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Confined Molecular Dynamics for Suppressing Kinetic Loss in Sugar Fuel Cell

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ABSTRACT

We corroborated substantial suppression of kinetic loss in sugar fuel cell owing to microscopic molecular dynamics at nanoporous electrodes. When electrochemical reaction is sluggish, exchange current density (j_0) is governed by how often the reactants encounter the surface of catalyst. This highly frequent interaction between reactant and electrode surface can be achieved by confined molecular dynamics in nanoporous electrode. Using sucrose molecule as an oxidant fuel, the performance of nanoporous Pt (L_2-ePt) with pore size of 1 to 2 nm was compared with that of thin layer of Pt nanoparticles (Pt NPs) that was electrodeposited on a polished Pt surface to exclude the effects of crystalline facets and defects. As sucrose is bulkier and less adsorptive than glucose and undergoes sluggish electrochemical oxidation, sucrose oxidation substantially benefits from the confined molecular dynamics at nanoporous electrode. The current density (J_{RSA}) normalized by real surface area (RSA) of sucrose oxidation at L_2-ePt was higher than Pt NPs. In fuel cell operation, open circuit voltage of L_2-ePt was measured to be 0.593 V, 4.4 times higher than Pt NPs and j_0 significantly increased at L_2-ePt. Moreover, maximum power density (P_{RSA}) of L_2-ePt was much higher by a factor of 15.7 than Pt NPs.

1. Introductions

The origins that decrease the electrode performance of fuel cells can be categorized into three; kinetic loss, *iR* loss, and overpotential due to mass transport [1]. In response to these challenges, various porous structures of catalytic electrode materials and/or underlying supports have been suggested [2], *e.g.*, ordered porous carbon [3], three-dimensional (3D) CNT [4,5], graphene [6,7], etc.. First of all, the surface area of these conducting materials was effectively enlarged, securing conductance to minimize *iR* loss at electrodes. And efficiency of macroscopic mass transport through the porous network can be attained by finely tuning pore regularity [8], interconnectivity, and pore size [9]. As for kinetic loss caused by sluggish electrochemical kinetics, intrinsic catalytic activity of given electrode material is undoubtedly the most crucial factor. It is well-known that Pt shows the highest electrocatalytic activity for oxygen reduction reaction (ORR), while its cost is the highest barrier that makes itself difficult to be commercialized [10]. In due course, a great deal of effort has been made to minimize the amount of Pt, i.e. engineering the surface properties of catalysts [11] such as crystalline facets [12], defects [13], and alloy [14]. Indeed, several Pt based catalysts show adequate ORR activity, which is similar or even higher than a target (0.4 A mg^{-1}) of US DOE (Department of Energy)[1]. However, no catalyst has been proven to achieve high voltage and durability at low Pt loading for cost-efficiency yet. This means that impressive electrocatalytic ability of catalyst is not sufficient to meet the challenges posed by large scale fuel cell. As for substituting less expensive catalyst for Pt [15–17], it is still far to reach non-noble metals or metal free catalysts that possess catalytic activity comparable to Pt. [1,18] Therefore, we need new strategy to break through the trade-off between energy efficiency and cost efficiency by making the amount of Pt minimized or needless.

When electron transfer kinetics at a given electrode surface is too sluggish during the average period of molecular adsorption, the adsorbed reactants are likely to leave the surface without electron transfer. The desorbed reactants randomly diffuse in solution until they arrive at another region of the electrode surface. Under this condition, the rate of electron transfer is controlled by how often the reactants encounter the electrode surface, which can be parameterized as collision frequency [19,20]. Considering that high collision frequency means more interaction with the electrode surface within reaction zone for given period [21], any factor augmenting effective collision frequency could enhance the

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number of successful electron transfer events occurring for a given period. If the reactant is confined in nanopore[22], collision frequency is predicted to significantly elevate owing to geometric confinement so that the reactant should have more opportunities to stay longer at the electrode surface. This possible scenario is called *nano-confinement effect or confined molecular dynamics,* which was theoretically investigated in terms of Knudsen diffusion [22,23] and Brownian motion [24]. In our previous works, we suggested the confined molecular dynamics as a new electrocatalytic mechanism by showing appreciable enhancement in ORR and H_2O_2 reduction [25–28]. Both cathodic and anodic J_{RSA} (the current density divided by real surface area) of nanoporous Pt exhibited nearly reversible redox behavior of H_2O_2. The onset potential of ORR at nanoporous Pt shifted by *ca.* 100 mV in the positive direction. Erlebacher and coworkers supported this geometric effect by measuring ORR activity of nanoporous Ni/Pt alloy nanoparticles [29]. Furthermore, Mahmoud and El-Sayed reported that the frequency factor of the Arrhenius equation in 4-nitronphenol reduction inside hollow nanoparticles was higher than solid nanoparticles [30]. Computer simulations [25] as well as experimental studies [28] were carried out to assess how much the confined molecular dynamics affects heterogeneous electron transfer rate of weakly adsorptive reactants. Here we demonstrate that the microscopic confined molecular dynamics can bring about substantial suppression of kinetic loss in fuel cells by adopting sucrose as a fuel.

2. Experimental

2.1. Materials

All the chemicals including hydrogen hexachloroplatinate hydrate, Triton X-100, sulfuric acid, sodium chloride, potassium hydroxide, glucose, sucrose, and Pt wire were purchased from Aldrich and used without further purification. All electrochemical tests were carried out at room temperature.

2.2. Instrumentation

Cyclic voltammetry (CV), linear sweep voltammetry (LSV), and cell potential measurements were performed using an electrochemical analyzer (model CHI660A, CH Instruments Inc.). Reference 600 equipped with EIS300 electrochemical impedance spectroscopy software (Gamry Instruments) was used for the electrochemical impedance spectroscopy (EIS) experiments. EIS was performed by applying 10 mV AC amplitude at frequencies between 0.01 Hz and 100 kHz. Hg/HgO (1 M NaOH, CH Instruments Inc.) and Hg/Hg_2SO_4 (saturated K_2SO_4) were used as a reference electrode for CV in alkaline solution and sulfuric acid, respectively. Pt wire or mesh was used as a counter electrode. Pt disk electrodes (dia. 1 mm) were used as substrate electrodes for electrodeposition. The real surface areas (RSA) of working electrodes were determined from the areas under the hydrogen adsorption/desorption peaks in the cyclic voltammograms at 200 mV s^{-1} in 1 M sulfuric acid solution based on 210 $\mu C\ cm^{-2}$ of the conversion factor [31,32].

2.3. Preparation and modification of nanoporous Pt (L_2-ePt) electrode

Hydrogen hexachloroplatinate hydrate (5 wt%), 0.3 M NaCl (45 wt%), and Triton X-100 (50 wt%) were mixed and heated to 60 °C. The mixture as made was transparent and homogeneous. The temperature of the mixture solution was maintained around 40 °C using a thermostat, and therein electrodeposition of L_2-ePt was carried out on Pt disk electrodes at −0.2 V vs. Ag/AgCl. The resulting L_2-ePt electrode was immersed in distilled water for 1 h to remove the Triton X-100, and such a washing process was repeated 3–4 times. Then the electrode was electrochemically cleaned by cycling potential between +0.68 and −0.72 V vs. Hg/Hg_2SO_4 in 1 M sulfuric acid until a steady cyclic voltammogram was obtained.

2.4. Fuel cell setup and operation

The electrodes for the house made sucrose fuel cell in this work were not conventional MEAs. The cathode and anode were immersed respectively in two solution compartments that were separated by the anion exchange membrane (fumasep® FAA-3-PK-130, Fumatech GmbH, 0.13 mm thickness) like a normal salt bridge for electroanalytical cell. This was to more precisely analyze the molecular confinement effect. Thus, there was no physical contact between Pt electrode and membrane unlike conventional fuel cells. The anodic chamber was filled with nitrogen-saturated 0.1 M KOH solution containing 10 mM sucrose while oxygen-saturated 0.1 M KOH solution was in the cathodic chamber. Two half cells were assembled and then the open circuit voltage (V_{oc}) was continuously monitored by a CHI 660A electrochemical station. Once V_{oc} reached a steady-state, polarization curves were obtained by recording the cell voltage for 30 s at given constant currents. All tests were performed at ambient conditions.

3. Results and Discussion

3.1. Slow electrooxidation kinetics of a bulky sucrose molecule

One of the reasons we chose sucrose is its sluggish electrochemical kinetics. The sucrose oxidation at copper-modified gold electrode in alkaline solution is slower by 12 times than glucose to 44 times than fructose [33]. Other disaccharides such as maltose and cellobiose are electrochemically oxidized faster than sucrose as well [33]. Another reason is its size *ca.* 1.02 nm in diameter [34], which is a little smaller than pore size of nanoporous Pt that was used in this work. Both sluggish kinetics and appropriate size of sucrose are expected to allow us to see the considerable contribution of confined molecular dynamics to faradaic enhancement and performance of fuel cell. Incidentally, sucrose is the most widely available saccharide in our daily lives so as to be more indicative of evolvement to a practical fuel cell, which may be expedited by nanoporous electrochemistry based on confined molecular dynamics.

3.2. Linear sweep voltammograms of polished Pt, Pt NPs, and L_2-ePt

We used 3D nanoporous Pt, the so-called L_2-ePt, which consisted of closely packed Pt nanoparticles with a diameter of 3 nm functioning as ligaments and had pore size of 1 to 2 nm [35]. The amount of Pt loaded was about 1.16 µg. Metal nanoparticles by themselves can make electrocatalytic effects, which are currently believed to come from various crystalline facets [36,37] and defects [13,38]. In order to investigate pure confined molecular dynamics, we electrodeposited Pt nanoparticles (Pt NPs) onto carefully polished Pt substrates in a L_2-ePt plating solution for a short time (<10 s) to use it as planar geometry. The resulting Pt NPs had a roughness factor (R_f) of 6.2, which was only three times larger than the polished Pt (R_f 2.6). Such a low R_f of Pt NPs is reasonable because only a limited number of Pt NPs are scattered in the form of submonolayer. The interstitial space among neighboring Pt NPs on the flat substrate is too shallow for electroactive species to be confined. The molecules are likely to escape to the bulk solution rather than trapped between neighboring Pt NPs. Therefore, the effect of "confined molecular dynamics" among Pt NPs is negligible