



Short communication

In situ spectroscopic investigation of CO accumulation and poisoning on Pd black surfaces in concentrated HCOOH

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ARTICLE INFO

Article history:

Received 12 August 2011

Received in revised form 8 October 2011

Accepted 10 October 2011

Available online 20 October 2011

Keywords:

Infrared spectroscopy

Formic acid

Palladium black

Carbon monoxide

Deactivation

Nanocatalyst

ABSTRACT

Attenuated total reflection-infrared (ATR-IR) spectroscopy is extended to investigate the surface poisoning species in the processes of (electro)chemical decomposition of formic acid (FA) on a state-of-the-art commercial Pd black catalyst in 5 M FA solution. During the FA decomposition under different potential settings including the open circuit potential (OCP, ca. 0.06 V vs. RHE), the constant potential 0.4 V (vs. RHE) and the scanned potentials between 0.1 and 0.5 V (vs. RHE), CO is clearly confirmed as a surface poisoning species with its vibrational frequencies located over ~ 1845 to 2016 cm^{-1} , featuring different CO bonding configurations (including the triple-, bridge- and linear-bonded CO species) on Pd black surfaces. CO_{ad} coverage increases with increasing operation time and decreasing operation potential. Once formed, CO_{ad} can only be removed at a much higher oxidation potential, corresponding to the reactivation of the Pd black surfaces. The present results provide a molecular level insight into an important aspect of the deactivation issue for a real Pd nanocatalyst in a practical FA concentration relevant to the anode operations of direct formic acid fuel cells (DFAFCs).

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1. Introduction

With Pd-based catalysts, formic acid (FA) may serve as the anode liquid fuel for direct formic acid fuel cells (DFAFCs) [1–7] or as the *in situ* hydrogen source to drive portable H_2 – O_2 fuel cells [8]. However, the critical deactivation of the Pd catalysts obstructs their commercial applications, calling for the need to deeply understand this issue [9–16].

Two main causes were assumed to be responsible for the deactivation of the Pd anode during FA electrooxidation after long-term operation: (1) the aggregation of Pd nanoparticles as observed by TEM measurement [9]; (2) more importantly, the accumulation of certain surface poisoning species. The identity of this poisoning species was mainly deduced from none-spectroscopic investigations [9–15]. By using electrochemical impedance spectroscopy (EIS) [9,10] and on-line mass spectroscopy [11], a small amount of strongly adsorbed intermediate was detected. Recent anodic stripping measurements on Pd nanocatalysts [9,12,13] that were pre-polarized in concentrated FA solutions for hours and then *ex situ* transferred to a HClO_4 electrolyte suggested the presence of so-called ‘ CO_{ad} -like residues’ on Pd surfaces. Notably, it was also reported that the existence of Pd-O(H) species [14] or the application of a high potential of 1.0 V (RHE) [15] to the Pd electrode may

facilitate the removal of this ‘CO-like’ species and hence recover the performance of a DFAFC.

Regarding relevant spectroscopic studies on CO_{ad} formation on Pd surfaces in FA solutions [17–21], no consensus has been reached owing probably to different methods, Pd surfaces, FA concentrations and potentials used. Traditionally, CO was regarded as the product of the dehydration pathway in parallel to the dehydrogenation pathway [22]. With conventional infrared reflection absorption spectroscopy (IRAS) or surface enhanced infrared absorption spectroscopy in ATR configuration (ATR-SEIRAS), CO_{ad} was not detected during FA decomposition on either Pd(111) [17], Au/Pd(111) [18] or Pd/Pt(111) [19] electrodes. In contrast, very weak CO bands around 1730 – 1840 cm^{-1} were detected on chemically deposited Pd film electrodes in 25 mM FA during a positive potential scan from 0.22 V (RHE) by high-sensitivity ATR-SEIRAS [20]. Most recently, we have identified a stronger CO band around 1838 – 1849 cm^{-1} on electrodeposited Pd overfilm electrodes in 0.5–2 M FA by SEIRAS, and proposed that CO formation may mainly proceed via the reduction of FA hydrogenation product CO_2 [21]. Nonetheless, all the above Pd materials and FA concentrations for spectroscopic measurements are not practically used in DFAFCs. Instead, carbon-supported or unsupported Pd nanocatalysts in more concentrated FA solutions (2–10 M) are normally adopted for the latter case. It is thus of great significance and urgency to probe at the molecular level whether such a poisoning species may form and how it effects on the deactivation of a practical catalyst under conditions to some extents mimicking the DFAFC anode operations.

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Unfortunately, no pertinent reports have shown up in the literature to address this practically more interested concern.

In this work, we have applied *in situ* ATR-IR spectroscopy to probe the CO_{ad} accumulation and its poisoning nature in FA (electro)decomposition on a state-of-the-art Pd black catalyst in 5 M FA solution at the open circuit potential (OCP, ca. 0.06 V vs. RHE), 0.4 V (RHE) and scanned potentials between 0.1 and 0.5 V (RHE). These potential conditions more or less correspond to the chemical decomposition, typical potentiostatic oxidation, and 'on' and 'off' switch output operations of a DFAFC anode, respectively.

2. Experimental

The Pd black catalyst suspension was prepared by mixing 1 mg of Pd black (High surface, Sigma–Aldrich, particle size ca. 8 nm), 950 μL of ethanol, and 50 μL of Nafion (5 wt.%, Aldrich) with ultrasonication for 30 min, and 80 μL of the suspension was then pipetted onto a clean Au film (~ 50 nm thick) pre-deposited on the reflecting plane of a hemicylindrical Si prism for electrochemical ATR-IR measurement, or onto a glassy carbon (GC) rotating disc electrode (RDE) (Pine) for electrochemical measurement to attain a same Pd loading of 45 $\mu\text{g cm}^{-2}$. The catalyst ink was dried slowly at room temperature with a N_2 flow atmosphere. The catalyst-layer was rinsed thoroughly with Milli-Q water (≥ 18.2 M Ω cm, Millipore) and then served as the working electrode in subsequent (spectro)-electrochemical measurements with a Au foil and a saturated calomel electrode (SCE) as the counter and reference electrodes, respectively. A CHI 633 electrochemistry workstation (CH Instruments, Shanghai) was employed for the potential control. All the potentials are converted to the corresponding values with respect to RHE. The electrolyte solutions were prepared by using Pro Analysis (P.A.) grade FA, suprapure HClO_4 (Sinopharm, China), and Milli-Q water. The details for chemical deposition of the Au underfilm on Si and the setup of the ATR cell were described elsewhere [23,24].

A Varian 3100 FT-IR Excalibur Series spectrometer equipped with an MCT detector was used for ATR-IR measurements at a resolution of 8 cm^{-1} with unpolarized IR radiation at an incidence angle of ca. 65°. All the spectra were shown in the absorbance unit as $-\log(I/I_0)$, where I and I_0 represent the intensities of the reflected radiation of the sample and reference spectra, respectively. The successive time " t " indicated in the following plots correspond to the ending moment in acquiring a spectrum over a designated period of 5 or 10 s in real-time IR measurements.

3. Results and discussion

3.1. CO accumulation at open circuit potential

FA decomposition at OCP is practically important in refueling an anode of a DFAFC without an output current and in producing hydrogen to drive a portable H_2 – O_2 PEMFC [8]. Shown in Fig. 1A are the time-evolved IR spectra for the Pd black/Au electrode that were recorded upon injecting a pre-mixed 5 M FA + 0.1 M HClO_4 solution in the spectral cell at OCP (ca. 0.06 V) with the single-beam spectrum acquired before the injection used as the reference spectrum. The very strong bands at 1720, 1400 and 1214 cm^{-1} arise from the interfacial high concentration of FA [17]. The weak band at 2345 cm^{-1} can be safely assigned to the interfacial CO_2 from FA dehydrogenation, whose intensity initially increased and then gradually decreased with time, reflecting the interplay of the CO_2 production at Pd surfaces and the CO_2 diffusion to the bulk solution. Unlike the external IRAS mode which can trap the CO_2 product dissolved in its thin-layer-structured electrolyte with a much longer optical path, the ATR mode is not so sensitive to detect the

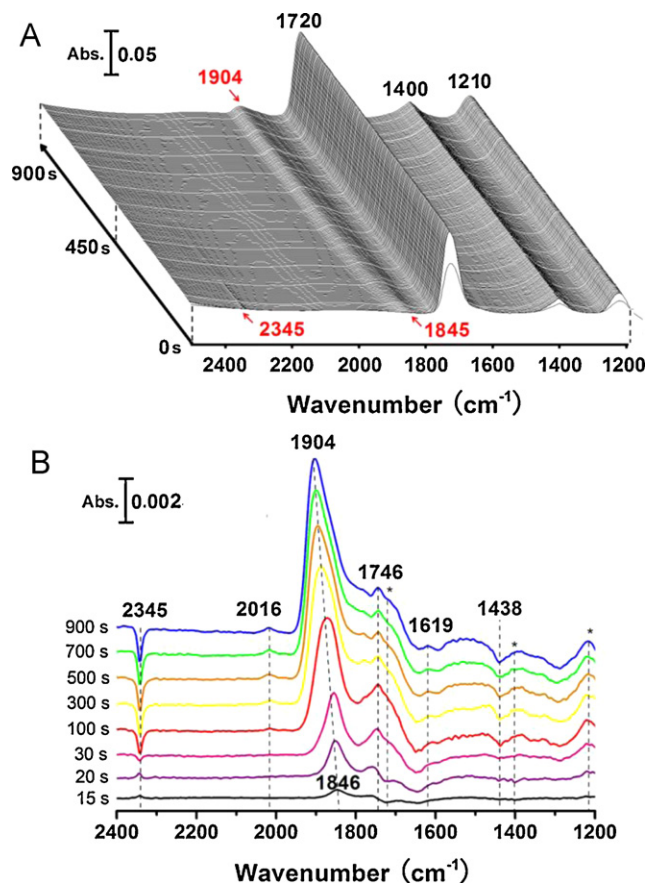


Fig. 1. (A) Time-evolved IR spectra of the Pd black/Au electrode recorded after injecting a pre-mixed 5 M FA + 0.1 M HClO_4 solution to the spectral cell. Reference spectrum was recorded in air before the injection; (B) replotted spectra selected from (A) with the single-beam spectrum taken at 10 s after the injection of 5 M FA + 0.1 M HClO_4 to the cell as the reference spectrum. The acquisition time for each single-beam spectrum is 5 s.

interfacial dissolved CO_2 product due to the relative facile mass transport of CO_2 to the bulk solution as well as the limited evanescent light penetration depth. Nevertheless, the band intensity may qualitatively reflect the variation of interfacial CO_2 concentration.

On the other hand, a few seconds after the Pd black surfaces were immersed in the above solution, a band at ca. 1845 cm^{-1} emerged and then grew in intensity with its frequency blue-shifted slowly to 1904 cm^{-1} . To minimize the interference of strong bulk FA signals and highlight other weak bands, the single-beam spectrum taken at 10 s after the electrolyte injection (to ensure that all Pd black surfaces are in contact with 5 M FA) was selected as the reference spectrum to yield the time-evolved absorption spectra as shown in Fig. 1B. As can be seen from Fig. 1B, only minor residual bulk FA bands were left as indicated with the asterisks. In addition, two negative-going bands and four positive-going ones can be identified. The two negative-going bands at 2435 and 1438 cm^{-1} can be attributed to the interfacial CO_2 and the HCO_3^- species at the Pd black surfaces [25], respectively. The major band initially at 1846 cm^{-1} grew rapidly over the first 300-s domain with its frequency blue-shifted to ca. 1904 cm^{-1} , accompanied by less conspicuous growth of two minor bands at 1746 and 1619 cm^{-1} . Additionally, at ~ 100 s, a very weak band located at 2016 cm^{-1} appeared. These bands at 1746, 1846–1904, and 2016 cm^{-1} are characteristic of multi-, triple- or bridge- and linear-bonded CO species (denoted as CO_M , CO_T or CO_B and CO_L , respectively) on Pd black surfaces [26,27] and the band at 1619 cm^{-1} may be assigned to the co-adsorbed H_2O . It should be mentioned that the frequencies and relative intensities from different configurations of CO_{ad}

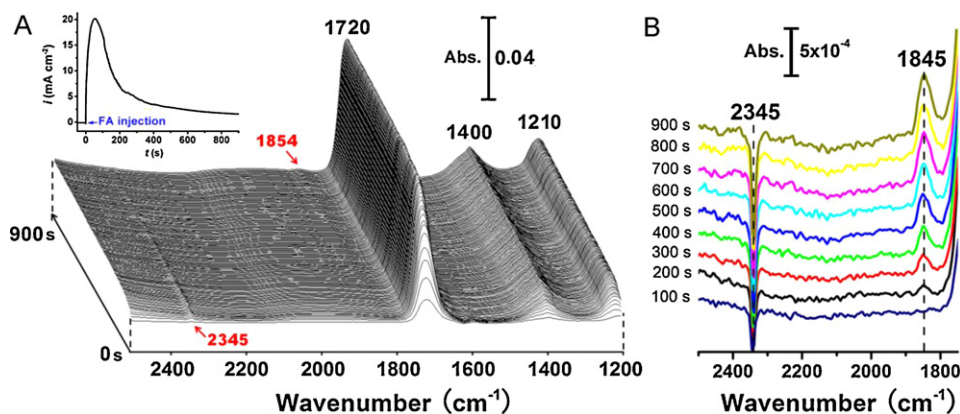


Fig. 2. (A) Time-evolved IR spectra for the Pd black/Au electrode at 0.4 V after the injection of aliquot of 96 wt.% FA (at 0 s) in 0.1 M HClO₄ to attain a final concentration of 5 M FA under Ar bubbling. Reference spectrum was recorded in blank 0.1 M HClO₄ solution (Insert is the corresponding chronoamperometric curve.) (B) Replotted and selected spectra with the single beam spectrum acquired at 50 s after FA injection as the reference spectrum from (A). The acquisition time for each single-beam spectrum is 5 s.

on Pd surfaces are strongly dependent on the overall CO coverage as well as the surface states (such as the facets, defects and coadsorbates on Pd surfaces). The spectral feature obtained here suggests a much lower CO coverage compared to that for saturation adsorption, as demonstrated with the delicately controlled CO bubbling experiments on Pd film electrodes [20,21]. In accompany with increasing CO coverage on Pd surfaces with time, the CO₂ output decreased, so did the weakly adsorbed HCO₃⁻, suggesting that the strongly adsorbed CO blocked the surface active sites accommodated for FA dehydrogenation.

3.2. CO accumulation at 0.4 V

0.4 V (RHE) corresponds to a typical working potential for the anode to sustain the output voltage of ~0.5 V for a DFAFC single cell, and thus was often used in assessing the chronoamperometric response of a Pd-based catalyst for FA electro-oxidation [2]. In order to further testify if any CO_{ad} forms at this potential, the time-evolved IR spectra for the Pd black/Au electrode in 0.1 M HClO₄ were recorded at 0.4 V upon adding aliquots of 96 wt.% FA to attain a final concentration of 5 M FA under Ar bubbling (achieved possibly after tens of seconds). The spectra obtained are shown in Fig. 2A with the single-beam spectrum taken in blank 0.1 M HClO₄ as the reference. Two distinctive spectral features can be seen as compared with those for OCP (Fig. 1A), i.e., stronger CO₂ and much weaker CO_{ad} band intensities. Displayed in Fig. 2B are the selected spectra calculated with the single beam spectrum at 50 s after introducing FA as the reference spectrum, indicating that the CO_T band at 1845 cm⁻¹ appeared and increased from about 100 s after FA injection. Throughout the whole process of 900 s, the CO_T band remained significantly lower than the major CO band detected at OCP, and neither CO_L nor CO_B band could be seen at 0.4 V. These results suggest the CO_{ad} formation and accumulation at 0.4 V is much slower than at OCP (ca. 0.06 V), in accordance with our recent observation on the Pd film electrode in lower concentrations of FA [21]. The CO_{ad} species may originate from the dehydration of FA [2,22] and the reduction of FA dehydrogenation product CO₂ on H-covered Pd surfaces [21]. According to our latest spectroelectrochemical study in conjunction with a flow cell design on a Pd film electrode in FA solutions of lower concentrations, the CO₂ reduction pathway could be predominant, which may account for the observation that a lower potential favors a higher CO coverage [21].

Meanwhile, the chronoamperometric curve for the Pd black/Au electrode is shown as the inset of Fig. 2A. The initial current rise reflects the process of increasing interfacial concentration to 5 M after injecting aliquots of 96% FA to 0.1 M HClO₄ solution with

Ar bubbling. The peaked FA oxidation current decayed from the ca. 20 mA cm⁻² at 40 s to ~3 mA cm⁻² at 900 s, in company with decreasing CO₂ band intensity in Fig. 2A and B. The fast current decay may be deemed from four contributions: (1) the insufficient supply of FA from the bulk to the surface due to the rapid oxidation consumption; (2) the surface inhibition due to CO₂ bubbles [28]; (3) the decrease in the catalysts surface due to the aggregation of Pd nanoparticles [9]; and (4) last but not least, the surface poisoning of strongly adsorbed 'CO-like' species. The first two can be largely solved by increasing mass transport with an improved design of the anode, and the last two are more relevant to the irreversible deactivation of Pd nanocatalysts. Based on electrochemical measurements, surface poisoning was suggested to be more important than nanoparticle aggregation in deactivating the Pd catalyst in a long-working DFAFC [9]. By using EIS [9,10], on-line mass spectroscopy [11], and anodic stripping measurements [9,12,13], the so-called 'CO_{ad}-like' residues were assumed on Pd surfaces without molecular level evidences. On the other hand, no relevant molecular spectroscopic reports have been found in literature in addressing the nature of poisoning species on genuine Pd nanocatalysts. In this regard, we have for the first time provided molecular level evidences to clarify the presence of CO poisoning species on a Pd black nanocatalyst in practically used 5 M FA during (electro)chemical decomposition of FA by using high surface sensitivity ATR-IR spectroscopy. For comparison, parallel experiments were also run on the bare Au film electrode and the Pd black/Au electrode without incorporating Nafion in the ink under otherwise the same conditions, respectively (not shown). No CO_{ad} was detected on the bare Au film electrode, and CO_{ad} was similarly detected on Pd black surfaces in the absence of Nafion.

3.3. CO poisoning and removal at changing potentials

To further assess CO poisoning at changing potentials to some extent mimicking the anode polarization of a DFAFC under repetitive 'on' and 'off'-output conditions as well as to examine the effect of so-called 'reactivation' through a sufficiently positive potential excursion.

In Fig. 3B, two sets of current vs. time curves were plotted for the Pd black/Au electrode in 5 M FA + 0.1 M HClO₄ solution during potential cycling between 0.1 and 0.5 V at 10 mV s⁻¹. The potential waveform scheme is shown in Fig. 3A, indicating that how the spectral and current data for potential cycling were acquired. Notably, before the initial potential scan, the electrode was left at OCP for 400 s to mimic the anode refueling and storing processes without output currents. After ten cycles of potential scan, the electrode was

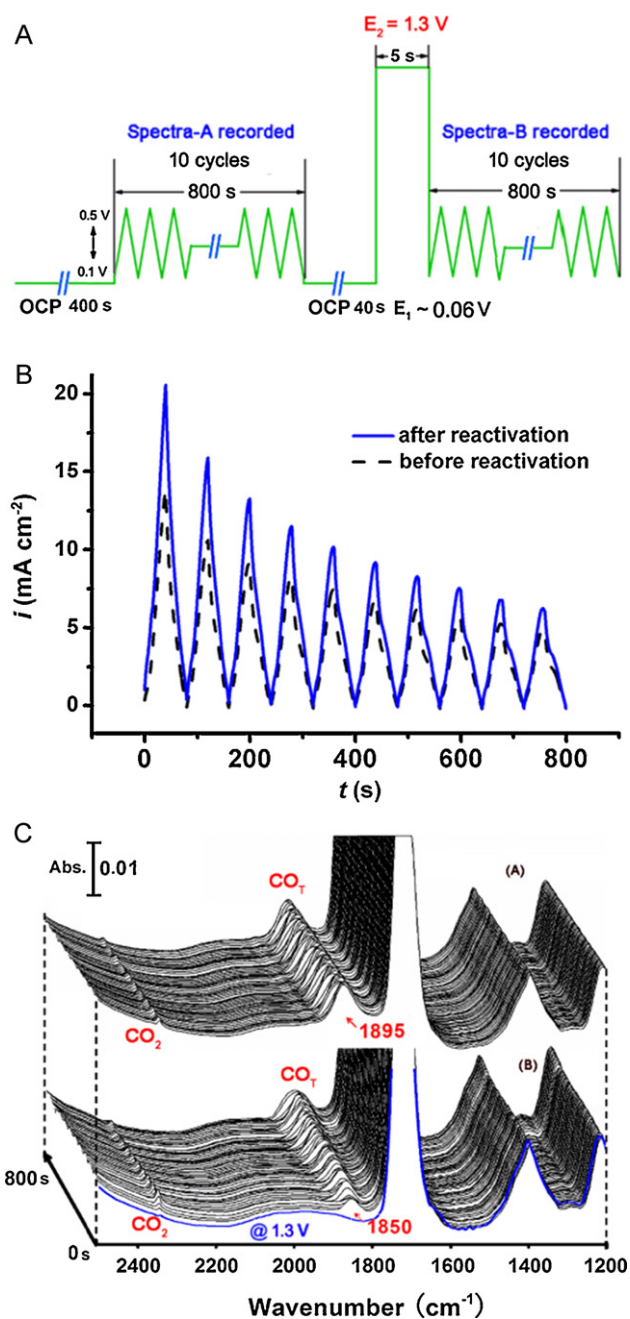


Fig. 3. (A) Potential working function used for the measurements. (B) Chronoamperometric curves for the Pd black/Au electrode in 5 M FA + 0.1 M HClO₄ solution for two potentiodynamic measurements between 0.1 and 0.5 V at 10 mV s⁻¹ before and after reactivation at 1.3 V. (C) Corresponding time-evolved IR spectra for the same Pd black/Au electrode in the two runs of potentiodynamic measurements. The acquisition time for each single-beam spectrum is 10 s. The spectrum obtained after polarizing the electrode at 1.3 V for 5 s is inserted for comparison (blue line).

left at OCP again for 40 s and was then stepped to 1.3 V and held at this potential for 5 s to strip CO_{ad} followed by another ten cycles of potential scan. Two sets of time-evolved spectra were recorded in potential scanning with an acquisition time of 10 s for each single-beam spectrum, yielding four spectra in a half cycle. Displayed in Fig. 3C are spectra calculated in absorbance unit with the single-beam spectrum acquired in blank 0.1 M HClO₄ as the reference. The periodic shift of the band frequency of CO_T is due to four periodically changing average potentials at which the spectra were obtained.

From Fig. 3B, it can be seen that for both potential cycling tests, the oxidation currents decayed with increasing cycle. As discussed

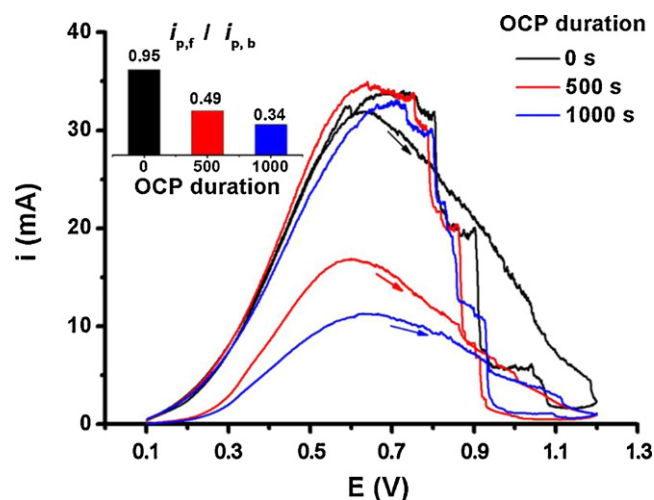


Fig. 4. Cyclic voltammograms recorded for a Pd black covered GC RDE electrode in 5 M FA + 0.5 M HClO₄ at 50 mV s⁻¹ with different preconditioning times at OCP (0, 500 and 1000 s) before initializing potential scans. The column inset shows the values of $i_{p,f}/i_{p,b}$ for the three cases.

above, the current decay may arise from four contributions, among which the CO poisoning is an important cause for the irreversible deactivation of Pd surfaces. Careful examination of the two sets of current vs. time curves and the corresponding spectra reveals the following facts: first, after polarization at 1.3 V for 5 s, CO_{ad} accumulated so far can be effectively removed as no CO_T band can be seen in the inserted spectrum in Fig. 3C (blue line) from another independent measurement; second, after the potential-triggered reactivation, the maximum current increased from 4.8 (the 10th cycle of the first run) to 20.6 mA cm⁻² (the 1st cycle of the second run), in response to a substantially reduced CO_T band intensity; third, for each same sequence of cycle in the two runs of spectro-electrochemical measurements, the currents after the reactivation are larger than the ones before reactivation, accompanied with generally much lower CO_T band intensities. These observations further support the poisoning nature of CO_{ad} species formed on Pd surfaces in FA solutions. Also notable is that the CO_T band intensity is largely decided by the OCP duration, suggesting that special attention should be paid to the OCP control in operating a DFAFC, as well as in transferring a tested Pd electrode from concentrated FA solutions to other electrolytes for *ex situ* surface examination.

The effect of the OCP-staying duration on the electrocatalytic activity of a Pd black electrode was further demonstrated in Fig. 4, in which three cyclic voltammograms for a Pd black covered GC RDE were recorded at 1000 rpm in 5 M FA + 0.5 M HClO₄ under otherwise the same conditions except different OCP durations before the measurements. The RDE was used to control the mass transport condition and to reduce the possible block of CO₂ bubbles on the Pd surface and 0.5 M HClO₄ was adopted to lower the overall IR ohmic drop. As shown in Fig. 4, it is revealed that the longer duration at OCP for the electrode, the smaller oxidation peak current in the forward-scan ($i_{p,f}$). However, in the backward scan, the oxidation peak current ($i_{p,b}$) is largely independent of the OCP-staying duration. This result is better demonstrated by the decreasing value of $i_{p,f}/i_{p,b}$ with increasing OCP staying duration from 0 to 1000 s as shown in the inset, which can be qualitatively understood based on the above spectral results. As already known, CO formation is more significant at a lower potential, actually, the CO_T formation is negligible for a short period of oxidation at potentials higher than 0.4 V (RHE) [21]. A longer stay at OCP produces a relatively higher coverage of CO_{ad}, leading to a smaller oxidation in the forward scan. Since CO_{ad} can be oxidized as the potential was scanned to 1.2 V

(RHE), in the backward scan, the surfaces are initially absent of CO poisoning since a slow CO accumulation may occur only at potentials lower than 0.5 V, giving rise to the roughly same oxidation currents in the three cases.

Briefly, our results lend molecular level support to the claim that applying a high potential to a deactivated Pd electrode may largely regenerate the activity of the anode catalyst in a DFAFC [15]. Along this line, it appears that future durable Pd-based anode catalysts should be developed in the direction of anti-CO poisoning on Pd sites. Moreover, the potential-dependent CO_{ad} accumulation suggests more attention should be paid to the expected and unexpected OCP operations in practice.

4. Conclusion

In this report, we have applied *in situ* electrochemical ATR-IR to investigate the accumulation and removal of CO poisoning species on practically important Pd black nanocatalyst in 5 M FA for different potential patterns, mimicking to some extents the working conditions of a DFAFC anode. Concrete spectral evidence of CO_{ad} accumulation with time at Pd black surfaces is provided during the (electro)chemical decomposition of FA. The CO_T, CO_B and CO_L band could be detected at the OCP while the CO_T band could be directly seen at 0.4 V. The spectral and electrochemical results reveal that CO_{ad} is more seriously accumulated at a low potential, e.g., OCP, attributing greatly to a decreased activity of the Pd black towards FA electrooxidation. The CO-poisoned surfaces can be reactivated largely through a high oxidation potential excursion.

Acknowledgements

This work is supported by NSFC (Nos. 20833005, 20873031 and 21073045), SMCST (Nos. 08JC1402000 and 08DZ2270500). MOST (No. 2009AA033701) provides partial support for purchasing chemicals and DFG IRTG program (No. GRK1215/2) supports the international cooperation.

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