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ORIGINAL PAPER

Effects of iron-tetrasulfophthalocyanine on the catalytic activities of Pt/C, PtRu/C, and Pd/C catalysts in a multi-anode direct formic acid fuel cell

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Abstract This paper reports a systematic study of the effects of a promoter, iron-tetrasulfophthalocyanine (FeTSPc), on the catalytic activities of carbon supported Pt, PtRu, and Pd catalysts (Pt/C, PtRu/C, and Pd/C) for formic acid oxidation. A multi-anode direct formic acid fuel cell (DFAFC) was used to compare the effects on each catalyst of adding FeTSPc to the fuel stream. The FeTSPc significantly enhanced the activity of the Pt/C catalyst, but had little effect on the PtRu/C catalyst. The activity of the Pd/C catalyst was inhibited by the FeTSPc. A FeTSPc modified Pt/C was also evaluated in a conventional 5 cm^2 DFAFC.

Keywords Iron-tetrasulfophthalocyanine (FeTSPc) · Carbon supported catalysts · Multi-anode direct formic acid fuel cell (DFAFC) · Array membrane electrode assembly (MEA) · Catalytic activity

1 Introduction

Using formic acid as fuel in polymer electrolyte membrane (PEM) based fuel cells was first introduced in 1996 [1]. Through only a few years of research, direct formic acid fuel cell (DFAFC) technology has shown electro-catalytic oxidation activity superior to that of direct methanol fuel cells (DMFCs) and in some cases performances approaching those of H_2-fed polymer electrolyte membrane fuel cells (H_2-PEMFCs) [2]. Compared with DMFCs, DFAFCs have the multiple advantages of high electromotive force, limited fuel crossover, and high practical power densities at low temperatures. Therefore, the DFAFC system has recently been considered as a promising portable power source [3].

Pt-based and Pd-based catalysts are usually used in the anodes of DFAFCs [1–35]. Pd-based catalysts usually show higher activities than Pt-based catalysts, but tend to lose their activity under DFAFC conditions [2, 12]. The catalytic activities of Pt-based catalysts are generally stable but relatively low. Therefore, improvements of either the activities of Pt-based catalysts or the stabilities of Pd-based catalysts are two important aspects of the development of high performance DFAFCs.

Advances in high performance fuel cell catalysts have usually been focused on the development of bi-metallic (or tri-metallic) catalyst systems. A number of Pt alloy, inter-metallic, or surface modified catalysts (Pt/Ru, Pt/Pd, Pt/Au, and Pt/Pb), have been reported as the anode catalysts for DFAFCs, and these catalysts have shown better cell performance than pure platinum [6, 7, 14, 19, 20, 33]. As well, a few Pd-based bi-metallic catalysts (Pd/Au, Pd/P, and Pd/Pt) have also been demonstrated in DFAFC systems, and have shown better cell performance than pure palladium [15, 26, 27].

Recently, an interesting iron-tetrasulfophthalocyanine (FeTSPc) modified Pt co-catalyst for the electro-oxidation of formic acid has been reported [19, 31, 35]. Zhou et al. [19, 31, 35] found that the catalytic activity of a Pt electrode could be enhanced by modification with adsorbed FeTSPc. In this paper, the effects of FeTSPc on the catalytic activities of commercial Pt/C, PtRu/C, and Pd/C anode catalysts are compared. The better activities of PtRu and Pd for formic acid oxidation, relative to Pt, make these attractive candidates for further improvement with FeTSPc.

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The lower cost of Pd is a further incentive for this work. In addition, a comparison of the effects of FeTSPc on the activities of Pt/C, PtRu/C, and Pd/C provides mechanistic insight into the role of the FeTSPc.

Conventional catalyst studies are usually performed in a single fuel cell. In order to avoid the effects of uncontrolled variations between experiments, a multi-anode DFAFC was used in this study, which allows comparison of several different catalysts simultaneously.

2 Experimental

2.1 Catalysts and chemicals

Catalysts employed in this study were 40% Pd/C (40% palladium on Vulcan XC-72, E-TEK), 20% Pt/C (20% platinum on Vulcan XC-72, E-TEK), and 20% PtRu/C (20% platinum-ruthenium (Pt:Ru = 1:1) on Vulcan XC-72, E-TEK). Formic acid from Alfa Aesar (ACS, 88 + % + 12% water, Lot# H13S025) was diluted with de-ionized water. FeTSPc was from Sigma–Aldrich.

2.2 Preparation of electrodes

The catalyst was dispersed, by sonication for 10 min, in a mixture of pure water and a volume of Nafion solution® (5%, DuPont) required for a net Nafion to catalyst ratio of 1:4 (w/w). The resulting ink was deposited onto carbon fiber paper (Toray TGP-H-090) and dried in air for 1 h at ambient temperature. The loading was maintained at 1.6 mg cm^{-2}, including the carbon support and Nafion.

Pre-modified FeTSPc Pt/C electrodes were prepared as follows: 10 mg E-TEK 20% Pt/C catalyst was mixed with 0.25 mL FeTSPc solution (with various net amounts of FeTSPc as indicated) and 0.05 mL of 5% Nafion solution, and sonicated for 10 min. The resulting ink was deposited onto carbon fiber paper and dried in the air for 1 h at ambient temperature. The loading was 1.6 mg cm^{-2}, including the carbon support, Nafion and FeTSPc.

2.3 Conventional three-electrode experiments

A Pt wire and Hg/Hg_2SO_4 electrode were used as the counter electrode and the reference electrode, respectively. The potentials in these experiments are quoted against Hg/Hg_2SO_4. The working electrode was prepared by spreading 1.6 mg cm^{-2} catalyst onto 1 cm^2 of carbon fiber paper, as described in Sect. 2.2. The electrolytes were 0.5 M H_2SO_4 or 0.5 M HCOOH + 0.5 M H_2SO_4, with or without 0.1 mg mL^{-1} FeTSPc added as indicated.

2.4 Fuel cell performance tests

2.4.1 Preparation of anode-array membrane and electrode assemblies (MEAs)

Membrane and electrode assemblies with anode arrays were prepared with a Nafion 115® membrane (Ion Power), a 5 cm^2 cathode consisting of 4 mg cm^{-2} Pt black on carbon fiber paper, and nine 0.23 cm^2 anodes which were cut from a single larger electrode prepared as described in Sect. 2.2 with a catalyst-layer loading of 1.6 mg cm^{-2}. This gives very good reproducibility of the catalyst loading on each electrode, as indicated by the reproducibility between electrodes in Fig. 3, for example. The electrodes were hot pressed onto the Nafion at 135 °C and 200 kg cm^{-2} for 90 s.

2.4.2 Cell performance tests

A multi-anode, liquid-feed fuel cell that has been previously described [36] was used. It is based on a commercial (Electrochem®) 5 cm^2 active area cathode plate, and a custom anode plate with 9 (3 × 3 array) electronically isolated graphite rod anode current collectors embedded in a Lexan plate.

The operation of the multi-anode DFAFC was controlled with a multi-channel potentiostat (Arbin®). The cell was operated with aqueous formic acid (with or without FeTSPc added) fed to the anode at a flow rate of 0.2 mL min^{-1}, and dry oxygen delivered to the cathode at a flow rate of 100 sccm without back pressure. All experiments were conducted at ambient temperature.

3 Results

3.1 Evaluation of FeTSPc effects with a conventional three-electrode cell

3.1.1 Effects of FeTSPc on the catalytic activities of Pt/C, PtRuC, and Pd/C catalysts

The effects of FeTSPc on the catalytic activities of carbon supported Pt, PtRu, and Pd catalysts for formic acid oxidation were first investigated with a regular 3-electrode electrochemical cell. Figure 1 shows linear sweep voltammograms for 40% Pd/C, 20% Pt/C, and 20% PtRu/C electrodes in a 0.5 M formic acid + 0.5 M H_2SO_4 solution with and without FeTSPc added to the solution. It can be seen that the addition of FeTSPc significantly impaired the catalytic activity of the 40% Pd/C (Fig. 1a), while it significantly enhanced the activity of the 20% Pt/C (Fig. 1b). The effect of FeTSPc on the 20% PtRu/C catalyst was relatively minor (Fig. 1c), with some enhancement at low potentials and inhibition at high potentials.

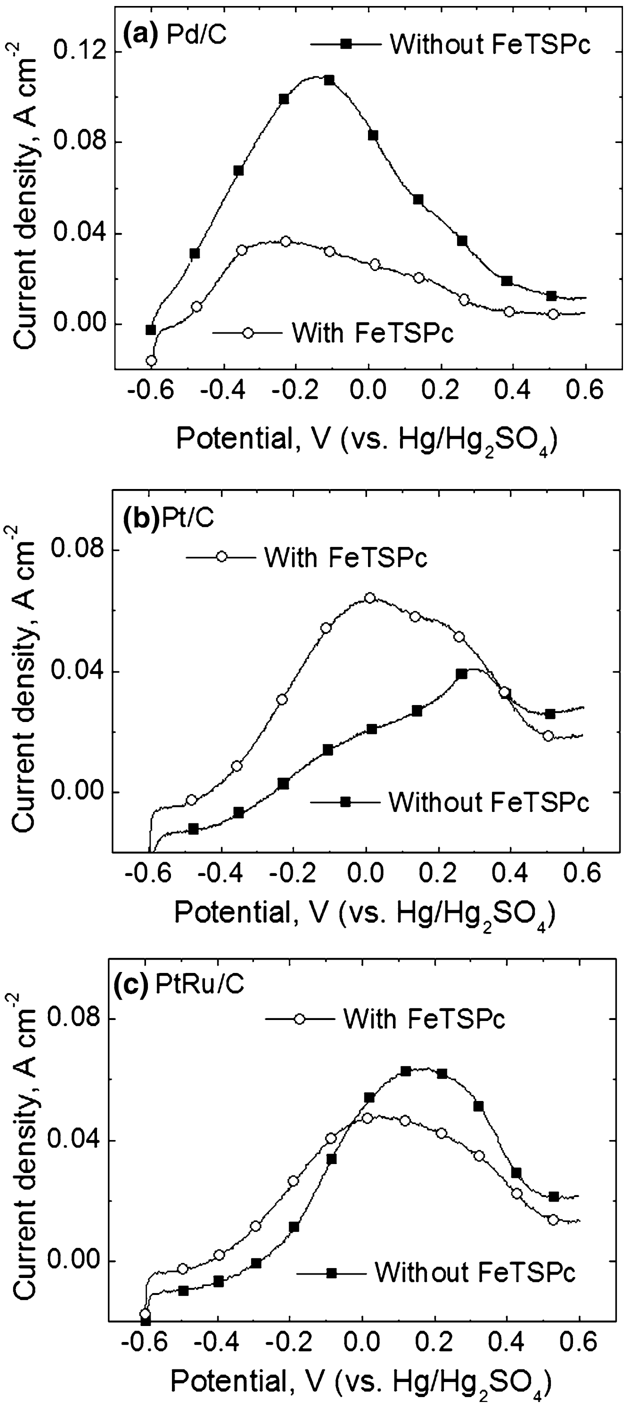

Fig. 1 Linear sweep voltammograms at 20 mV s^{-1} for **a** 40% Pd/C; **b** 20% Pt/C; and **c** 20% PtRu/C electrodes in a liquid electrolyte (0.5 M HCOOH + 0.5 M H_2SO_4 + 0.1 mg mL^{-1} FeTSPc as indicated), 3-electrode cell

3.1.2 Quantitative study of the effect of FeTSPc on the catalytic activities of Pt/C

Since the catalytic activity of the Pt/C catalyst was significantly improved by adsorption of FeTSPc, the effect of FeTSPc was quantitatively studied with pre-modified FeTSPc/Pt/C catalysts. Figure 2 shows linear sweep voltammograms for electrodes pre-modified with various amounts of FeTSPc. For the catalyst loading of 1.6 mg cm^{-2} (including Pt/C catalyst, Nafion and FeTSPc) employed in this study, the maximum promotion effect was obtained at a FeTSPc loading of 0.032 mg cm^{-2}. Additional FeTSPc in the catalyst layer did not significantly change the catalytic activity.

3.2 Effects of FeTSPc on the performance of DFAFCs with Pd/C, PtRu/C, and Pt/C catalysts

3.2.1 Multi-anode DFAFC performance

The effects of FeTSPc on the catalytic activity of the Pd/C, PtRu/C, and Pt/C catalysts were further studied in a multi-anode DFAFC by employing an anode array membrane electrode assembly (MEA). The array MEA was prepared with three electrodes each of 40% Pd/C, 20% PtRu/C and 20% Pt/C, as illustrated in Fig. 3a. Polarization curves were obtained by applying a potential staircase in which the anodes in the array were simultaneously polarized from the cells' open circuit voltages (OCV) to a final voltage of 0.3 V for the Pd/C anodes, and to a final voltage of 0.1 V for the Pt/C and PtRu/C anodes. The step size was –15 mV and the step time was 30 s. Continuous polarization curves were obtained by returning the cell voltages to their initial OCV at the end of each polarization, and the next polarization was begun immediately.

Figure 3b shows a series of continuous polarization curves of the multi-anode cell obtained with the 40% Pd/C, 20% PtRu/C and 20% Pt/C anode catalysts, and with 5 M HCOOH fuel without FeTSPc. As seen in the figure, the Pd/C catalyst provided the best initial (first polarization

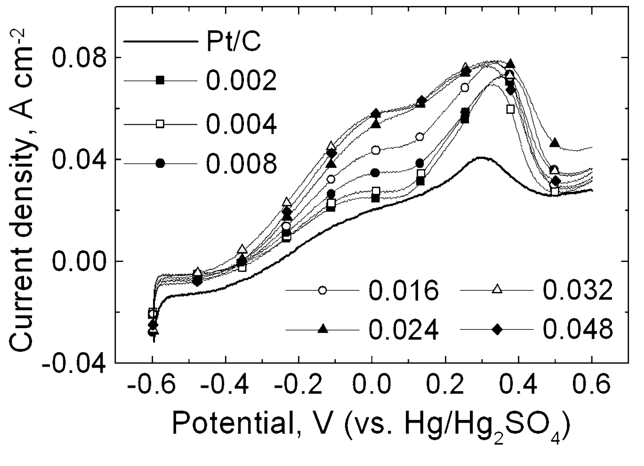

Fig. 2 Linear sweep voltammograms (20 mV s^{-1}) for electrodes prepared with 20% Pt/C and various amounts (0.002, 0.004, 0.008, 0.016, 0.024, 0.032 0.048 mg cm^{-2}) of FeTSPc. The electrolyte was 0.5 M HCOOH + 0.5 M H_2SO_4 (3-electrode cell)

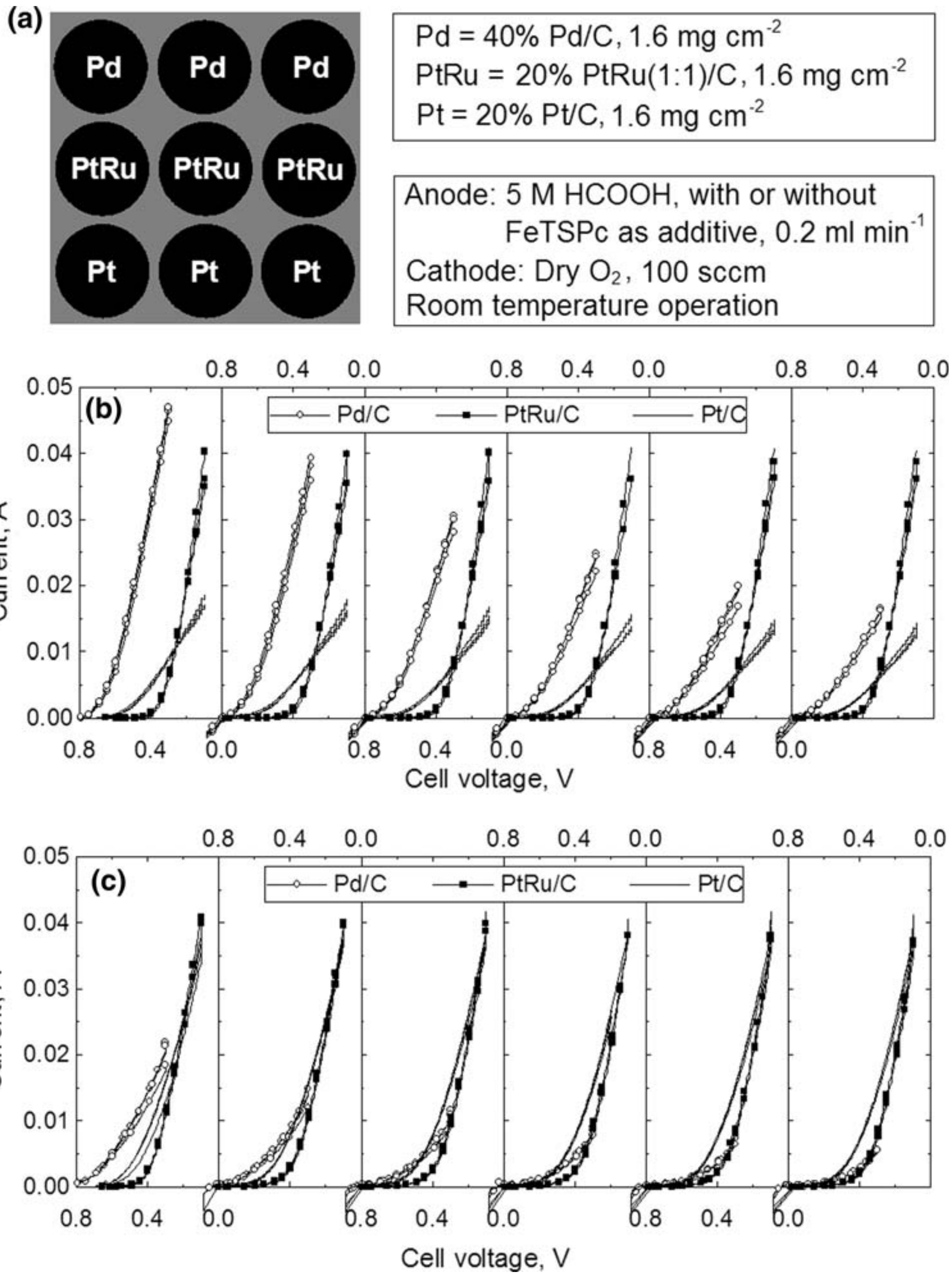

Fig. 3 **a** Schematic, **b** consecutive polarization curves without FeTSPc, and **c** consecutive polarization curves with 0.1 mg mL^{-1} added to the 5 M HCOOH fuel, for a multi-anode DFAFC with Pd/C, Pt/C, and PtRu/C anodes

experiment) cell performance. However, the performances of the Pd/C electrodes decreased seriously during repeated polarization. The PtRu/C performed better than the Pt/C at low cell voltages, but surprisingly was inferior at higher cell voltages. The PtRu/C and Pt/C electrodes exhibited some performance decay with time, but much less than for the Pd/C electrodes.

Figure 3c shows continuous polarization curves for the same array MEA as in Fig. 3b, but with 0.1 mg mL^{-1} FeTSPc added to the 5 M HCOOH fuel. It should be noted that in order to avoid the influence of the deactivation of the Pd/C electrodes during the previous polarization experiment (Fig. 3b), the Pd/C electrodes were reactivated at a cell voltage −0.3 V for 5 s before the polarization experiments shown in Fig. 3c [36]. Comparing the results shown in Fig. 3c with those in Fig. 3b, it can be seen that while the performance of the Pd/C was seriously impaired by the addition of FeTSPc, the performance of the Pt/C was greatly enhanced. The performance of PtRu/C was not significantly influenced by the FeTSPc. These results are consistent with those obtained in the liquid electrolyte cell (Fig. 1).

The effects of FeTSPc on the Pd/C, PtRu/C, and Pt/C catalysts under DFAFC conditions were further studied by monitoring the cell currents during operation of the multi-anode cell at fixed cell voltages of 0.3 V (Fig. 4) and 0.5 V (Fig. 5), with and without FeTSPc added to the 5 M formic

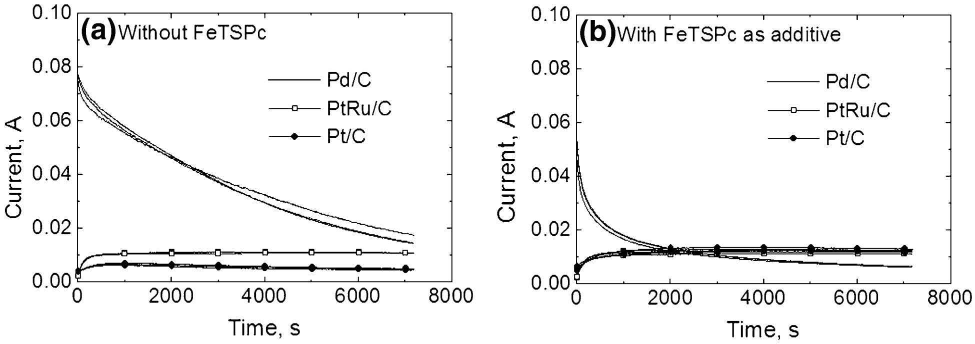

Fig. 4 Current versus time curves for Pd/C, PtRu/C, and Pt/C electrodes in a multi-anode DFAFC during operation at a constant cell voltage of 0.3 V. **a** Without FeTSPc in the fuel; **b** with 0.1 mg mL^{-1} FeTSPc added to the fuel

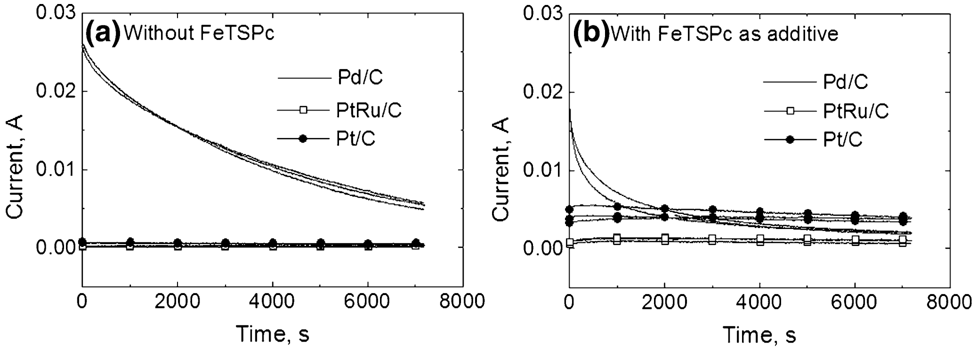

Fig. 5 Current versus time curves for Pd/C, PtRu/C, and Pt/C electrodes in a multi-anode DFAFC during operation at a constant cell voltage of 0.5 V. **a** without FeTSPc in the fuel; **b** with 0.1 mg mL^{-1} FeTSPc added to the fuel

acid fuel. The Pd/C electrodes were reactivated between each constant voltage experiment. As observed in the polarization experiments (Fig. 3), addition of FeTSPc to the formic acid fuel seriously impaired the performance of the Pd/C, improved the performance of Pt/C, and had a relatively small effect on PtRu/C. After 2-h operation at 0.3 V, the presence of FeTSPc decreased the average current at the Pd/C anodes by a factor of ca. 2.5, while it increased the average current at the Pt/C anodes by a factor of ca. 3.

At constant cell voltages of 0.5 V (Fig. 5), the effect of FeTSPc of the performance of the Pt/C was even more pronounced, with the average current at 2 h increasing by a factor of ca. 8 when FeTSPc was added to the fuel. At this voltage, FeTSFPc also significantly enhanced the performance of the PtRu/C. This is consistent with the results obtained in the liquid electrolyte cell (Fig. 1), where FeTSPc was seen only to enhance the low potential performance of PtRu/C.

3.2.2 *Single cell (5 cm^2 electrode) performance with a pre-modified FeTSPc/Pt/C catalyst anode*

The screening results described above clearly indicate that the catalytic activity of Pt for formic acid oxidation is enhanced by FeTSPc. Therefore, a pre-modified FeTSPc/Pt/C catalyst (with the optimum FeTSPc loading of 0.032 mg cm^{-2}) was further investigated in a single cell prepared with a 5 cm^2 anode. A single cell was also prepared with a 5 cm^2 unmodified Pt/C anode for comparison. In this investigation, 5 M HCOOH was used as the fuel without FeTSPc added.

Figure 6a, b shows polarization curves and the corresponding power plots obtained with the Pt/C and FeTSPc/Pt/C anode catalysts in single DFAFCs. Both the currents and the powers in these polarization plots were normalized on the basis of the Pt mass. With the FeTSPc/Pt/C catalyst, the cell can generate a maximum power of 90 mW (mg Pt)$^{-1}$, about 2.5 times higher than with the unmodified Pt/C catalyst.

Figure 7a, b shows current versus time curves for the single cells at voltages of 0.3 and 0.5 V, respectively. At both cell voltages, the normalized current for the FeTSPc/Pt/C anode was much higher than for the unmodified Pt/C anode. After 2 h operation, the normalized current at the FeTSPc/Pt/C anode was about 3 times higher than at the unmodified Pt/C anode at 0.3 V, and was about 5 times higher at 0.5 V.

3.3 CO stripping of the Pd/C, Pt/C, and PtRu/C catalyst electrodes with FeTSPc as additive

In order to further understand the effects of FeTSPc on the activities of the Pd/C, Pt/C, and PtRu/C catalysts, CO stripping experiments were carried out. As seen in Fig. 8, addition of FeTSPc to the electrolyte decreased the height of the CO stripping peak (first cycle) for all three catalysts.

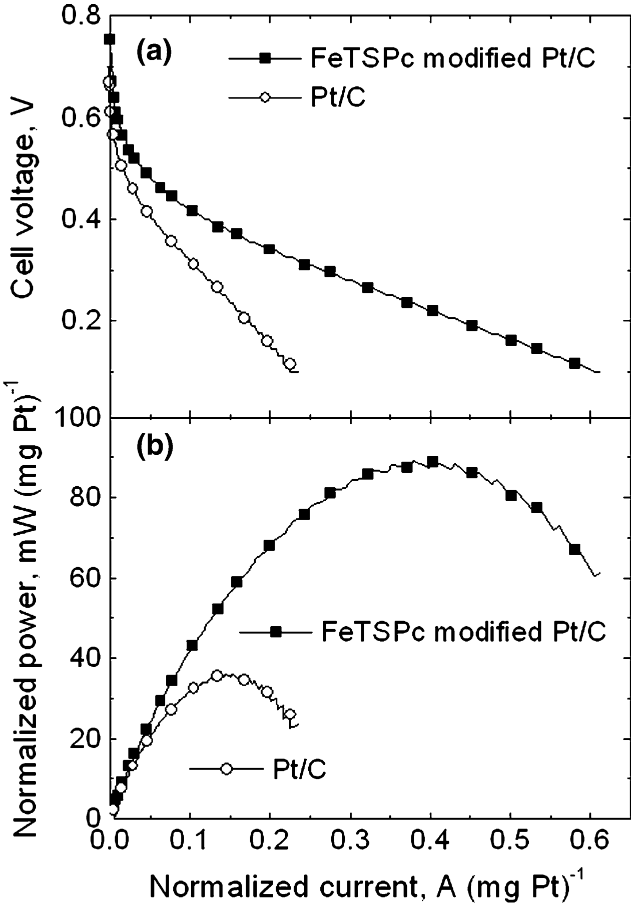

Fig. 6 **a** Polarization curves and **b** power plots obtained with the Pt/C and FeTSPc modified Pt/C anodes in a 5 cm^2 DFAFC

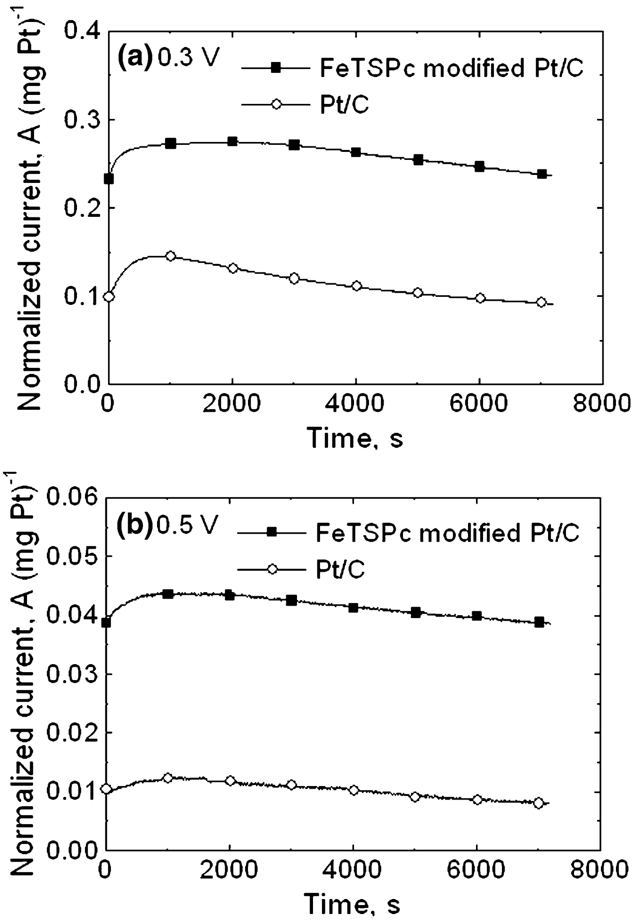

Fig. 7 Current versus time curves for 5 cm^2 DFAFCs with Pt/C and FeTSPc modified Pt/C anodes at cell voltages of **a** 0.3 V and **b** 0.5 V

This can be attributed to partial coverage of the catalyst surface by adsorbed FeTSPc, since the presence of FeTSPc also decreased the H-adsorption/desorption charge (2nd cycle). The presence of FeTSPc had no influence on the position of the CO stripping waves for Pd and PtRu, but caused a shift to lower potentials for Pt. This indicates that FeTSPc assists in the removal of adsorbed CO from Pt, but not from Pd or PtRu.

A third effect seen in Fig. 8 is that for Pt and PtRu the H-adsorption/desorption waves are not completely suppressed by the CO when FeTSPc is present. This indicates that some Pt sites are protected from CO poisoning by the adsorbed FeTSPc, but are still exposed to the electrolyte.

The coverage of the catalysts by the FeTSPc adsorption can be estimated by integration of the CO oxidation peaks of the Pd/C, Pt/C, and PtRu/C electrodes with and without the presence of FeTSPc in the electrolyte. Comparison of the areas of the CO oxidation peaks shown in Fig. 8 indicates that the coverages of the Pd/C, Pt/C, and PtRu/C catalysts by adsorbed FeTSPc were ca. 42, 36, and 50%, respectively.

4 Discussion

Platinum and platinum–ruthenium have commonly been used as anode catalysts in direct alcohol (such as methanol and ethanol) fuel cells [37–40]. As well, Pt and PtRu anode catalysts were used in the first DFAFC, for which Weber et al. [1] found that the PtRu catalyst was more active than Pt-black for formic acid oxidation. However, in DFAFC systems, PtRu catalysts have not always shown better performance than pure Pt. We have previously found [36], and again show in Fig. 3b, that the polarization curves of DFAFCs with Pt/C and PtRu/C anode cross at intermediate potentials. Thus, at low cell voltages, the performance of PtRu/C is much better than for Pt/C as expected, while at higher cell voltages, the performance of PtRu/C is a little lower than for Pt/C. This phenomenon also appears in some other published results [7], and can be explained as follows.

Ru is known to improve the activity of Pt for methanol oxidation through a bi-functional mechanism. The enhanced activity of PtRu alloys is attributed to oxygenated species

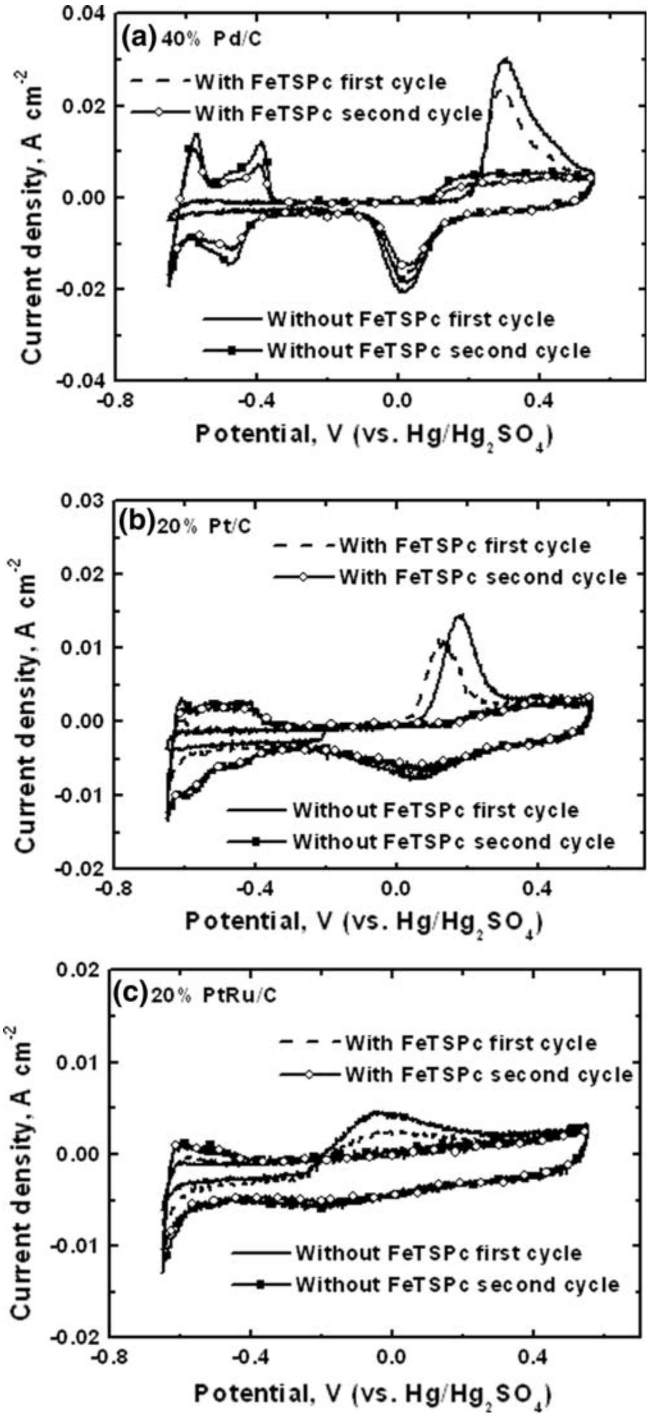

Fig. 8 CO stripping results for **a** 40% Pd/C; **b** 20% Pt/C, and **c** 20% PtRu/C electrodes in 0.5 M H2SO4 with (*dashed line*: first cycle; *open circle*: second cycle) or without FeTSPc (*solid line*: first cycle; *filled square* second cycle)

generated from the dissociation of water at Ru sites, which can accelerate the oxidation of CO to CO_2 and thus remove adsorbed CO from Pt sites [41–43]. Oxidation of formic acid on Pt is relatively well understood, and is recognized to follow a “dual-pathway” mechanism, as described in Eqs. 1 and 2 [44].

$$\text{Pathway 1}: \ \mathrm{HCOOH} \rightarrow \mathrm{CO_2} + 2\mathrm{H^+} + 2\mathrm{e^-} \qquad (1)$$

$$\begin{aligned}\text{Pathway 2}: \ \mathrm{HCOOH} &\rightarrow -\mathrm{CO_{ads}} + \mathrm{H_2O}\\ &\rightarrow \mathrm{CO_2} + 2\mathrm{H^+} + 2\mathrm{e^-}\end{aligned}$$

As seen in Fig. 1b, voltammograms for oxidation of formic acid at Pt/C exhibits two peaks at about −0.05 V and 0.30 V that have been attributed to the electro-oxidation of formic acid through the direct “dehydrogenation pathway” (Eq. 1) and indirect “CO pathway”

(Eq. 2), respectively [31, 45]. The current density for the 0.30 V peak is higher than at −0.05 V, suggesting that the oxidation of formic acid on Pt is mainly via the CO pathway. The superiority of PtRu/C over Pt/C in DFAFCs appears at low cell voltages (high anode potentials), at which the oxidation of formic acid mainly follows the indirect (CO) pathway, and the buildup of CO on Pt is serious [31, 45]. However, at high cell voltages oxidation of formic acid is slow and the direct (dehydrogenation) pathway can dominate. Furthermore, since there are fewer Pt active sites on the PtRu it shows less activity than pure Pt (Fig. 3b).

The promoting effect of FeTSPc on the electro-oxidation of formic acid at Pt has been proposed to be due to either hindering of the formation of intermediate species (CO_{ad}) or weakening of the adsorption strength of the poisoning CO_{ad} [19, 31]. The stripping results in Fig. 8b support these proposals, since they show that less CO is adsorbed when FeTSPc is present, and that part of the Pt surface remains free of both CO and FeTSPc. In addition, the stripping results also show that FeTSPc promotes the oxidation of adsorbed CO (on Pt) at lower potentials. Like Ru, it therefore appears to participate in a bi-functional mechanism and promote formic acid oxidation via the CO pathway (Eq. 2). Since this pathway is dominant for electro-oxidation of formic acid on pure Pt [45], the promoting effect of FeTSPc is very strong. It is tempting to speculate that the sites that are active for H-adsorption/desorption in the presence of both adsorbed FeTSPc and CO (Fig. 8b; dashed line) surround the adsorbed FeTSPc molecules. Formic acid oxidation at these sites would then obtain the maximum benefit of the adjacent FeTSPc sites.

Addition of Ru to Pt provides a facile route for the oxidation of adsorbed CO, as can be seen by comparing the stripping voltammograms (without FeTSPc) in Fig. 8b, c. The presence of FeTSPc, which is less effective at promoting CO oxidation (compare Fig. 8b and c), therefore does not produce a significant additional promoting effect for formic acid oxidation on the PtRu/C catalyst. As seen in Fig. 1c, addition of FeTSPc to the electrolyte only slightly increased the current at the PtRu/C electrode in the “direct pathway” potential range (−0.5 to +0.1 V).

Although the above discussion provides a reasonable explanation of the role of FeTSPc in terms of its influence on CO oxidation, it is important to note that there are many other possible effects [46]. Other adsorbed intermediates and poisons, such as carboxylic acid species, formate species, surface oxides, and adsorbed anions have been implicated. However, CO appears to be the major poison, and its accumulation appears to be the main factor limiting the performances of Pt based catalysts.

The mechanism of formic acid oxidation on Pd is not well established, although Pd is known to facilitate formic acid oxidation through the direct dehydrogenation pathway [47]. CO is a possible poison on Pd, but since FeTSPc does not promote CO oxidation on Pd (Fig. 8a) it would not be expected to mitigate the effects of CO adsorption during formic acid oxidation. On the contrary, the adsorption of FeTSPc appears to block active sites on the Pd (see Fig. 8a). Comparison of Fig. 4a with b (or Fig. 5a with b) implies that the deactivation of the Pd/C catalyst by FeTSPc occurs via a chemical (adsorption) process, since the initial currents at the Pd/C electrodes were seriously decreased by addition of FeTSPc to the fuel.

As seen from Figs. 4 and 5, the Pd/C showed much higher initial performances than both the Pt/C and PtRu/C catalysts. Although suffering a serious deactivation, over the 2-h timeframe employed in this study, the best performances were obtained with Pd/C without FeTSPc. However, by comparing Fig. 4a with b, or by comparing Fig. 5a with b, it can be seen that the currents at the FeTSPc modified Pt/C electrodes approached those of the Pd/C electrodes at the end of the 2-h experiments. At longer cell operating times, the FeTSPc modified Pt/C electrodes would likely exceed the performances of the Pd/C electrodes, due to the continuous performance decay of the Pd/C catalyst (documented elsewhere [36]), and the apparently stable performance of the FeTSPc modified Pt/C catalyst.

5 Conclusions

Iron-tetrasulfophthalocyanine (FeTSPc) has been confirmed to be an effective promoter of formic acid oxidation on a carbon supported Pt fuel cell catalyst. Voltammetric and DFAFC results support the view that the presence of the FeTSPc on the Pt surface mitigates the effects of CO poisoning and promotes the oxidation of formic acid through the direct pathway. This hypothesis is further supported by results for PtRu/C and Pd/C, which show only minor promotion for PtRu/C and inhibition for Pd/C.

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