon disk electrode (0.07 cm²) was pretreated as mentioned above. A 3.0 μ L aliquot of the above suspension was loaded onto the glassy carbon disk and dried at room temperature in air to yield a smooth film that covered the entire surface of the electrode and a loading of 39.4 μ gPt/cm² (geometric) was obtained.

Oxygen reduction reaction was studied in 0.1 M H₂SO₄ using a conventional two-compartment Pyrex glass container. Milli-Q water (Millipore, Japan) was used to prepare all solutions. Prior to each experiment, O₂ gas was bubbled directly into the cell for 30 min to obtain an O₂-saturated solution, and during the measurements O₂ gas was flushed over the cell solution.

Electrochemical measurements were performed at 25 ± 1 °C using a BAS 100 B/W electrochemical analyzer. The current density was calculated on the basis of the geometric surface area of the underlying GC electrode. Deaeration of the electrolyte solu-

tions was, if necessary, carried out by bubbling N₂ gas for at least 30 min prior to electrochemical measurements. A conventional three-electrode cell of around 20 ml was used for the cyclic voltammetric measurements, while in the case of hydrodynamic voltammetric measurements the working electrode compartments was 200 cm³ to eliminate any possible changes in the O₂ concentration during the measurements. Steady-state voltammograms were conducted at rotating ring-disk electrode (RRDE) with Pt-disk ($\phi = 6.0$ mm in diameter) and Pt-ring using a rotary system from Nikko Keisoku, Japan. O₂-saturated solutions were obtained by bubbling O₂ gas for 30 min prior to each experiment and O₂ gas was flushed over the solutions during the measurements. The Pt disk-Pt ring RRDE was mechanically polished to a mirror surface in the same manner as the poly-Pt electrodes and then was cleaned ultrasonically in milli-Q water. Electrolyte solutions were, if necessary, deaerated by bubbling N₂ gas for at least 30 min prior to electrochemical measurements.

SO₂ poisoning solution was prepared by introducing 0.1 M Na₂SO₃ in 0.1 M H₂SO₄ solution. In this case Na₂SO₃ (Kanto, Japan) was completely converted to SO₂ soluble in the aqueous solution. That is to say a certain volume of the aforementioned solution was used to prepare the desired concentration of SO₂ in 0.1 M H₂SO₄. Then poisoning was done in 5×10^{-4} M SO₂ containing N₂-saturated 0.1 M H₂SO₄ by scanning the potential of the electrode (for one cycle) at 0.1 V s⁻¹ between 0.8 and -0.1 V vs. Ag/AgCl/KCl (sat.). Next the electrode was transferred into SO₂-free 0.1 M H₂SO₄ solution for electrochemical characterization.

3. Results and discussion

Platinum nanoparticles (nano-Pt) modified glassy carbon electrode (nano-Pt/GC) was prepared by applying bi-potential steps as mentioned in Section 2. Fig. 1 shows a typical SEM image of the nano-Pt/GC electrode. A reasonably uniform size and density distribution of Pt nanoparticles can be confirmed from this micrograph. The size of the particles is in the range of 30–50 nm.

Fig. 2 shows the CVs obtained at (A) poly-Pt, (B) nano-Pt/GC and (C) nano-Pt_{comm}/GC electrodes ((a, c and e) fresh and (b, d and f) poisoned electrodes) in N₂-saturated 0.1 M H₂SO₄ solutions. First the CVs of the fresh electrodes (curves a, c and e) were obtained. Then these three electrodes were submitted to one potential cycle in the potential range (0.8 to -0.1 V) in the poisoning solution (0.5 mM Na₂SO₃ + 0.1 M H₂SO₄). Next these electrodes were washed with milli-Q water and then the voltammetric responses in N₂-saturated 0.1 M H₂SO₄ solution were obtained (curves b, d and f). At the fresh electrodes (curves a, c and e) the well-known peaks of the hydrogen adsorption-desorption ($H_{ads/des}$) and the peaks corresponding to the Pt/PtO_x couple are clearly observed, while at the poisoned electrodes (curves b, d and f) the $H_{ads/des}$ peaks are completely suppressed indicating a severe poisoning of the electrodes by the adsorbed sulfur species (the major species is the elemental S) [19]. Note that the surface coverage of sulfur at the nano-Pt/GC is smaller compared with that at the poly-Pt and nano-Pt_{comm}/GC electrodes (see Table 1). Small cathodic peaks shown in curves b and d around -0.1 V correspond to the reduction of the adsorbed SO₂ partially remaining after the cathodic scanning of potential in the poisoning solution (in the preparation of poisoned electrodes) [20].

It is noteworthy to mention that HClO₄ solutions are usually used for the study of the electrochemical behavior of oxygen reduction because the perchlorate is nonadsorbable anion, similarly to the solid acid (Nafion) used in the PEM fuel cells. The poisoning effect of bisulfate is severe at Pt(1 1 1) single crystalline electrode, but the effect is smaller at the other two low facets, i.e., Pt(1 1 0) and Pt(1 0 0). Thus the potential of the oxygen reduction peak at Pt(1 1 1) single crystalline electrode in H₂SO₄ solutions has been reported

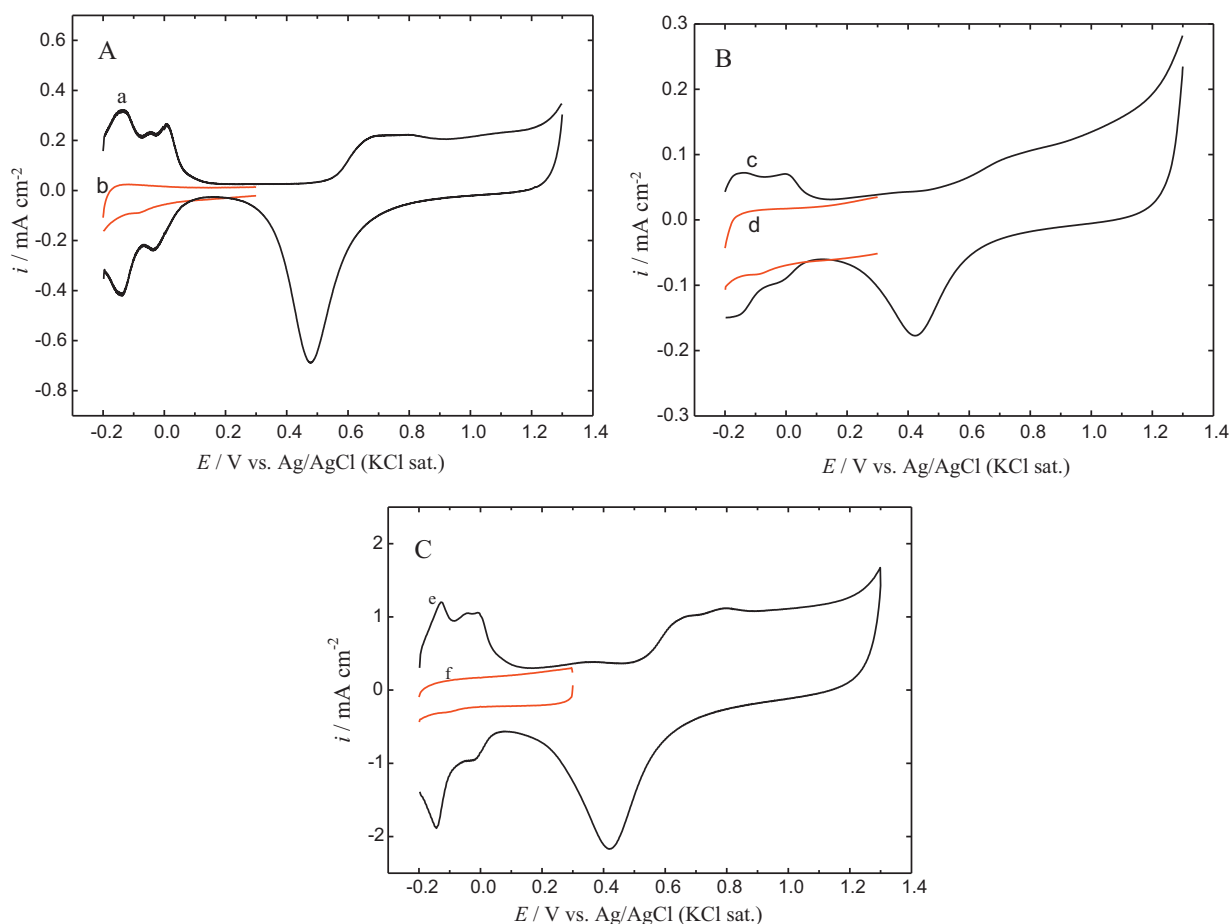


Fig. 2. CVs obtained at (A) poly-Pt, (B) nano-Pt/GC and nano-Pt_{comm}/GC electrodes in N₂-saturated 0.1 M H₂SO₄ solution. Curves (a, c and e): the fresh electrodes and curves (b, d and f): the poisoned electrodes. Scan rate: 100 mV s⁻¹.

to be negatively shifted compared with that obtained in HClO₄, while that at Pt(110) and Pt(100) single crystalline electrodes are almost the same [20]. In the present case, using polycrystalline Pt electrode, using low concentration H₂SO₄ is expected not to significantly affect the kinetics of the oxygen reduction as it has been reported that the adsorption of SO₄²⁻ has little effects on the kinetics of the ORR in acid sulfate medium [20]. Also it has been reported that the poisoning effect of bisulfate in PEM fuel cells is minimized by humidity [9]. Thus in solutions, in the present case, it could be expected that the effect of bisulfate adsorption is negligible.

Owing to the severe deleterious effect of SO₂ poisoning of platinum catalysts in PEMFCs, there have been several methods for its recovery [11,15]. In situ voltammetric method is considered to be an efficient and convenient one for the removal of the adsorbed

sulfur species. In the present case two procedures for the recovery of the electrodes were achieved by cycling the electrode potential in the narrow and wide potential ranges (NPR and WPR) of 0–0.8 V and –0.2 to 1.3 V, respectively, at 0.1 V s⁻¹. Fig. 3 shows the CVs for the ORR obtained at the (A) poly-Pt, (B) nano-Pt/GC and nano-Pt_{comm}/GC electrodes. Curves a and b were obtained at the fresh and poisoned electrodes, respectively. Curves c and d show the response after recovery of the two electrodes by the NPR and WPR procedures, respectively. In the NPR the potential was scanned for 10 cycles, in the potential range between 0.8 and 0.0 V in O₂-saturated H₂SO₄ solution, and only the 10th cycle is presented (curve c). In the WPR the potential was scanned in the potential range of –0.2 to 1.3 V. In curve d the 2nd cycle is presented in the case of the nano-Pt/GC and nano-Pt_{comm}/GC electrodes and the 4th cycle in the

Table 1
Electrochemical surface active area (A_r , A_p) and surface coverage (θ) of sulfur for fresh and poisoned poly-Pt, nano-Pt/GC and nano-Pt_{comm}/GC electrodes and for the electrodes recovered by the NPR and WPR recovery procedures.

Electrode	A_r, A_p (cm ²)			θ^a		
	Poly-Pt	Nano-Pt/GC	Nano-Pt _{comm} /GC	Poly-Pt	Nano-Pt/GC	Nano-Pt _{comm} /GC
Fresh	0.057	0.028	0.49	0.0	0.0	0.0
Poisoned ^b	0.003	0.006	0.0	0.95	0.79	1.0
NPR ^c	0.009	0.023	0.08	0.84	0.18	0.16
WPR ^d	0.044	0.026	0.48	0.24	0.07	0.02

^a As estimated from the charge consumed during the hydrogen desorption using a reported value of 210 $\mu\text{C cm}^{-2}$ [16].

^b The electrodes were poisoned by scanning the potential at 0.1 V s⁻¹ in 0.1 M H₂SO₄ solution containing 0.5 mM SO₂ in the potential range of –0.1 to 0.8 V.

^c The electrodes were recovered by scanning the potential at 0.1 V s⁻¹ for 10 cycles in the potential range of 0–0.8 V.

^d The electrodes were recovered by scanning the potential between –0.2 and 1.3 V at 0.1 V s⁻¹; two cycles for the nano-Pt/GC and nano-Pt_{comm}/GC electrodes and four cycles for the poly-Pt electrode.

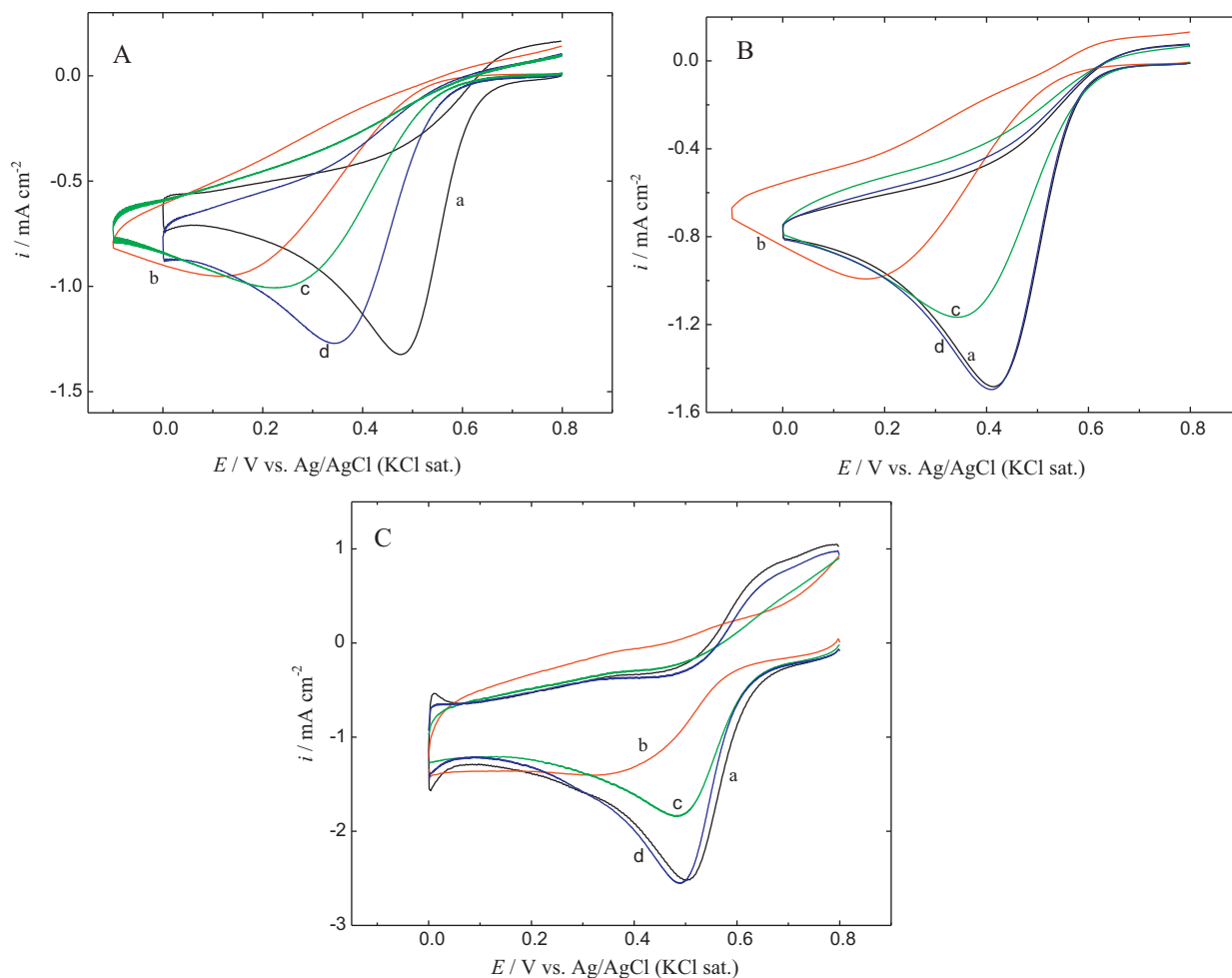


Fig. 3. CVs obtained at (A) poly-Pt, (B) nano-Pt/GC and nano-Pt_{comm}/GC electrodes ((a) fresh and (b) poisoned) in O₂-saturated 0.1 M H₂SO₄. (c) and (d) are CVs obtained at the electrodes recovered by the NPR and WPR procedures, respectively. Scan rate: 100 mV s⁻¹.

case of the poly-Pt electrode. This figure reflects several interesting points;

1. On poisoning the poly-Pt electrode the ORR peak potential is cathodically shifted by ca. 350 mV (compare curves a and b in Fig. 3A), while poisoning of the nano-Pt/GC electrode shifted the potential by ca. 250 mV (compare curves a and b in Fig. 3B). In the case of nano-Pt_{comm}/GC electrode the oxygen reduction peak at the poisoned electrodes is ill defined. Roughly the potential is shifted by ca. 150 mV (compare curves a and b in Fig. 3C).
2. The current of the poisoned electrodes (poly-Pt, nano-Pt/GC and nano-Pt_{comm}/GC) significantly decreased compared with each fresh electrode. The decrease in the current in all cases could be attributed either to the decrease in the electrochemical active area of the three electrodes (see Table 1) or to the change in the selectivity of the oxygen reduction, i.e., the change of the oxygen reduction mechanism from 4e reduction (formation of water) to 2e reduction pathway (formation of H₂O₂). To clarify this point the steady-state voltammograms at fresh and poisoned poly-Pt and nano-Pt/GC electrodes and the corresponding ring currents (*i_R*, upper panel) for H₂O₂ oxidation at the Pt-ring electrode at rotation rate of 800 rpm. The Pt-ring electrode was potentiostated at 1.1 V at which the oxidation of H₂O₂ is diffusion-controlled. Potential scan rate of the disk electrode is 10 mV s⁻¹. At the

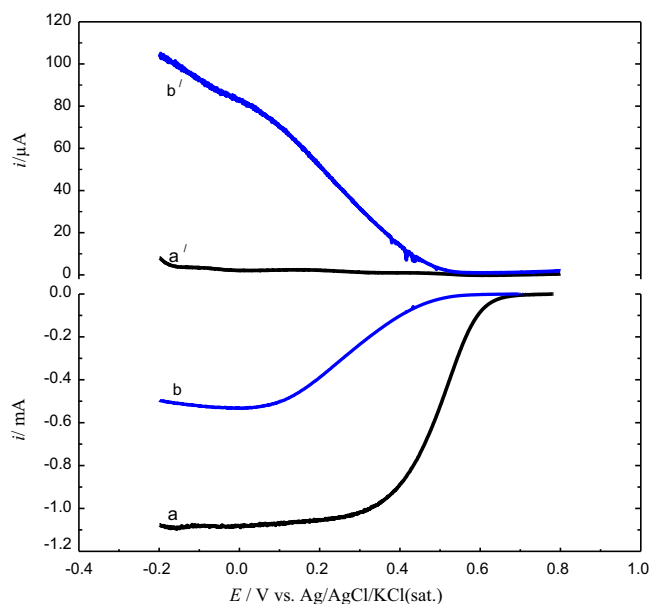


Fig. 4. Steady-state voltammograms for the ORR obtained at (a) fresh and (b) poisoned poly-Pt disk electrodes and for H₂O₂ oxidation at (a', b') Pt ring electrode in O₂-saturated 0.1 M H₂SO₄ solution. Rotation rate 800 rpm and the Pt ring was potentiostated at 1.1 V vs. Ag/AgCl (KCl sat.). Potential scan rate = 10 mV s⁻¹.

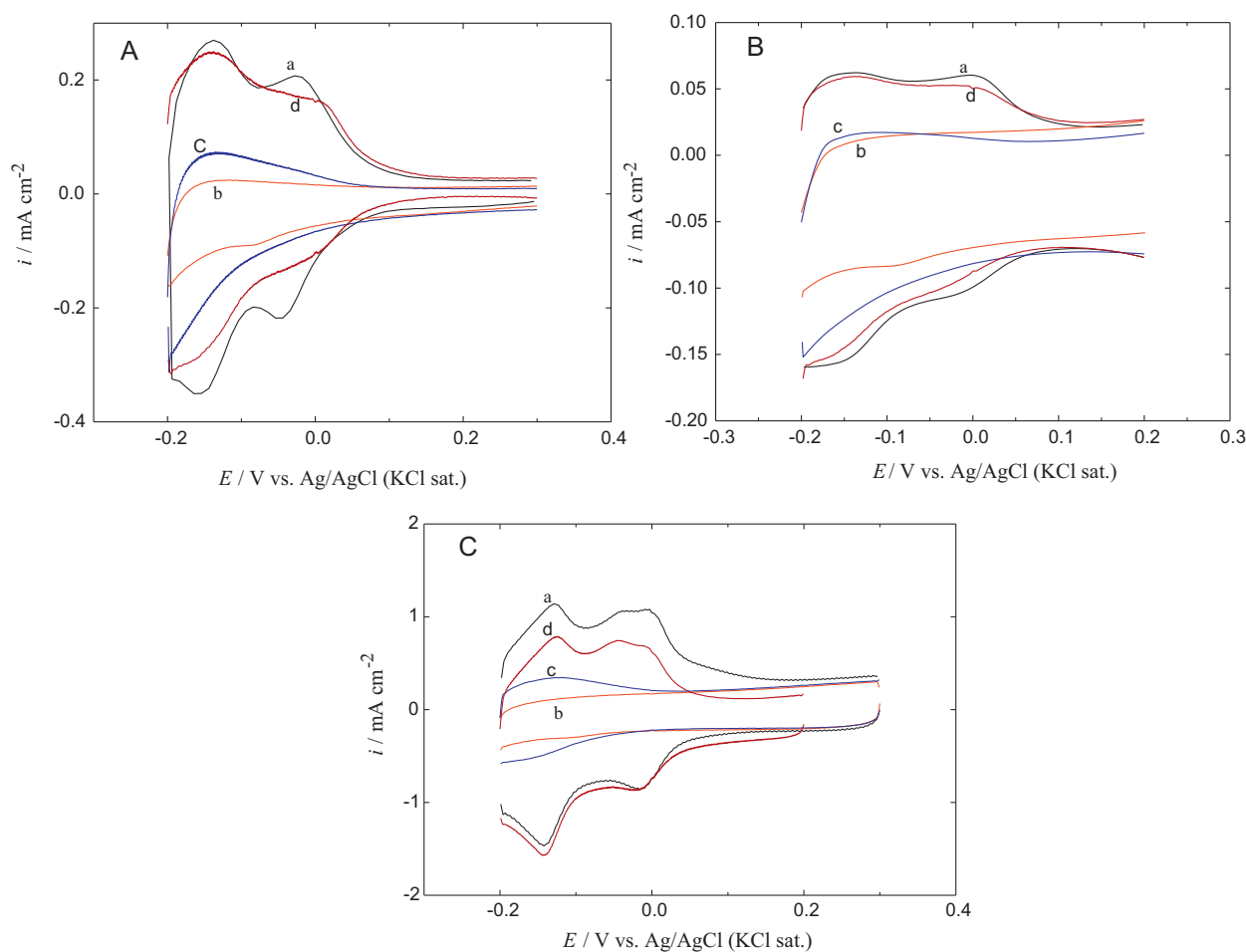


Fig. 5. CVs obtained at (A) poly-Pt, (B) nano-Pt/GC and nano-Pt_{comm}/GC electrodes ((a) fresh and (b) poisoned) in N₂-saturated 0.1 M H₂SO₄. (c) and (d) are CVs obtained at the electrodes recovered by the NPR and WPR procedures, respectively. Scan rate: 100 mV s⁻¹.

Pt-disk electrode (curve a), as expected, the ring current is significantly small indicating the exclusive 4-electron reduction of O₂ to H₂O. Whereas, in the case of the poisoned poly-Pt electrode (curve b) the scanning of the disk potential to the cathodic direction is accompanied by a significant increase in the ring current which starts to flow at ca. 0.5 V. This indicates the significant contribution of the 2e pathway (formation of H₂O₂) due to the adsorption of sulfur species which might partially change the adsorption pattern of molecular oxygen from a parallel mode to an end top mode. Such a change in the ORR mechanism occurs because of the decrease in the number of adjacent adsorption sites necessary for the breaking of the O–O bond [8,11].

- At the poly-Pt electrode the NPR recovery procedure is not remedial; after 10 potential cycles only 15.5% (see Table 1) of the oxygen reduction peak current was recovered ($\theta = 0.84$) and the cathodic peak potential was around 250 mV. By the WPR procedure the behavior is improved but still not satisfactory; the recovery is around 76%, and still the peak potential is negatively shifted compared to the fresh electrode. It has been reported that the recovery of the poly-Pt electrode needs at least seven potential cycles (in the potential range between the hydrogen and oxygen evolution (WPR) [21,4,22–26]. At high anodic potential the adsorbed S is removed by oxidative desorption as soluble SO₄²⁻ [21].
- At the nano-Pt/GC electrode, interestingly, the NPR recovery procedure is more efficient than in the case of the poly-Pt electrode.

That is to say, the nano-Pt/GC could be recovered in the potential range of the ORR, avoiding the dissolution of Pt when applying a high anodic potential. Moreover the WPR procedure in this case is remedial: the electrode is completely recovered after only two potential cycles. The CV for the electrode recovered by the WPR procedure almost coincides with that for the fresh electrode (curves a and d (Fig. 3B)). Similarly, the NPR recovery procedure is efficient at the nano-Pt_{comm}/GC electrode. The peak potential of the oxygen reduction after this recovery is almost as same as that of the fresh electrode. The NPR almost completely recovered the CV behavior in such a way that the CVs at the fresh electrode and at the electrode after being subjected to WPR are almost the same.

The extent of recovery of the three electrodes was quantified by estimating the electrochemical active area (*A*) from the amount of charge consumed during the hydrogen desorption [27] after discounting the double layer charge, for the fresh and poisoned electrodes and those recovered by the NPR and WPR procedures. Fig. 5 shows the *H*_{ads/des} at the (A) poly-Pt, (B) nano-Pt/GC and (C) nano-Pt_{comm}/GC electrodes in N₂-saturated 0.1 M H₂SO₄. Curves a and b were obtained at the fresh and poisoned electrodes, respectively. Curves c and d were obtained after the electrodes were recovered by the NPR and WPR procedures, respectively. Hydrogen adsorption occurs only on the adsorbate-free Pt electroactive sites and thus it can be considered as a reflection for the activity of the electrode. The surface coverage (θ) of sulfur was calculated

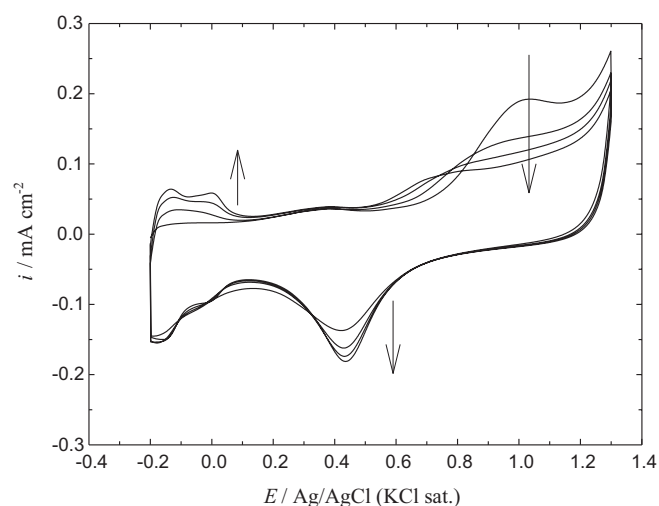


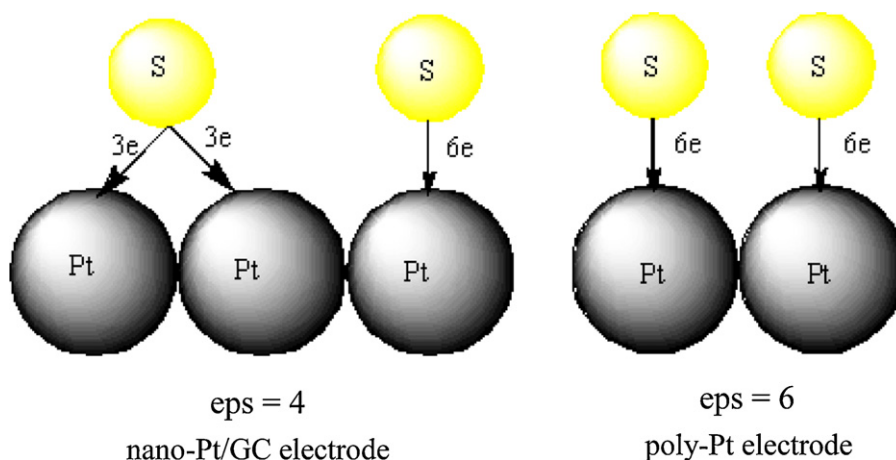
Fig. 6. A sequence of CVs obtained at the poisoned nano-Pt/GC electrode in N_2 -saturated 0.1 M H_2SO_4 . Potential scan rate: $0.1 V s^{-1}$.

from the following equation;

$$\theta = \left(1 - \frac{A_p}{A_f}\right) \times 100 \quad (1)$$

where A_f is the electroactive area of the fresh electrode and A_p is the electroactive area of the poisoned electrode, or recovered either by the NPR or WPR procedure. The values of A_f , A_p and θ for poly-Pt, nano-Pt/GC and nano-Pt_{comm}/GC were estimated and given in Table 1. The data in this table consistently agrees with the results deduced from the oxygen reduction, i.e., the efficient recovery was obtained at the nano-Pt/GC and nano-Pt_{comm}/GC electrodes, while the poly-Pt electrode was not completely recovered by using either the NPR or WPR procedure. It is noteworthy to mention that the sulfur surface coverage at nano-Pt/GC electrode is smaller than that at the poly-Pt electrode, even though the former electrode is of lower active surface area. This might be attributed to the different mode of adsorption of sulfur in both cases. It is reported that S may adsorb on Pt via one or two fold adsorption mode [28]. In the present case the adsorption of S onto the nano-Pt is considered to be a mixture of the two modes, as indicated below based on the number of electron per active site (eps) for the oxidation of S to SO_4^{2-} , calculated using Eq. (2) [28].

$$\text{eps} = \frac{Q_s}{Q_H} \quad (2)$$



Scheme 1. Models for the adsorption of sulfur onto poly-Pt and nano-Pt/GC electrodes.

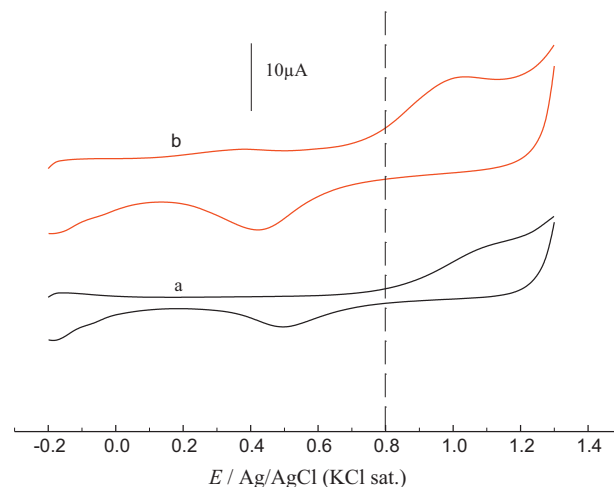


Fig. 7. CVs obtained at poisoned poly-Pt (a) and nano-Pt/GC (b) electrodes in N_2 -saturated 0.1 M H_2SO_4 . Scan rate: $100 mV s^{-1}$.

where Q_s is the charge consumed during the complete oxidative desorption of adsorbed S. $Q_s(\sum_n Q^a - Q^c)$ is calculated by the summation of the difference between the charge (Q^a) consumed during the oxidation in the entire potential range (0.4–1.3 V) and the charge (Q^c) consumed in the reduction of the platinum oxide formed and Q_H is the charge consumed during the H desorption at the clean electrode. Q_s was estimated from Fig. 6 in which the poisoned electrode was submitted to several potential cycles in clean N_2 -saturated H_2SO_4 until the characteristic CV of the clean electrode was obtained. Then Q_s for the all cycles was summated and divided by Q_H for the calculation of eps. In the case of the nano-Pt/GC electrode, eps was found to be equal to 3.7. This value indicates a single and multi coordination of S to the nano-Pt (see Scheme 1). On the other hand, eps was found to be 6 for the adsorption of S onto the poly-Pt electrode which is indicative of a single coordination of S as schematically represented in Scheme 1. Among the electrodes studied the nano-Pt_{comm}/GC electrode is the best one regarding the recovery performance. This may indicate a strong effect of the particle size on the recovery of sulfur-poisoned electrodes. This point needs further investigation which is under way.

The less susceptibility of the nano-Pt/GC electrode compared with the poly-Pt electrode to the SO_2 poisoning and the ease of the recovery could be explained based on the electrochemical response of the two fresh electrodes in 0.1 M H_2SO_4 in a wide range of potential (Fig. 2 (curves a and c)). The platinum oxide (PtO_x) reduction

at the nano-Pt/GC electrode (at ca. 0.4–0.5 V) occurs, as a whole, at relatively more negative potential compared with the poly-Pt electrode. This indicates that the PtO_x bonding at the nano-Pt/GC electrode is stronger than that on the poly-Pt electrode. The negative shift of the PtO_x reduction is coupled with a negative shift in the PtO_x formation. This is reflected in the less catalytic activity of the nano-Pt/GC electrode compared with the poly Pt electrode towards oxygen reduction (compare curve a in Fig. 3A and B). It has been reported that S oxidation is catalyzed by the formation of adsorbed oxygen species [29]. This is obvious from Fig. 7 in which the voltammetric behaviors obtained in a wide potential range at the poisoned poly-Pt and nano-Pt/GC electrodes in N₂-saturated 0.1 M H₂SO₄ are shown. It is clear that the onset potential of the oxidation of adsorbed sulfur at the nano-Pt/GC electrode is relatively less positive compared with that at the poly-Pt electrode (see the vertical dashed line). Thus it is thought that the easier electrochemical formation of the PtO_x species at the nano-Pt/GC electrode compared with the poly-Pt electrode plays an important role in the efficient recovery of the former electrode. This may also explain the efficient recovery at the nano-Pt/GC electrode using the NPR recovery procedure (0–0.8 V). At 0.8 V the oxidation of adsorbed S is significant at the nano-Pt/GC electrode, while it is negligible at the poly-Pt electrode. Moreover, it has been reported that sulfur species may be removed chemically via the reaction of electrochemically formed PtO_x with adsorbed S [30,31].

4. Conclusions

Nano-Pt/GC electrode showed an improved resistance to SO₂ poisoning compared with the poly-Pt electrode. Also the poisoned nano-Pt/GC electrode, in contrast to the poisoned poly-Pt electrode, was significantly recovered by in situ electrochemical treatment, i.e., several potential cycles in the potential range of the oxygen reduction and only two cycles in the potential range between the onset potentials of the hydrogen and oxygen evolutions.

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