



Deactivation/reactivation of a Pd/C catalyst in a direct formic acid fuel cell (DFAFC): Use of array membrane electrode assemblies

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ABSTRACT

Palladium-based catalysts exhibit high activity for formic acid oxidation, but their catalytic activity decreases quite rapidly under direct formic acid fuel cell (DFAFC) operating conditions. This paper presents a systematic study of the deactivation and electrochemical reactivation of a carbon supported palladium catalyst (Pd/C) employing anode arrays in a DFAFC. Deactivation of Pd/C is caused by the electro-oxidation of the formic acid, and does not occur significantly at open circuit. Its rate increases sharply with increasing formic acid concentration but is only dependent on potential at high cell voltages. Reactivation can be achieved by driving the cell voltage to a reverse polarity of -0.2 V or higher. The use of array membrane electrode assemblies allows the rapid generation of statistically significant information on differences between catalysts, and the effects of operational parameters on the deactivation and reactivation processes.

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1. Introduction

The demand for power sources with superior performance is ever growing as a result of the continuous growth in the use of portable electronic devices. Direct formic acid fuel cell (DFAFC) systems have recently been considered as an interesting alternative candidate for portable power sources. Compared with their primary small portable fuel cell contenders, H_2 -PEMFCs (H_2 -fed polymer electrolyte membrane fuel cells) and DMFCs (direct methanol fuel cells), DFAFCs have the advantages of high electromotive force, limited fuel crossover, and high practical power densities at low temperatures [1].

Pt-based catalysts were mainly used as the anode catalyst in the early stages of DFAFC development [2–4] and a number of Pt-M (M = a second metal other than platinum) bimetallic catalysts (such as Pt/Ru, Pt/Pd, Pt/Au and Pt/Pb) have been successfully demonstrated in DFAFC systems [5–10]. Pd-based catalysts, which generate higher power densities than Pt, have been used increasingly in recent years. Pd is a metal known for its ability to catalyze the oxidation of CO and of hydrocarbons [11], and to favor formic acid oxidation via a direct dehydrogenation pathway [1]. In order to reduce the noble metal loading, carbon supported catalysts are usually preferred in fuel cell systems. Carbon supported palladium catalysts have therefore become a very important area in DFAFC

catalyst studies in recent years [12–17]. Such Pd-based/C catalysts, obtained by various syntheses routes, have demonstrated good activity along with more efficient palladium metal utilization and lower metal loadings [12–17]. However, a disadvantage of Pd-based catalysts is that their activity decreases with the cell operation time, consequently impairing the performance of the DFAFC. Thus deactivation of palladium catalysts has become a significant obstacle for their implementation in DFAFC development. Although the reason for the activity loss is still unclear, it has been found that almost full activity can be recovered by applying an anodic potential of ca. 1.0 V or more vs RHE [18,19]. However, neither of these two important issues, the deactivation and the reactivation of Pd catalysts under DFAFC conditions, has been systematically investigated.

The systematic screening and study of fuel cell catalysts can be efficiently conducted with array membrane electrode assemblies [20–28]. In this paper, we introduce a multi-anode, liquid-fed fuel cell developed for screening of DFAFC anode catalysts. Deactivation, as well as the electrochemical reactivation, of carbon supported palladium catalysts (Pd/C) under DFAFC operating conditions was systematically studied with this multiple anode cell by employing membrane electrode assemblies (MEAs) with anode arrays.

2. Experimental

2.1. Catalysts and chemicals

Catalysts employed in this study were: (1) 40% Pd/C (40% palladium on Vulcan XC-72, E-TEK; Lot# E0061101; average Pd particle

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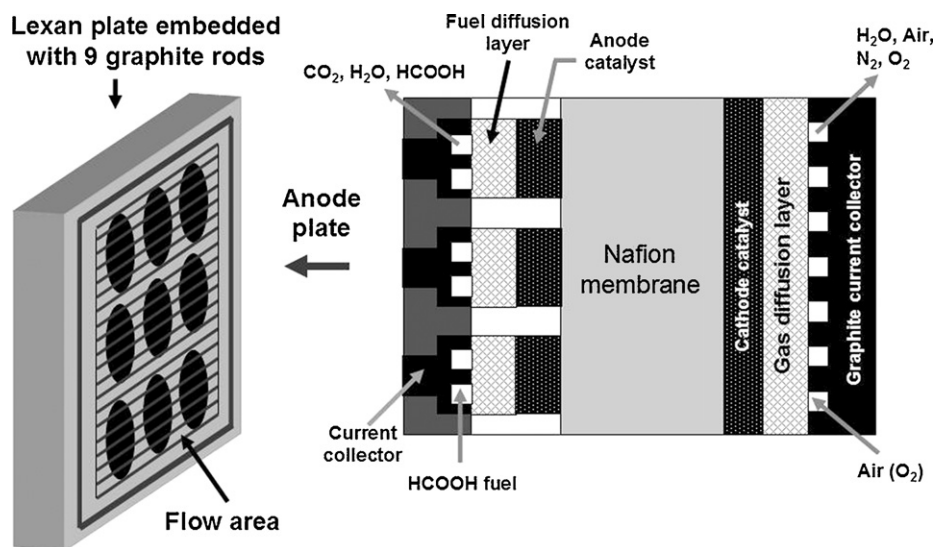


Fig. 1. Schematic of the multi-anode DFAFC.

size 4.2 nm from XRD (4.0 nm specified by E-TEK); (2) 20% Pt/C (20% platinum on Vulcan XC-72, E-TEK); and (3) 40% PtRu/C (40% PtRu on Vulcan XC-72, E-TEK). Formic acid from Alfa Aesar (ACS, 88% + 12% water, Lot# H13S025) was diluted with de-ionized water.

2.2. Preparation of electrodes

The catalyst powder was dispersed in a mixture of pure water and a certain volume of Nafion solution® (5%, DuPont) by sonication

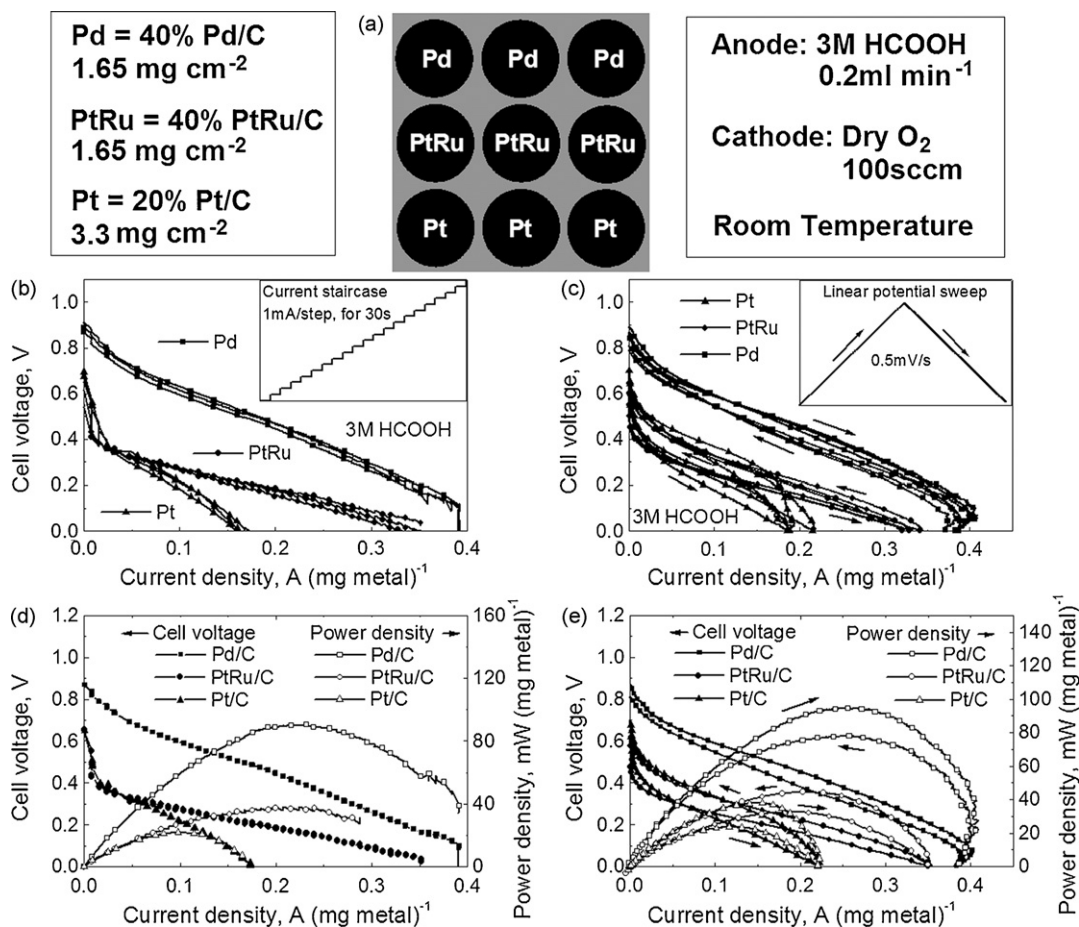


Fig. 2. Multi-anode DFAFC with Pt/C, PtRu/C and Pd/C anode catalysts: (a) schematic of the array; (b) polarization plots obtained in current staircase mode; (c) polarization plots obtained by cyclic voltammetry at 0.5 mV s⁻¹; (d) and (e) representative V-I plots and the corresponding power density plots for each type of catalyst derived from b and c, respectively.

for 10 min. The mass ratio of Nafion to the catalyst was maintained at 1:4. The resulting ink was deposited onto carbon fiber paper (Toray TGP-H-090) and dried in air for 1 h at room temperature. The loading of the catalyst + Nafion on the carbon fiber paper was varied (1.65 mg cm^{-2} for Pd/C and PtRu/C; 3.30 mg cm^{-2} for Pt/C) as required to provide a metal loading of 0.53 mg cm^{-2} . The Nafion loading was 0.33 mg cm^{-2} for Pd/C and PtRu/C, 0.66 mg cm^{-2} for Pt/C.

2.3. Conventional three-electrode electrochemical cell experiments

A Pt wire and Hg/Hg₂SO₄ electrode were used as the counter electrode and the reference electrode, respectively. The potentials in these experiments are quoted against Hg/Hg₂SO₄ (+0.616 V vs SHE). The working electrode was prepared by spreading 1.65 mg cm^{-2} Pd/C catalyst plus Nafion onto 1 cm^2 of carbon fiber paper.

2.4. Preparation of anode array membrane electrode assemblies

Anode array membrane electrode assemblies 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 punched from larger area pieces of catalyzed carbon fiber paper. The 5 cm^2 cathode and nine 0.23 cm^2 anodes were hot pressed (135°C , 200 kg cm^{-2} , 90 s) to the Nafion 115® membrane to form the membrane electrode assembly (MEA).

2.5. The multi-anode fuel cell

A multi-anode, liquid-fed fuel cell was developed for this work based on a design reported by Liu and Smotkin for DMFC catalyst evaluation [21]. A schematic diagram is shown in Fig. 1. 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 Lexan. A two-channel serpentine flow field was used to supply fuel to the anodes. Experiments with 9 identical electrodes demonstrated that the position in the array did not influence performance or deactivation/reactivation rates.

The operation of the multi-anode DFAFC was controlled with a multi-channel potentiostat (Arbin®). The cell was operated with aqueous formic acid 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 and discussion

3.1. Catalyst screening in the multi-anode DFAFC

Before the deactivation-reactivation studies on the Pd/C catalyst, the behavior of the multi-anode fuel cell was characterized. An anode array membrane electrode assembly (MEA) prepared with three electrodes each of carbon supported platinum (Pt/C), carbon supported platinum–ruthenium (PtRu/C) and carbon supported palladium (Pd/C), was used, as illustrated in Fig. 2a. Two polarization methodologies, a current staircase mode and slow cyclic voltammetry (linear potential sweep), were employed for measuring polarization curves. The current staircase polarization mode is illustrated in the inset of Fig. 2b. In this mode, the current applied to each of the anodes was stepped in 1 mA intervals from zero, with 30 s at each current for the potential to stabilize. For the cyclic voltammetry mode shown in the inset of Fig. 2c, the potential of each anode was scanned from the open circuit voltage (OCV)

to 0V at a scan rate of 0.5 mV s^{-1} . All potentials were measured relatively to the common 5 cm^2 cathode.

As seen in Fig. 2b and c, whatever mode was applied, the reproducibility of the polarization measurements for each type of catalyst was acceptable. Furthermore, for each type of catalyst, the averages of the currents on the forward and backward scans obtained by cyclic voltammetry were consistent with the polarization curves obtained in current staircase mode. Fig. 2d and e shows representative V–I plots (cell voltage vs. current density) and the corresponding power density plots, derived from Fig. 2b and c, for each type of catalyst. Both the current density and the power density in these polarization plots were normalized on the basis of metal weight (unit mass of Pt, PtRu or Pd). Interestingly, as evident in the polarization curves obtained by cyclic voltammetry (Fig. 2c and e), the current response in the backward scan was always higher than that in the forward scan for the Pt/C or PtRu/C anodes, which is consistent with literature results [9,17,29,30]. However, the current response was generally higher on the forward scan for the Pd/C anodes, presumably due to slight deactivation of the Pd/C catalyst during the forward scan (discussed in the following sections).

It is clear from the results in Fig. 2 that on a metal loading basis the Pd/C catalyst provided the best cell performance, while PtRu/C showed better cell performance than Pt/C. This is consistent with literature results [1], and provides a good illustration of the value of the multi-anode cell for screening catalysts under consistent conditions. The use of multiple electrodes of each type provides statistical information that can be used to determine the significance of differences between catalysts. From inspection of the data in Fig. 2, it is quite clear that the differences in performances between the three catalysts are much larger than the random variations between electrodes of the same type.

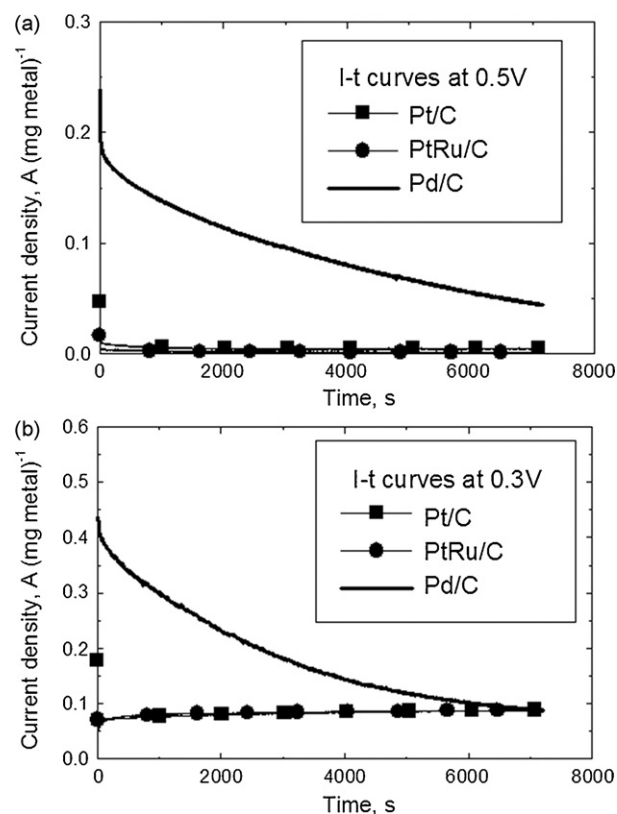


Fig. 3. Representative current vs. time curves for operation at various fixed cell voltages for a multi-anode DFAFC with Pt/C, PtRu/C and Pd/C anode catalysts: (a) cell voltage = 0.5 V; (b) cell voltage = 0.3 V.

Under the DFAFC conditions of this study (anode catalyst loading of $0.53 \text{ mg metal cm}^{-2}$; 3 M HCOOH at 0.2 ml min^{-1} ; dry O_2 at 100 sccm ; ambient temperature) the maximum power densities obtained were $88 \text{ mW mg}^{-1} \text{ Pd}$, $37 \text{ mW mg}^{-1} \text{ PtRu}$ and $20 \text{ mW mg}^{-1} \text{ Pt}$. The result for Pd is somewhat higher than the ca. 70 mW mg^{-1} reported by Larsen et al. [12] for a single 5 cm^2 cell, indicating that the small anodes of our multi-anode cell perform well.

The stabilities of the Pt/C, PtRu/C and Pd/C catalysts were compared by monitoring the current during operation of the cell at fixed anode voltages of 0.5 and 0.3 V (relative to the cathode). As shown in Fig. 3, the current was stable (increasing slightly) for the Pt/C and PtRu/C catalysts, while it decayed seriously with time for the Pd/C catalyst. After 2 h at 0.3 V, the performance advantage of Pd over Pt and Pt/Ru was completely lost.

3.2. Deactivation of Pd/C

The activity decay for the Pd/C catalyst was initially studied with a regular three-electrode electrochemical cell, with a Hg/HgSO₄ reference electrode. Fig. 4 shows current versus time curves at various potentials, and in various concentrations of formic acid solution (with $0.5 \text{ M H}_2\text{SO}_4$ as a supporting electrolyte). As seen in Fig. 4, the activity of the Pd/C catalyst decayed at all potentials from -0.1 to -0.5 V (vs. Hg/HgSO₄), which cover the potential range of the anode

under DFAFC operating conditions. The rate of decay did not show any clear dependence on the applied potential but was strongly dependent on the concentration of HCOOH in the electrolyte. At high concentrations of HCOOH ($10\text{--}20 \text{ M}$) the electrodes became inactive within the 2 h timeframe of the experiments.

The deactivation of the 40% Pd/C catalyst was investigated further under DFAFC conditions by employing an anode array membrane electrode assembly in a multi-anode direct formic acid fuel cell. The 9 anodes in the array were prepared with the same Pd/C catalyst (40% Pd on Vulcan XC-72 carbon black, E-TEK Inc.[®]), and with the same loading of 1.65 mg cm^{-2} ($0.53 \text{ mg Pd cm}^{-2}$) on carbon fiber paper. Catalyst arrays were tested simultaneously in a single cell, by sharing one integrated cathode (4 mg cm^{-2} Pt black). A schematic of the anode array (3×3) membrane electrode assembly is shown in Fig. 5a. Each group of three electrodes was subjected to a different procedure in order to explore the effects of various parameters in a statistically meaningful way. Polarization curves were obtained in a potential staircase mode, as illustrated in the inset of Fig. 5b. The arrays of anodes were simultaneously polarized from the cell's open circuit voltage (OCV) of 0.9 V to a final voltage of 0.3 V , with voltage steps of -15 mV . The current at each step was allowed to stabilize for 30 s. Fig. 5b shows polarization curves of the nine Pd/C anodes. There was excellent reproducibility between anodes.

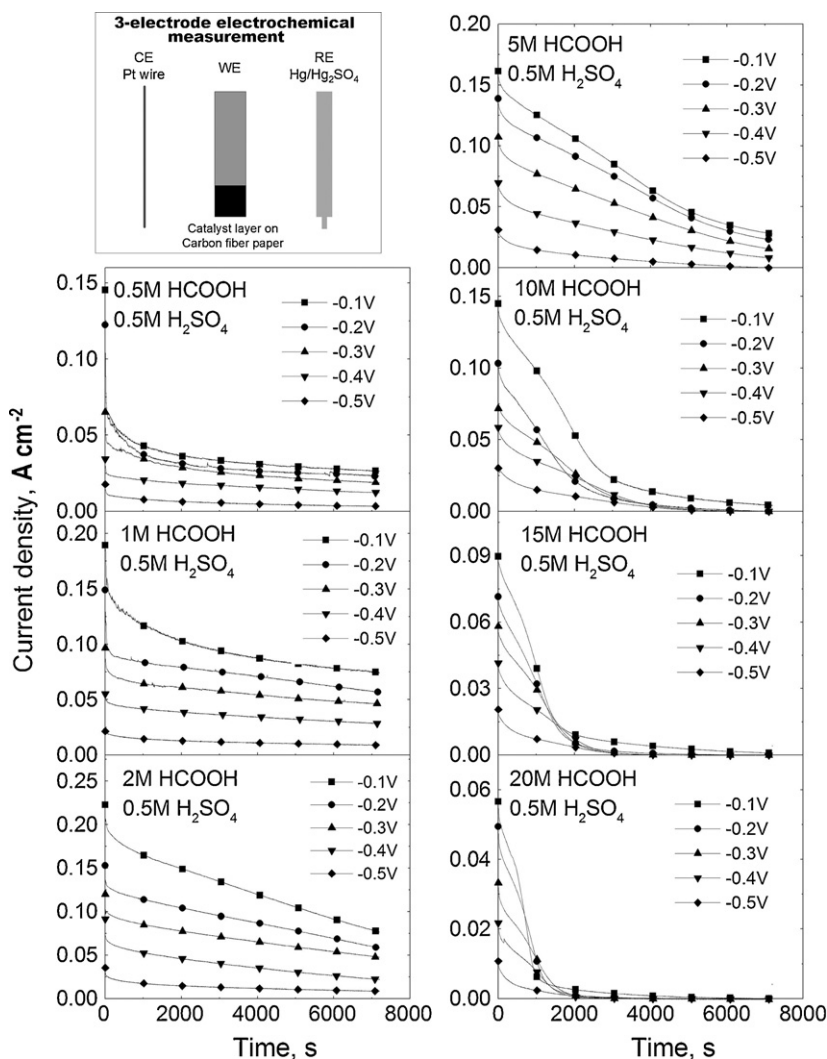


Fig. 4. Current decay with time in a conventional 3-electrode cell for Pd/C electrodes at various potentials (vs. Hg/HgSO₄), and in various concentrations of formic acid.

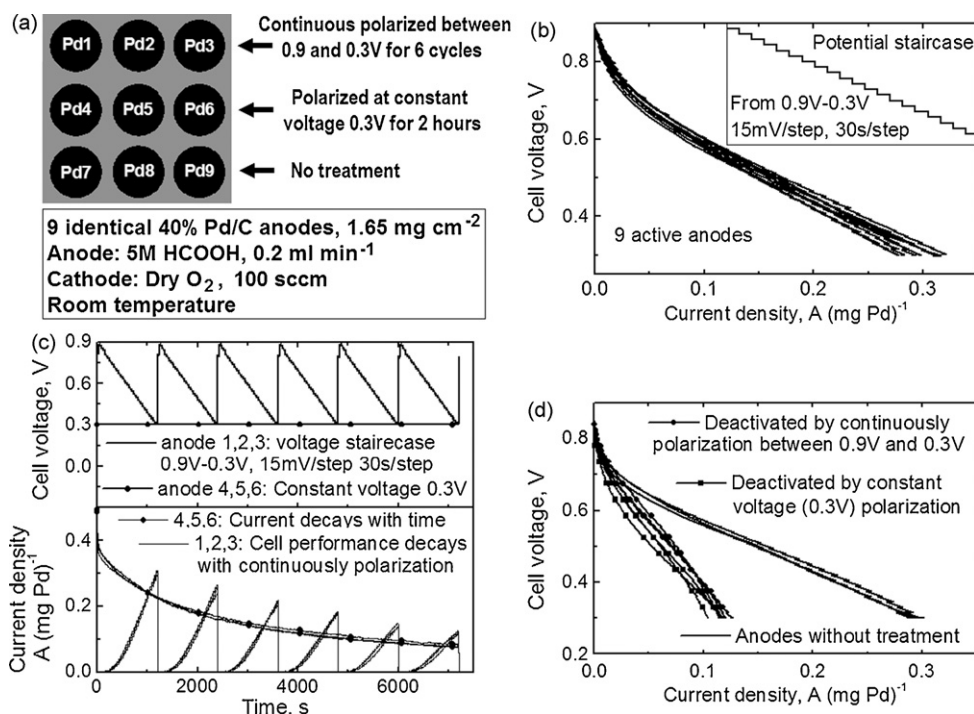


Fig. 5. Deactivation of Pd/C electrodes in a multi-anode DFAFC: (a) schematic of the array MEA with nine identical Pd/C anode catalysts; (b) initial polarization plots obtained in voltage staircase mode; (c) applied voltage vs. time (top), consecutive polarization curves for anodes 1–3 (bottom), and current vs. time for anodes 4–6 which were polarized at fixed cell voltage of 0.3 V (bottom); (d) final polarization curves (voltage staircase) of all electrodes.

In the following experiments, three of the anodes (7–9) were kept at open circuit to act as a control. Electrodes 1–3 were continuously polarized between cell voltages of 0.9 and 0.3 V for 6 cycles (Fig. 5c), while electrodes 4–6 were simultaneously polarized at a fixed cell voltage of 0.3 V for 2 h (Fig. 5c). As seen in Fig. 5c, the performances of the electrodes decreased substantially both during repeated polarization experiments and at constant voltage. The maximum current density during the six polarization cycles (electrode 1–3) dropped from ca. $0.30 \text{ A mg}^{-1} \text{ Pd}$ to ca. $0.12 \text{ A mg}^{-1} \text{ Pd}$, while the decay at a fixed potential of 0.3 V was somewhat faster. There is clearly some dependence of the deactivation rate on the applied potential, but it is weak.

Following the deactivation of six of the anodes in the array, as shown in Fig. 5c, a single polarization experiment was performed simultaneously on all 9 anodes (Fig. 5d). The control anodes (7–9) that had been kept at open circuit, but otherwise subjected to the same conditions as the deactivated electrodes, showed no deactivation. The anodes (1–3) subjected to 6 polarization experiments remained severely deactivated, while those (4–6) that had been held at 0.3 V for 2 h were deactivated to a somewhat greater extent.

The potential dependence of the deactivation process was investigated by polarizing nine identical Pd/C anodes for 2 h at various cell voltages from 0.8 to 0.2 V. Following this procedure, polarization curves were obtained simultaneously for all electrodes. Examples are shown in Fig. 6a. Current densities at two selected polarization voltages are shown in Fig. 6b as a function of the deactivation voltage for many experiments. It was found that deactivation was minor at 0.8 V, but substantial at 0.7 V and lower potentials, with little potential dependence below 0.7 V.

Although the loss of activity of Pd catalysts in DFAFCs is well documented, the mechanism by which this occurs is not clear. Generally, the deactivation of Pd is considered to be due to adsorbed intermediates formed during the oxidation of formic acid. Adsorbed CO has been identified as the main poison for Pt based catalysts, and so it was originally thought that the activity decay of Pd catalysts

was due to the build-up of adsorbed CO species on the Pd surface. CO or related species are formed during oxidation of formic acid via the dehydration pathway (Eq. (1)).

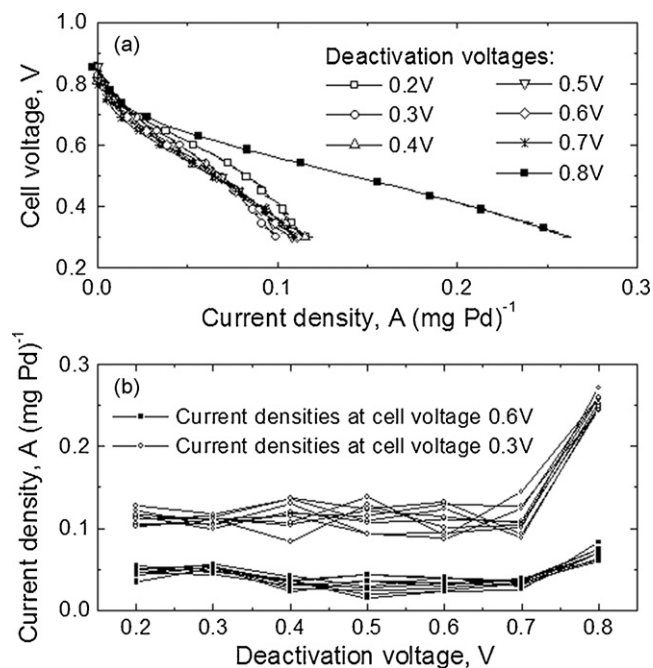
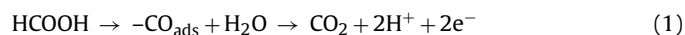


Fig. 6. Polarization plots (a) and current densities at 0.3 and 0.6 V for multiple experiments at each deactivation potential (b) for Pd/C anodes that had been deactivated for 2 h at various cell voltages from 0.8 to 0.2 V.

However, adsorbed CO has not been detected during formic acid oxidation on Pd [31,32]. Therefore, an alternative hypothesis was proposed that adsorbed $-OH$, or other adsorbed anions, could be the poisoning species [31]. In a recent impedance spectroscopy investigation [33] it was speculated that a non-CO, organic poisoning species occurred during palladium catalyst deactivation. The poisoning of palladium catalysts in DFAFC by impurities, such as methyl formate and acetic acid in the formic acid fuel, has recently been reported [34]. Regardless what the poisoning species is, the results shown in Figs. 5 and 6 clearly indicate that the deactivation of the Pd/C catalysts is caused by the electrochemical oxidation of the formic acid, rather than a chemical adsorption process of impurities in the formic acid fuel.

Although the results presented here do not provide sufficient information for us to suggest the source of the deactivation of Pd in a DFAFC, they do provide evidence against the adsorption of $-OH$ being responsible. The potential dependence (Fig. 6) does not agree with this hypothesis, since $-OH$ adsorption on Pd occurs at much higher potentials [31] than the ca. 0.1–0.2 V vs RHE (0.7 V cell voltage) required for deactivation at the maximum rate. In addition, rapid reactivation would be expected at the beginning of each polarization experiment (e.g. in Fig. 5c and d), since adsorbed $-OH$ should desorb at high cell potentials, or at open circuit in the presence of formic acid. The adsorption of other anions (e.g. formate, Nafion, impurities) also seems unlikely since these processes should also require higher potentials (i.e. cell voltages significantly lower than 0.7 V), and be reversible at cell voltages above 0.7 V.

3.3. Electrochemical reactivation of Pd/C

Ha et al. [18] reported that the initial cell performance of a palladium anode DFAFC could be recovered by applying a potential of 1.0 V vs. DHE to the anode for 5 s, while the same group later reported use of 1.2 V for a few seconds [19]. Jung et al. reported reactivation at 1.0 V vs. DHE for less than 3 s. Although very fast and effective, these methods require reversal of the cell voltage, which is an inconvenient and expensive capability to build into a fuel cell system. There is therefore a need for a more detailed investigation of the potential dependence of the reactivation process. This was undertaken here with the aid of the 9-anode DFAFC.

Polarization curves were obtained simultaneously for nine identical Pd/C anodes (Fig. 7a), which were then deactivated in the DFAFC by running six consecutive polarization experiments to 0.3 V.

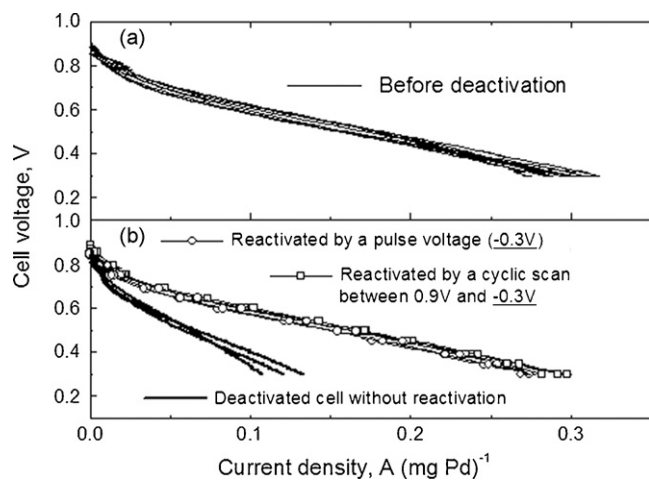


Fig. 7. Polarization curves (voltage staircase) obtained in a multi-anode DFAFC for nine Pd/C electrodes before deactivation (a), and for three of these electrodes following deactivation (solid lines), three following reactivation with a 0.9–0.3 V scan (squares) and three following reactivation at -0.3 V for 1 s (circles).

Three of these electrodes were reactivated at a cell voltage of -0.3 V (i.e. reversed cell polarity) for 1 s. This is roughly equivalent to $+1.0$ V vs DHE at the anode, since the cathode potential would be ca. 0.7 V vs DHE [35]. Another three electrodes were reactivated by applying a cyclic potential scan between cell voltages of 0.9 V and -0.3 V at 20 mV s^{-1} , while the remaining three electrodes were maintained at open circuit. Fig. 7 shows polarization curves of the nine anodes following these procedures. It can be seen that the electrodes held at open circuit remained deactivated, while the cycled electrodes and those held at -0.3 V were returned almost to their initial activity. Similar results were obtained when the nine anodes were deactivated at a constant cell voltage of 0.3 V.

These results confirm literature reports that reactivation can be accomplished within a matter of seconds at ≥ 1.0 V vs DHE (cell voltage ≤ -0.3 V). However, reactivation at a cell voltage of 0 V or higher is required from a practical perspective. Arrays of deactivated anodes were therefore subjected to various cell potentials from 0 to -0.3 V, for various times in order to probe the rate of reactivation as a function of potential. Fig. 8 shows polarization curves obtained following reactivation of the electrodes under the specified conditions. All electrodes were deactivated by running ten consecutive polarization experiments between 0.9 and 0.3 V.

As seen in Fig. 8a, there was some reactivation during 1 s at -0.2 V, but it was incomplete. However, 1 min at this cell voltage produced almost complete regeneration of the catalyst (cf. Figs. 8b, 8c and 5b). It is evident from the data in Fig. 8 that reactivation of the anodes is very slow at a cell voltage of -0.1 V, and that only partial reactivation is practical at this voltage. At a cell voltage of 0 V, no reactivation was apparent within 10 min.

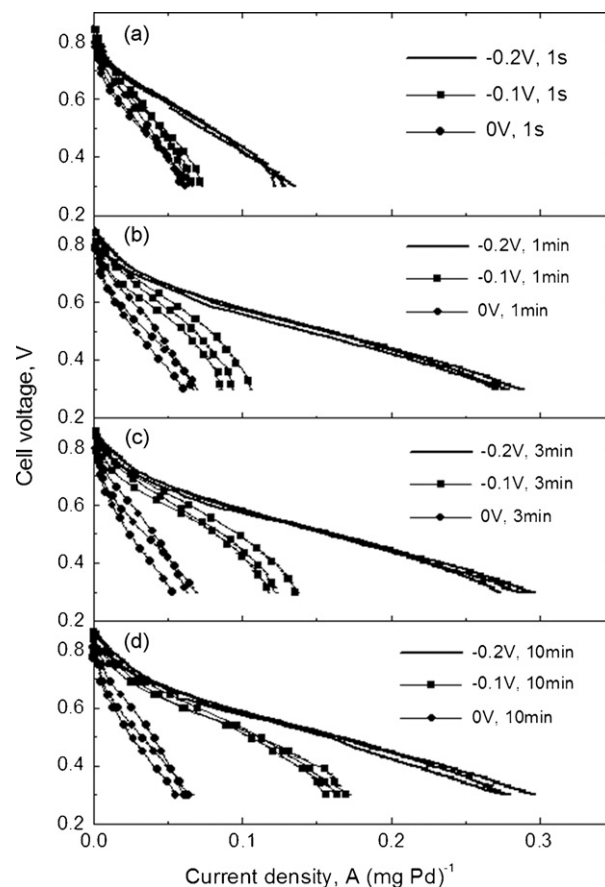


Fig. 8. Polarization curves obtained in a multi-anode DFAFC for deactivated Pd/C electrodes following application of cell voltages of -0.2 , -0.1 and 0 V for 1 s (a), 1 min (b), 3 min (c) and 10 min (d).

These results show that reactivation of Pd DFAFC anodes under normal operating conditions is currently impractical. Approaches other than simply changing the cell voltage are therefore required.

4. Conclusions

A multi-anode, liquid-fed fuel cell has been developed for rapid study of direct formic acid fuel cell (DFAFC) anode catalysts. The cell provided good reproducibility between electrodes and allowed definitive conclusions to be drawn regarding the activity of different anode catalysts under identical operating condition. Deactivation, as well as the electrochemical reactivation of a Pd/C catalyst under DFAFC operation conditions was systematically studied with the potential and time dependence of both processes being elucidated. Deactivated anodes can only be electrochemically reactivated by reversing the cell voltage, and reactivation is slow (>1 min) if the voltage is less negative than -0.2 V.

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