



## Short communication

# Acrylonitrile-contamination induced enhancement of formic acid electro-oxidation at platinum nanoparticles modified glassy carbon electrodes



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## H I G H L I G H T S

- FAO is unexpectedly enhanced at nano-Pt/GC electrodes poisoned with AcN.
- The extent of enhancement depends on the surface coverage ( $\theta$ ) of AcN.
- AcN favors the direct FAO at the expense of the indirect oxidation (CO pathway).
- Adsorption of AcN impurities alters the electronic properties of the underlying Pt surface.

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## A B S T R A C T

Minute amount ( $\sim 1$  ppm) of acrylonitrile (AcN), a possible contaminant, shows an unexpected enhancement for the direct electro-oxidation of formic acid (FAO) at Pt nanoparticles modified GC (nano-Pt/GC) electrodes. This is reflected by a remarkable increase of the current intensity of the direct oxidation peak ( $j_p^d$ , at ca. 0.3 V) in the presence of AcN, concurrently with a significant decrease of the second (indirect) oxidation current ( $j_p^{nd}$ , at ca. 0.7 V), compared to that observed in the absence of AcN (i.e., at the unpoisoned Pt electrode). The extent of enhancement depends on the surface coverage ( $\theta$ ) of AcN at the surface of Pt nanoparticles. AcN is thought to favor the direct FAO by disturbing the contiguity of the Pt sites, which is necessary for CO adsorption. Furthermore, XPS measurements revealed a change in the electronic structure of Pt in presence of AcN, which has a favorable positive impact on the charge transfer during the direct FAO.

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## 1. Introduction

Fuel cells have been emerged as a clean, efficient, reliable and durable electrical energy supply systems replacing the fossil fuels. In this regard, the direct formic acid fuel cells (DFAFCs) have shown superiority over the traditional hydrogen (HFCs) and direct methanol (DMFCs) fuel cells in providing electricity for portable electronic devices. This advantage is acquired from the easiness and safety concerns associated with storing and transporting formic

acid (FA). Moreover, the slow crossover of FA through the Nafion-based membranes and the reasonable oxidation kinetics of FA have also enriched the desire to DFAFCs [1–3]. The electro-oxidation of FA (FAO) is the essential anodic reaction in DFAFCs. So far, Pd-based and Pt-based electrodes are among the best catalysts for this reaction, nevertheless, Pd suffers from an inherent instability [2,4–8] and Pt electrodes suffer from the CO poisoning.

Generally, FAO on Pt-based electrodes follows a dual (direct and indirect) pathway mechanism. The direct (desirable) pathway involves the dehydrogenation of FA to CO<sub>2</sub> at relatively low anodic potential (with a peak current  $j_p^d$ ). On the other hand, the indirect (dehydration) pathway involves a non-faradaic dissociation of FA to CO (undesirable) which is adsorbed at the Pt surface and subsequently oxidized at higher potential (with a peak current  $j_p^{nd}$ ). The

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adsorption of CO on Pt surface causes a surface poisoning and thus impedes the direct oxidation pathway of FA to CO<sub>2</sub> [9–16]. The decoration of the surface of the Pt electrode with other metal and/or metal oxides is shown to overcome/reduce the CO poisoning and improve the electrode catalytic activity, mainly due to a favorable geometric and/or electronic modification which disfavors the CO adsorption. For instance, interruption of the Pt site contiguity by gold nanoparticles (AuNPs) could eventually hinder the CO adsorption leading to an outstanding electrocatalytic activity towards the direct FAO without passing by the CO intermediate [17–19]. Additionally, metal oxides could easily provide/exchange oxygen species which facilitate the oxidative removal of CO at reasonable potentials [2,6–8].

In order to commercialize the DFAFCs, the high price and the deterioration of the catalytic activity of the costly Pt catalyst should be overcome. In fact, the major influence for the efficiency loss in DFAFCs comes from the deterioration of the catalytic activity of the Pt catalyst by inevitable organic and/or inorganic contaminants, e.g., nitrogen- and/or sulfur-containing compounds (entering the cell with air), halides (where most of the high-surface area fuel cell catalysts are often synthesized from halide-containing educts), and hydrocarbons (if any defect appeared in piping, blowers, pumps and heat exchangers) [20–22]. Basically, the existence of these organic compounds at the Pt surface is able to alter the binding energies of Pt with key intermediates, which ultimately influence the reaction kinetics [23]. St-Pierre et al. [24] reported a significant loss in PEMFCs performance in the presence of some airborne hydrocarbon contaminants (e.g., acetonitrile and toluene), which is restored back after exposure to clean air. Moreover, acrylonitrile (AcN) is shown as a possible hydrocarbon contaminant from the materials making up the balance of plant (BOP) of PEMFCs such as accessories, piping, blowers, pumps and heat exchanger [21]. A severe poisoning for the kinetics of the oxygen reduction reaction was observed in the presence of a minute amount (~ ppm) of AcN at commercially available Pt/C catalysts in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> solution [20]. In this context, the investigation of the impact of AcN on the catalytic performance of the anodic part of PEMFCs has a prime importance.

Herein, unpredictable surprising enhancement for the direct FAO at Pt nanoparticles modified GC (nano-Pt/GC) electrodes is observed in the presence of a minute amount (in ppm) of AcN. The catalytic enhancement is shown to depend on the AcN concentration. The results are explained in view of the possible reaction pathways of FAO with the help of XPS measurements.

## 2. Experimental

Glassy carbon (GC,  $d = 3.0$  mm) and Pt ( $d = 1.6$  mm) electrodes (from ALS-Japan) were used as working electrodes after polishing with aqueous slurries of successively finer alumina powder on a microcloth. The Pt electrodes were further electrochemically cleaned by scanning the potential between the onset potentials of the HER and OER in 0.5 M H<sub>2</sub>SO<sub>4</sub> for several cycles until the characteristic cyclic voltammogram (CV) of a clean Pt surface was obtained. A spiral Pt wire and Ag/AgCl/KCl (sat) were used as the counter and reference electrodes, respectively.

The electrodeposition of PtNPs on the bare GC (nano-Pt/GC) electrode was done in 0.1 M H<sub>2</sub>SO<sub>4</sub> containing 1.0 mM H<sub>2</sub>[PtCl<sub>6</sub>] solution at a constant potential of 1 V for 300 s. This typically ends up with ca. 55 μg Pt loading ( $7.85 \times 10^{-4}$  g cm<sup>-2</sup>), as estimated from the amount of charge passed during the potentiostatic electrodeposition of Pt.

The electrochemical measurements were performed at room temperature ( $25 \pm 1$  °C) in a conventional two-compartment three-electrode glass cell using an EG&G potentiostat (model 273A)

operated with Echem 270 software. The electrocatalytic activity of the nano-Pt/GC electrode towards FAO was examined by measuring cyclic voltammograms (CVs) in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing 0.3 M FA in presence/absence of AcN (in ppm range). The real surface areas were evaluated in two ways; using the hydrogen adsorption/desorption peaks and using the CO stripping peak. Current densities are calculated on the basis of the geometric surface area of the working electrode (geometric area = 0.07 cm<sup>2</sup>). A field emission scanning electron microscope (FE-SEM, QUANTA FEG 250) coupled with an energy dispersive X-ray spectrometer (EDX) unit was employed to evaluate the electrode morphology and composition. X-ray photoelectron spectroscopy (XPS, operating with Al K $\alpha$  radiation) was employed in the determination of the electronic structure of the Pt catalyst. The binding energies derived from XPS measurements have been calibrated to the C1s spectrum (at 284.5 eV) of the carbon support.

## 3. Results and discussions

Fig. 1A shows an SEM micrograph for the nano-Pt/GC electrode, in which Pt nanoparticles with an average particle size of 80 nm are homogeneously covering the entire GC surface. A typical characteristic CV for a Pt substrate measured in 0.5 M H<sub>2</sub>SO<sub>4</sub> is observed with a broad oxidation peak for the Pt-oxide formation (commences at ca. 0.65 V and extends up to 1.4 V) coupled with a single reduction peak centered at ca. 0.45 V (Fig. 1B, curve a). The hydrogen adsorption/desorption ( $H_{\text{ads/des}}$ ) couple appeared in the potential

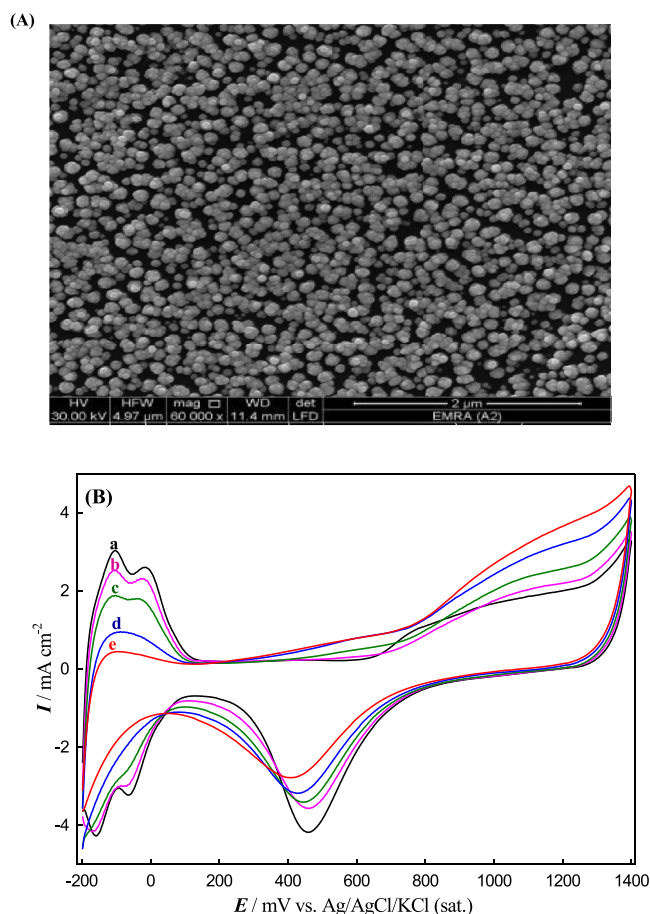


Fig. 1. (A) SEM micrograph for nano-Pt/GC. (B) CVs of the nano-Pt/GC electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing (a) 0, (b) 1, (c) 10, (d) 30, and (e) 50 ppm AcN. Potential scan rate: 100 mV s<sup>-1</sup>.

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