



# Electroactivity of nanoporous platinum depending on the porosity and potential for various electrode reactions



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## ABSTRACT

Electroactivity of nanoporous Pt (npPt) depending on the pore characteristics was studied for various electrode reactions having a range of electrode reaction kinetics: ferrocene oxidation, L-ascorbic acid (AA) oxidation, oxygen reduction reaction (ORR), H<sub>2</sub>O<sub>2</sub> reduction, and glucose oxidation. npPts with two different degrees of the porosities (npPt-1 and npPt-2) were electrodeposited on recessed Pt microdisk electrodes (100- $\mu$ m diameter), employing deposition solutions in which the composition ratios of Pt precursor, Triton X-100, and lead acetate were varied. npPt-1 has smaller microscale pores than npPt-2. The electroactivities of npPts were analyzed using amperometric sensitivities at mass-transfer-controlled and kinetic-controlled potential regions. Both npPt-1 and npPt-2 increased the sensitivities for all the reactions but reversible ferrocene oxidation remarkably compared to bare Pt. In the kinetic-controlled region, npPt-1 showed more greatly enhanced sensitivity compared to npPt-2 due to the smaller pores exerting more efficient confinement of a reactant near the Pt surface. In mass-transfer controlled region, npPt-2 was beneficial for relatively fast reactions (AA oxidation, ORR); while npPt-1 was advantageous for slower reactions (H<sub>2</sub>O<sub>2</sub> reduction, glucose oxidation). This suggests that the particle-to-particle distance of the npPt affects the electroactivity and an optimum degree of the porosity is different depending on the reaction kinetics.

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## 1. Introduction

Nanoporous Pt (npPt) has been of interest due to its high electrochemical catalytic activity (e.g. oxygen reduction reaction (ORR) [1–4], glucose oxidation [4–9], H<sub>2</sub>O<sub>2</sub> oxidation/reduction [2,4,10,11], pH measurement [12]), having wide applications such as fuel cell [1–3,6,13], chemical/biosensors [2,5,7–11,14], pH sensor [12], and immunosensors [15]. Enhanced electroactivity of npPt compared to bulk Pt had been mainly attributed to its enlarged surface area [3,10,16]. In recent years, however, the unique structural characteristic of npPt has been considered as another important factor increasing the electroactivity [17]. According to Han et al. [18], the confined space in nanoporous structures increases the collision efficiency of reactant molecules to Pt surface by capturing them in the pores. This confinement effect is also confirmed by the simulations [19,20].

Considering this confinement effect, the apparent electrocatalytic activity of npPt is anticipated to be affected by the pore sizes of the nanoporous structure. Some studies have reported the pore size effect of nanoporous materials on the electrocatalytic activity. Jung et al. [21] fabricated npPt thin films with various pore sizes (4–22 nm) by controlling composition and dealloying conditions of Pt–Si binary alloy. It showed that as the pore size increased, the methanol oxidation activity

improved and its charge-transfer resistance decreased. Honda et al. [22] made Pt-modified nanoporous honeycomb diamond films with two different pore sizes (60  $\times$  500 nm<sup>2</sup> and 400 nm  $\times$  3  $\mu$ m) using oxygen plasma etching of diamond films through anodic alumina masks with various pore dimensions followed by Pt deposition. The authors reported that a Pt-modified film with the widest pores showed greatly enhanced current densities for alcohol oxidation, reducing the reaction resistances. Du et al. [23] fabricated Pt nanoparticle-loaded nanoporous carbon which have pore sizes in a range of 4–19 nm. The catalytic activity of this material for ORR depended on the pore sizes. Wide pores made oxygen pass through them easily, but led to a large diffusion distance. The authors claimed that the optimum pore size for ORR was between 20 and 50 nm. These previous works showed that the pore size (i.e., particle-to-particle distance) could significantly affect the electrocatalytic activity of catalyst materials. However, they studied the pore size effect for a targeted specific single electrochemical reaction.

Instead, Park et al. [4] examined the activities of npPt with 1–2 nm sized pores [12] for a few electrode reactions (ORR, H<sub>2</sub>O<sub>2</sub> reduction, and glucose oxidation reactions) in phosphate buffer. It has been proven that sluggish ORR, H<sub>2</sub>O<sub>2</sub> reduction, and glucose oxidation reactions could be accelerated by npPt [3,5,10]. According to their results, for ORR and H<sub>2</sub>O<sub>2</sub> reduction reaction, the faradaic current increased with increasing the npPt thickness, but this value reached a plateau indicating that the further increased surface area did not contribute to the

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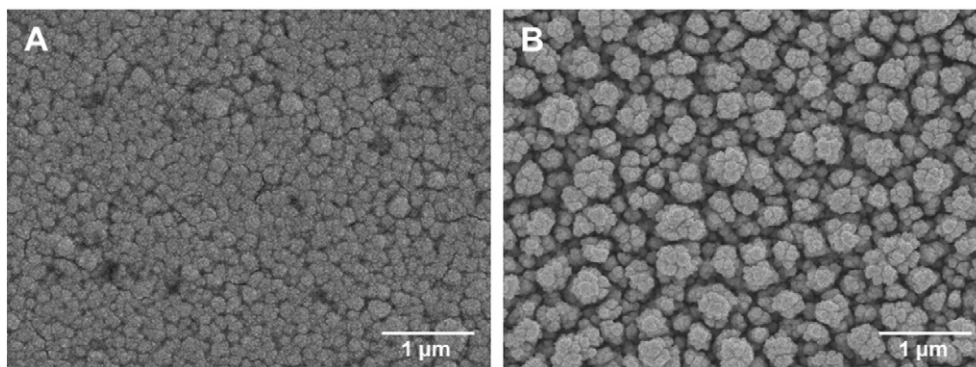


Fig. 1. Representative FE-SEM images of (A) npPt-1 and (B) npPt-2.

reactions. For glucose oxidation reaction, however, the faradaic current continuously rose with increasing the npPt film thickness showing that it was still in kinetic-controlled regime due to its very slow kinetics. A diffusion-controlled condition was achieved with very thick npPt films. This result suggested that npPt could enhance the catalytic activity more significantly for much sluggish reactions, due to not only enlarged surface area but also confinement effect. However, the npPt pore size effect on these various reactions with different electrode reaction kinetics was not studied.

In current study, we simply fabricated npPt with different pore sizes (npPt-1 and npPt-2) by electrodeposition varying the composition of a deposition solution. We investigated the local porosity effect on various electrode reactions with a range of electrode reaction rates systematically: ferrocene oxidation, L-ascorbic acid (AA) oxidation, ORR,  $H_2O_2$  reduction, and glucose oxidation reactions. Ferrocene oxidation is a well-known fast reversible reaction [24], while glucose oxidation is known as a sluggish totally-irreversible reaction [4]. AA oxidation, ORR, and reduction of  $H_2O_2$  which is an intermediate of ORR were studied as reactions having moderately slow electrode reaction kinetics. The electrocatalytic activities of npPt-1 and npPt-2 for all the tested reactions were analyzed and compared using amperometric sensitivities in two different potentials (i.e., mass-transfer-controlled and kinetic-controlled regimes).

## 2. Experimental

### 2.1. Chemicals

Pt microwire (100  $\mu\text{m}$  in diameter, 99.99%), Kimble microcapillary pipettes, NaCl ( $\geq 99.5\%$ ), Triton<sup>TM</sup> X-100, ferrocene (98%), acetonitrile (ACS reagent,  $\geq 99.5\%$ ), tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>, 98%),  $H_2O_2$  (35 wt.% solution in water), AA, D-(+)-glucose (ACS reagent), and  $H_2SO_4$  (95.0–98.0%) were from Sigma-Aldrich (St. Louis, MO). Phosphate buffer solution (PBS) was made by mixing  $NaH_2PO_4$  and  $Na_2HPO_4$  (BioXtra,  $\geq 99.0\%$ ) from Sigma-Aldrich. Carbon paste from BASi was used for electrochemical connection between an end of Pt wire and a copper wire (Hook-up wire, 28 AWG, Solid PTFE, Spool Green) from AlphaWire.  $H_2PtCl_6$  (Premion, 99.999%) was purchased from Alfa Aesar (Ward Hill, MA).  $Pb(CH_3CO_2)_2 \cdot 3H_2O$  ( $Pb \geq 99.5\%$ ) was supplied by Fluka (Steinheim, Germany). All solutions were prepared with 18 M $\Omega$  cm deionized water.

### 2.2. Electrode fabrication

An electrode was prepared by thermally sealing Pt microwires (100  $\mu\text{m}$  in diameter) under vacuum in glass capillaries (Kimble) and then by vertical polishing of the sealed end to expose Pt disk, as previously reported [25]. The resulting Pt microdisk electrode was etched in 1.2 M  $CaCl_2$  dissolved in acetone/water mixture (1:2 in volumetric ratio) by applying 3 V ac voltage (60 Hz) for 15 s with respect to

0.5 mm diameter Pt wire counter electrode using variable autotransformer (Staco Energy Products Co., Dayton, OH).

### 2.3. Electrodeposition of npPt films

Pt films with two different degrees of porosity (npPt-1 or npPt-2) were electrochemically deposited within the recessed pore of Pt disk with cyclic voltammetry (CV) with a Pt wire counter electrode and a saturated calomel reference electrode (SCE) as reported in our previous work [26]. Electrochemical deposition was performed using

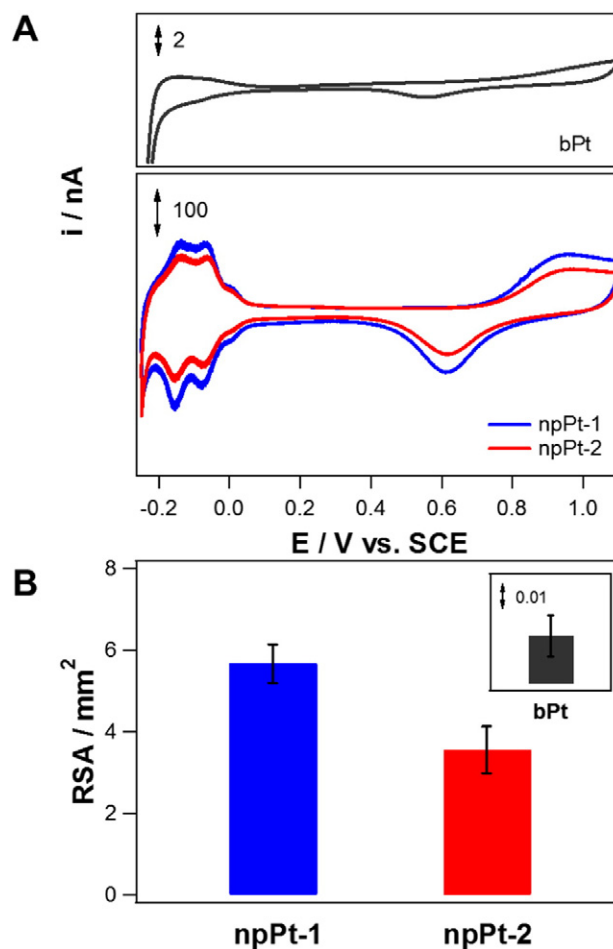


Fig. 2. (A) Cyclic voltammograms obtained in Ar-saturated 1 M  $H_2SO_4$  solution with a variety of electrodes: Pt disk, npPt-1, and npPt-2. Scan rate, 2  $\text{mV s}^{-1}$ . All the electrodes have the identical projected geometric area with a diameter of 100  $\mu\text{m}$ . (B) RSA of each electrode calculated by integrating the corresponding  $H_2$  adsorption/desorption peaks in the CV curve ( $n = 7$ ).

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