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Methanol electro-oxidation at platinum electrode: In situ recovery of CO poisoned platinum electrode

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Methanol oxidation at polycrystalline (poly-Pt) electrode in acid medium is retarded by the formation of carbon monoxide intermediate as a result of poisoning of the active sites upon the first potential scan and as a result of the dissociative adsorption of methanol. This retards the subsequent oxidation to carbon dioxide, which probably occurs at large anodic potential. In the present work the possible In situ recovery of the poisoned platinum electrodes using potentiodynamic and potentiostatic techniques are investigated. In potentiodynamic one, both short range recovery (SRR), i.e., in the potential range - 0.2 to 0.9 V and, long range recovery (LRR), i.e., in the range - 0.2 to 1.3 V are conducted. Recycling the potential according to the former scenario results in more poisoning of the electrode as reflected in the continuous decrease of the peak current of the methanol oxidation, while recycling the potential in the wide potential cycling. It is likely that the deactivation of the electrochemical response upon SRR is due to the accumulation of the CO intermediate, and the activation upon LRR is due to the sweeping of the formed CO as a result of the oxidation by the adsorbed hydroxide at large potential. In the potentiostatic one, the electrode is conditioned for various time period at either - 0.9 or - 1.3 V. Conditioning the potential at - 0.9 V activated the electrode, while at - 0 1.3 V recovered the activity.

Keywords: Methanol oxidation, platinum, poisoning, recovery.

1. INTRODUCTION

Polycrystalline platinum (poly-Pt) electrode is considered as the candidate for oxidation of methanol at which the electrochemical behavior of methanol has been extensively studied [1-3]. The methanol electro-oxidation at poly-Pt electrode surface, occurs either through direct or indirect pathway, is combined with several steps of dehydrogenation for the final oxidation to CO_2 [1-13]. However, the CO poisoning of the poly-Pt by CO formed during the methanol oxidation retards the commercial applications of direct methanol fuel cells for. Even though the equilibrium potential of methanol is

comparable to hydrogen, but the oxidation of the former occurs at relatively high potential because of the sluggish kinetics [9-13]. The potential should be high enough such that the electrode is free from adsorbed hydrogen and at the same time enough for the dissociation of water [14-19].

It has been reported that the coexistence of $Pt-OH_{ads}$ and Pt atoms at the electrode surface electrocatalyze methanol oxidation through what is the so called bi-functional mechanism [20-33] according the following equation;

In the present work, the In situ recovery of poisoned poly-Pt electrode during methanol oxidation is examoned via continuous scan of potential in a short range, i.e., in the potential range - 0.2 to 0.9 V and continuous scan of potential in a wide potential range, i.e., - 0.2 to 1.3 V, are conducted. In the potentiostatic one, the electrode is conditioned for various time period at either – 0.9 or – 1.3 V. A plausible explanation for different behaviors is given.

2. EXPERIMENTAL

2.1. Chemicals and solutions.

All chemicals used in the present work were analytical grade. Reagent grade Sulphuric acid (H₂SO₄, OmniTrace Ultra), methanol (CH₃OH, 99.9 % purity), and Bbismuth (III) nitrate pentahydrate were purchased from (Sigma-Aldrich). Sodium hydroxide (NaOH (99. 8% purity) was purchased from (BDH). Chemicals were used as received without any further purification.

2.2. Electrodes and Electrolytes.

Electrodes used are polycrystalline platinum (poly-Pt), 1.6 mm diameter, as working electrode, platinum spiral wire as the counter electrode and reference electrode as Ag/AgCl (KCl sat.). The working electrode used in this work was prepared by polishing procedure. The electrode was polished until the surface is visually smooth with sandpaper. Polishing start from Grit 1500 to 3000 and rinsed with deionized water. After that, using alumina powder (down to 0.06 μ m) and then ultrasonically cleaned in pure Deionized water for 15 min for removing any physically adsorbed species. Then, it was electrochemically pretreated in 0.5 M H₂SO₄ solution by repeating the potential sweep in the potential ranges (between – 0.2 to 1. 3 V vs. Ag/AgCl (KCl sat.)) until the cyclic voltammetric (CV) characteristic of a clean poly-Pt electrode was obtained. Potentiostat/galvanostat/ZRA model Reference 600 TM was

used. A conventional three-electrode cell of around 20 ml was used for the voltammetric measurements. All electrochemical measurements were performed at the room temperature.

3. RESULTS AND DISCUSSION

Fig. 1 shows the voltammetric behavior of poly-Pt electrode in (a) N₂-saturated 0.5 M H₂SO₄ containing (b, c) 0.5 M methanol, both in (b) a short range and (c) a wide range of potential. In the absence of CH₃OH (curve a), voltammetric pattern exhibited the features of poly-Pt surface chemistry [34], i.e., the one for the hydrogen region (in the potential range - 0.2 to 0.1 V) that shows the hydrogen under potential deposition (UPD) peaks in acid electrolyte. These pattern is suppressed after adding CH₃OH (curves b and c). Probably, this decrease is due to the poisoning of the hydrogen sites by CO_{ads} [35, 36]. The current for oxidation of methanol commences at about 0.4 V in the vicinity of charging of the double-layer region. In this region, adsorbed dissociated water is the oxygen source. The mean peak at around 0.68 V (accord to Eq. 2) is followed by the subsequent oxidation of adsorbed carbon monoxide to carbon dioxide (Eq. 3) as enhanced by the oxygenated adsorbed species, OH_{ads} that starts to form at potentials above 0.5 V (Eq. 4).

$$Pt-CH_3OH \rightarrow Pt-CO + 4H^+ + 4e^-$$
(2)

$$Pt-CO + H_2O \rightarrow Pt + CO_2 + 2H^+ + 2e^-$$
(3)

$$H_2O + OH_{ads} + H^+ + e^-$$
 (4)

At potentials above 0.8 V, the peak current of the oxidation of methanol decreases substantially . Probably this decreases is attributed to the extensive surface oxidation [35, 36]. On the reverse scan, a reverse anodic peak is observed. In the reverse scan and at the potential negative enough for the complete reduction of platinum oxide formed in the anodic sweep, again the oxidation of methanol increases. This is confirmed from scanning the potential of the electrode in a short range (curve c), where the reverse peak is not that sharp. The reverse anodic peak and the forward one does not coincide. The former one shifted slightly to more negative potentials than the former one. At more negative potentials, surface coverage of coverage of CO_{ads} increases and consequently the current decreases. This was recognized as the catalyst poison in oxidation of methanol on platinum electrode.

As clearly shown the scanning of potential to larger values (curve b) resulted in the recovery of the active sites as revealed from the appearance of the platinum oxide reduction peak at around 0.7 V as well as of the clear reverse peak which appears at the forward going shoulder at 0.35 V. In the scanning of the potential in short range (curve b), the reverse peak is not revealed. Thus the recovery of the poisoned electrode is tried in both ranges (see below).

Figs. 2 and 3 show the effect of cycling of the potential in a wide range on the CH₃OH oxidation at poly-Pt electrode in 0.5 M H₂SO₄. It is clear that scanning in a wide potential range, i.e., from -0.2 to 1.3 V, results in a continuous increase in the peak current values (Peaks II and III). This is due to the sweeping of the possible intermediate and its conversion to CO₂ and thus the active sites becomes available for methanol oxidation.



Figure 1. Cyclic voltammetry for Poly-Pt electrode recorded at a scan rate 100 V s⁻¹ in (a) 0.5 M H₂SO₄ containing (b, c) 0.5 M CH₃OH.



Figure 2. Cyclic voltammograms obtained at Poly-Pt electrode recorded at a scan rate 100 V s⁻¹ in 0.5 M H₂SO₄ containing 0.5 M CH₃OH. Various consecutive cycles, in a wide potential range, are shown.

The peak current and enhancing factors (the peak current obtained in cycles next to the first one with respect to the peak current of the first cycle), calculated by Eq. 5, are shown in Table 1. The current

is considered for peak II. As clearly shown the peak current increases with cycling of potential and the enhancing factor reaches 4 for cycle 40th. The increase in the peak current cease when the cycles reaches 50 cycles.

Enhancing factor =
$$I_{pa2}/I_{pa1}$$
 (5)

where I_{pa1} and I_{pa2} are the current obtained in the 1st and consecutive cycles, respectively.



Figure 3. Cyclic voltammograms obtained at Poly-Pt electrode recorded at a scan rate 100 V s⁻¹ in 0.5 M H₂SO₄ containing 0.5 M CH₃OH. Various consecutive cycles, in a wide potential range, are shown.

Table 1. Methanol peak current and enhancing factors obtained at various potential cycles over a wide potential range. Data are extracted from Figs 2 and 3.

Potential cycle	Peak current / µA	Enhancing factor
number		
1 st	127	
2^{nd}	239	1.90
5 th	261	2.15
10 th	303	2.38
20 th	404	3.18
30 th	467	3.67
50 th	519	4.08

In Fig. 4 in which the potential scanned in a short potential range, i.e., from -0.2 to 0.9 V, in contrary to scanning in a wide potential range (shown above), the peak current continuously decreases as a result of methanol oxidation to the poisoning CO species (Eq. 1). Thus for complete recovery of the poisoned electrode, its potential can be scanned in a wide potential range, i.e., from -0.2 to 1.3 V.

The peak current and deactivation factor (the peak current obtained in the first cycle with respect to the peak current of the consecutive one) are shown in Table 2. The current is considered for peak II. It is noteworthy to mention that the 1st cycle in Fig. 4 is similar to cycle 50th in Fig. 3, i.e., the results obtained in Fig. 4 was taken for the same electrode after conducting experiment for results presented in Figs 2 and 3. As clearly shown the peak current decreases with cycling of potential. The extent of deactivation is estimated using Eq. 5, given above and data are shown in Table 2. As shown in Table 2, the peak current obtained after 7 cycles decreased 28 % of the peak current of the first cycle.



Figure 4. Cyclic voltammograms obtained at Poly-Pt electrode recorded at a scan rate 100 V s⁻¹ in 0.5 M H₂SO₄ containing 0.5 M CH₃OH. Various consecutive cycles, in a short potential range, are shown.

Table 2. Methanol peak current and enhancing factors obtained at various potential cycles over a short potential range. Data are extracted from Fig. 4.

Potential cycle	Peak current / μA	Deactivation factor
number		
1 st	503	-
2 nd	421	0.84
3 rd	400	0.79
4 th	392	0.78
5 th	378	0.75
6 th	364	0.72
7 th	364	0.72

3.1. Potentiostatic recovery of the poisoned poly-Pt electrode

A typical cyclic voltammetry results when changing the holding time at a different holding potentials is shown in Figs. 5 and 6. At holding potential 0.9 V, with increasing holding time, the activity of the electrode initially decreases (holding time 1 s) as reflected on the positive shift of the peak of methanol oxidation, even though the peak current slightly increased. Probably this deactivation of the electrode is due to the initial accumulation of the CO at the electrode surface. However, upon increasing the holding potential to 5 s and more, the peak potential is retained in addition to the increase of the peak current. Interestingly, the recovery here is significant compared with the potentiodynamic recovery in the short range, i.e., from -0.2 to 0.9 V. When the potential is held at 1.3 V, the response is stable, no significant change in the voltammetric response, unlike the recovery using potentiodynamic mode. It has been reported that scenario of recovery poisoned platinum electrode is critical; for example while sulfur poisoned platinum electrode in polymer electrolyte membrane fuel cell could be partially recover by LRR (in the potential range between 0.06 and 1.26 V) (reversible hydrogen electrode, RHE) [37-41], it cannot be completely recovered even by holding the potential at 1.46 V (RHE). In the present case the potentiodynamic cycling of potential was remedial in the wide potential range rather than the short one.



Figure 5. Cyclic voltammograms obtained at Poly-Pt electrode recorded at a scan rate 100 V s⁻¹ in 0.5 M H₂SO₄ containing 0.5 M CH₃OH. The potential was hold at 0.9 V for various times.

The potentiostatic one was remedial at studied potentials. Probably, the difference is due to the nature of the poisoning species. Recovery of the poisoned electrode at lower potential avoid the possible dissolution of platinum at large potentials. Further study to clarify this point is underway. It has been reported that increasing the immunity of platinum and platinum based electrodes could be achieved via several scenarios including for example alloying of platinum with other species [42-45]. These species should have higher ability, compared with platinum, to adsorb water at lower anodic potentials. Among these species Ru with its oxophylic properties is considered as the candidate one [46, 47]. The immunity against CO poisoning has been reported also to increase at higher temperatures [48-51]. Another Alternative approaches is self induced performance recovery with neat air which is an effective strategy as it provide oxygen for the oxidation of adsorbed contaminant species in the anode electrode[52, 53]. Also the recovery of the performance loss of poly electrolyte membrane fuel cells (PEMFCs) has been reported to be largely restored by neat air operation and potential cycling between 0.08 V and 1.2 V vs. the hydrogen reference electrode [54]. Similar recovery procedure have been applied in PEMFCs [55, 56]. In the present case, successfully, the recovery could be achieved at lower potential avoiding the possible dissolution of platinum at large anodic potentials.



Figure 6. Cyclic voltammograms obtained at Poly-Pt electrode recorded at a scan rate 100 V s⁻¹ in 0.5 M H₂SO₄ containing 0.5 M CH₃OH. The potential was hold at 0.9 V for various times.

4. CONSLUSIONS

Methanol oxidation at polycrystalline platinum (poly-Pt) electrode is retarded by the formation of carbon monoxide due to the deactivation of the active sites. In the present work, two scenarios for the in situ recovery of the poisoned poly-Pt electrode are conducted, i.e., potentiodynamic and potentiostaic. In the former the potential of the electrode is cycled between lower and upper limits; between -0.2 V and -0.9 V (short range recovery (SRR)) and between -0.2 and 1.3 V (longe range recovery (LRR)).

In the potentiostatic one, the electrode is conditioned for various time period at either -0.9 or -1.3 V. It has been found that while LRR completely recovers the poisoned electrode, the SRR resulted in a continuous deactivation of the electrode. In contrary, in potentiostatic mode, conditioning the potential at -0.9 V activated the electrode, and conditioning at -1.3 V retained the activity of electrode towards methanol oxidation.

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