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# Conducting polymers inducing catalysis: Enhanced formic acid electro-oxidation at a Pt/polyaniline nanocatalyst

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## ABSTRACT

Research is moving rapidly to sustain convenient energy resources fulfilling the global climate legislations. Herein, a novel catalyst of platinum nanoparticles (PtNPs) dispersed onto polyaniline (PANi) is recommended for formic acid electro-oxidation (FAO); the fundamental anodic reaction in direct formic acid fuel cells (DFAFCs). The catalyst's preparation scheme allows a sequential electrodeposition of fibril PANi and spherical PtNPs (ca. 65 nm in size) on a glassy carbon (GC) substrate and permits a precise control over the deposition sequence and loading. Interestingly, incorporation of PANi into the catalyst's ingredients can significantly (ca. 16 times) improve the catalytic activity of the catalyst towards FAO by shifting the mechanism towards the desirable dehydrogenation pathway and mitigating the undesirable poisoning dehydration pathway. The catalytic efficiency is tuned by manipulating the deposition order and loading of different catalyst's ingredients. Several techniques are employed to confirm the successful deposition of the catalyst and to evaluate its morphology, composition and crystal structure. While PtNPs are essential for FA adsorption, PANi improves the dispersion of PtNPs and mediates FAO to facilitate the charge transfer and mitigate CO poisoning. A promising catalytic stability is achieved in a long continuous (150 CVs) electrolysis experiment.

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## Introduction

The global desire to reduce the carbon emissions, mostly released to the atmosphere from the traditional combustion of fossil fuels, is motivating research to realize alternative environment-friendly and efficient power sources for future prosperity. In this regard, fuel cells (FCs—the galvanic device

converting the chemical energy into electricity in a continuous feeding manner) appeared promising for stationary and many diverse portable applications. Of these promising FCs, the DFAFCs have shown superiority over the long-investigated H<sub>2</sub>–FCs (HFCs) and the next recommended the direct methanol FCs (DMFCs) [1–5]. While the HFCs experienced potential hazards associated with the H<sub>2</sub> production, transportation and storage, in addition to its low gas-phase

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energy density, the DMFCs are still encountering a fuel-crossover problem through Nafion<sup>®</sup> membranes that typically limits the fuel concentration and the voltage gain. On the other hand, the DFAFCs feature a higher theoretical open-circuit potential (1.40 V) if compared to HFCs (1.23 V vs. RHE) and DMFC (1.21 V), which probably intensifies the voltage gain. Alternatively, FA (as a fuel) exhibits a less toxicity, faster oxidation kinetics and a smaller crossover through Nafion<sup>®</sup> membrane, which permits using a higher concentration of the fuel and thinner membranes.

Most of recent reports indicated a preponderance of platinum-based materials in the catalysis of FAO, the principal oxidation reaction in DFAFCs [6]. Perhaps, this originated from the measurable affinity of Pt surfaces for the de-protonation of FA to formate; the corresponding conjugate base of FA, according to simple Brønsted–Lowry acid–base concepts [7]. There is almost an agreement for proceeding the FAO on Pt-based surfaces in the two parallel pathways; dehydrogenation and dehydration [5–10]. The first (dehydrogenation), involving the direct oxidation of FA into CO<sub>2</sub>, is actually desirable as it consumes less energy with no emergence of poisoning intermediates. The other (undesirable) pathway involves a “non-faradaic” dissociation (dehydration) of FA to release CO; the critical poisonous for Pt surfaces. The release of CO consumes a significant ratio of Pt active sites imparting a potential deactivation towards FAO. Biasing the potential far to the positive side (high energy) until the Pt surface gets hydroxylated allows the oxidative desorption of CO to retrieve the Pt surface active again for FAO. The simple definition of both avenues rationalizes the increasing interest driving the manipulations dedicated to stimulate processing the FAO exclusively in the direct pathway. In this regard, increasing the basicity of the Pt surface with a chemisorbed layer of oxygen could successively impart a recognized activity (6–7 fold increase) for the Pt surface towards the dehydrogenation pathway of FAO [8]. This could be achieved by doping the Pt surface with different transition metal oxide nanostructures, which could provide the oxygen moiety required for enhanced CO oxidation at a relatively lower potential [9–11]. In fact, the impact of doping the Pt surface with foreign materials may extend to induce rather a geometrical enhancement for FAO. As pointed earlier, the CO poisoning of Pt surfaces requires the existence of three active Pt sites contiguously in a specific geometry [12,13]. Interruption of this contiguity by foreign atoms could successively steer the FAO towards the direct mechanism [9,14,15]. Similarly, the enhanced electrocatalytic activities that have been recently reported by Gong et al. for FAO on AuPt@Pt bimetallic and Pd@PtNi trimetallic nanostructures of tunable geometry can be understood [16,17].

Recently, conducting polymers (CPs) such as polyaniline (PANi) [18–20], polypyrrole [21,22], polyindole [23–26] and polycarbazole [24,27] have exhibited potential applications in electrocatalysis, and several Pt/CPs composites were developed for particular applications. For example, the electro-oxidation of small organic molecules demonstrated a particular enhanced activity at Pt/CPs composites, where the activity was correlated to the unusual improvement in the particle's distribution and surface area of the Pt catalyst [18,28]. PANi, in particular, has received exceptional attention owing to its large surface area, simple and low-cost production, outstanding

tunable electronic and electrical conductivity, perfect mechanical and chemical (below 100 °C) stability, that associate a wonderful conjugated polymeric structure [18,28].

Herein, a new Pt/PANi nanocomposite is recommended for FAO. The catalyst's preparation involved a sequential deposition for Pt nanoparticles (PtNPs) and PANi onto the surface of a glassy carbon (GC) electrode in a way permitting a control over the deposition sequence and loading. The Pt/PANi nanocomposite exhibited a unique catalytic activity towards FAO, and experiments were designed to reveal the origin of enhancement.

## Experimental

Chemicals of high quality (ultra pure) were purchased from trusted vendors (as Sigma–Aldrich, Fluka) and were used without prior purification treatment. Electrochemical and electrocatalytic measurements were performed in a two-compartment three-electrode conventional glass cell, in which an unmodified/modified GC (d = 3.0 mm) rod, a Ag/AgCl/KCl (sat.) electrode and a spiral Pt wire served, respectively, as the working, reference and counter electrode. All potentials will be displayed, even if not stated, in reference to Ag/AgCl/KCl (sat.). These measurements were all performed at room temperature (25 ± 1 °C) under Ar-saturated (i.e., O<sub>2</sub>-free) atmosphere using an EG&G scanning potentiostat (model 273A) operated with Echem 270 software. Typical cleaning procedure was applied for the GC and PtNPs modified GC (Pt/GC) electrodes before targeting the electrochemical measurements [2]. PANi was deposited electrochemically from 0.5 M H<sub>2</sub>SO<sub>4</sub> containing 0.1 M aniline at a constant potential of +0.9 V for 60 s, while PtNPs were electrodeposited from 0.2 M H<sub>2</sub>SO<sub>4</sub> containing 1.0 mM H<sub>2</sub>PtCl<sub>6</sub> solution using a potential step electrolysis from 1 to 0.1 V for various durations. The catalytic activity towards FAO was investigated in an aqueous solution of 0.5 M H<sub>2</sub>SO<sub>4</sub> containing 0.3 M FA. Multi diverse techniques were employed to confirm a successful catalyst's preparation, evaluate its morphology, composition and crystal structure and measure its catalytic activity and stability. These included cyclic voltammetry (CV), linear sweep voltammetry (LSV), field-emission scanning electron microscopy (FE-SEM-QUANTA FEG 250), energy dispersive X-ray spectrometry (EDS—attached the FE-SEM machine) and X-ray diffraction spectroscopy (XRD— PANalytical, X'Pert PRO operated with Cu target (λ = 1.54 Å)). High resolution transmission electron microscopy (HR-TEM) was conducted using FEI microscope (Tecnai G20, Super twin, double tilt - Netherland). The bright field mode of imaging was employed at electron accelerating voltage 200 kV using lanthanum hexaboride (LaB<sub>6</sub>) electron source gun. Eagle CCD camera with (4k × 4k) image resolution was used to acquire and collect transmitted electron images. Imaging & Analysis (TIA) software was used to spectrum acquisition.

## Results and discussion

### Electrochemical and morphological characterizations

The electrochemical characterization was pursued first due to its capacity to detect electroactive surface species even those

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