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Effect of electrode size on catalytic activity

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Abstract

In the field of catalyst research, synthesis innovations have allowed for the production of nanoparticle catalysts less than 2 nm in size. With this decrease in catalyst size, new questions have arisen with respect to the overall effect of size on catalytic activity. It is generally accepted that as catalyst particles decrease in size, the surface area to volume ratio of the catalyst is increased, resulting in higher catalytic performance. This paper introduces a novel technique for producing electrode structures with specific catalyst sizes. Through the use of electrochemical impedance spectroscopy and chronoamperometry, these different electrode sizes are compared with respect to the hydrogen evolution reaction. From this work, it is shown that for the given reaction, there exists a critical size at which catalytic activity begins to increase. A proposed explanation for the observed change in catalytic performance is introduced.

Keywords: Size effect; Catalytic activity; Template synthesis; Electrochemical impedance spectroscopy; Capacitance

1. Introduction

Through the development and refinement of a variety of synthesis techniques, it has become possible to fabricate nanostructures with controlled sizes and geometries [1–6]. Specifically, in the areas of fuel cells and batteries, nanostructured catalysts have received considerable research focus due to their ability to increase electrocatalytic activity while minimizing catalyst loading [7,8].

Using current techniques, it is now possible to synthesize nanoparticle catalysts with a mean particle diameter less than 2 nm [7]. With this decrease in catalyst size, new questions have arisen with respect to the effect of size on electrocatalytic performance. It has been accepted in literature that with a decrease in particle size, there is an increase in electrocatalytic performance. However, it has also been noted that this increase in catalytic performance only continues to a certain size [8–10].

Through the work done by Chen and Goodman [9], it was shown that low-temperature oxidation of CO on supported Au particles had a marked increase in reaction rate down to 3.5 nm. As the particle size was reduced below this point, a decrease in catalytic activity was observed. Despite efforts to explain this behaviour, no current atomic-level understanding exists [9].

In fuel cell catalysts, this same trend has been identified. As an explanation, researchers have used theories such as the ''particle size effect'' and ''territory theory'' [8]. These theories address changes in particle morphology and particle distribution. It is proposed that if particles are loaded too close together, mutual influence of diffusion and other parameters can render catalytic particles inactive.

To clarify these issues and develop a relationship between particle size and catalytic performance, a novel approach has been used to produce electrodes of controlled sizes. Using a technique known as template synthesis, flat gold electrodes ranging from 10 nm to 800 nm in diameter have been produced.

Using electrochemical impedance spectroscopy and chronoamperometry, these different sized electrodes have been tested with respect to the hydrogen evolution reaction. Through comparison of relative current densities, a relationship has been established for the effect of particle

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size on catalytic performance. Currently, more data is needed for particle sizes less than 10 nm in diameter to establish a complete trend.

2. Experimental

Gold nanowires of 10, 15, 30, 50, 100, 400 and 800 nm in diameter were synthesized through a combination of electroless deposition and template synthesis as described in a previous article [1]. This deposition utilized track-etched polycarbonate membranes that contained nanopores of the given sizes. To insure consistent grain size and microstructure between the different sized nanowires, each sample was subjected to the same bath chemistry, deposition temperature and bath pH.

After deposition was completed on a membrane, gold was removed from one surface of the membrane using a lab wipe. The membrane was then placed into a furnace at 230 °C for 5 min to seal the polycarbonate membrane to the gold nanowire surface. This procedure was done to insure that during electrochemical testing, electrolyte would not be able to wet the interface between the membrane and nanowires.

To form electrodes, the side of the membrane still coated in gold was carbon painted to a flat copper plate. This copper plate was spot welded to a copper wire and the entire assembly was coated in Amercoat 90HS® epoxy to leave just the ends of the nanowires exposed. A depiction of the overall electrode assembly can be seen in Fig. 1.

These electrode assemblies were then tested using electrochemical impedance spectroscopy so that a relative catalytically active surface area could be determined for each electrode. This testing was carried out in a 10 mMol NaCl solution at −0.4 V over the frequency range of 60 000 Hz–0.6 Hz. Through fitting the impedance data to an electrochemical model, the double layer capacitance for each electrode was determined based on the equation,

$$C_{\mathrm{dl}} = \frac{1}{2\pi\omega R_{\mathrm{ct}}} \tag{1}$$

where C_{dl} represents the double layer capacitance in farads (F), ω represents the frequency at maximum height in hertz (Hz) and R_{ct} represents the charge transfer resistance in ohms (Ω). Through comparing this double layer capacitance for each electrode, the relative surface area was determined.

After the surface area for each electrode was determined, chronoamperometry was used to test the current density of each electrode with respect to the hydrogen evolution reaction. The chronoamperometry was performed at −0.8 V until the current reached steady state. The data was then compared.

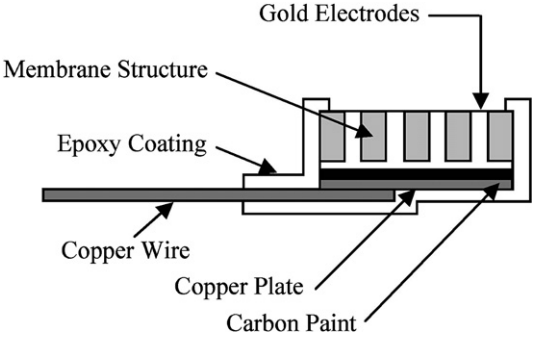

Fig. 1. Side-view of overall electrode assembly outlining the different components involved.

3. Results and discussion

Template synthesis was chosen to develop a relationship between electrode size and catalytic activity. Due to the nature of the templates used and the uniformity of pore sizes within the templates, electrode assemblies could be easily and reproducibly made over a wide spectrum of sizes. The inherent spacing of pores on polycarbonate track-etched membranes exceeds the size range at which territory theory (diffusion) exhibits a dominant role.

3.1. Nanowire characterization

Scanning transmission electron microscopy (STEM) and ultra-microtoming were used to verify that the electroless deposition procedure produced solid nanowires that were continuous throughout the nanopores of the membrane. An SEM image of the top surface of a membrane showing electrode size and spacing can be seen in Fig. 2.

3.2. Catalytically active surface area measurements

Electrochemical impedance spectroscopy (EIS) was used to determine the catalytically active surface area for each sized electrode. A 10 mmol NaCl solution at 25 °C was chosen for running the EIS data due to its benign nature with respect to both gold and polycarbonate. Using results from cyclic sweeps of a flat bulk gold electrode as a stan-

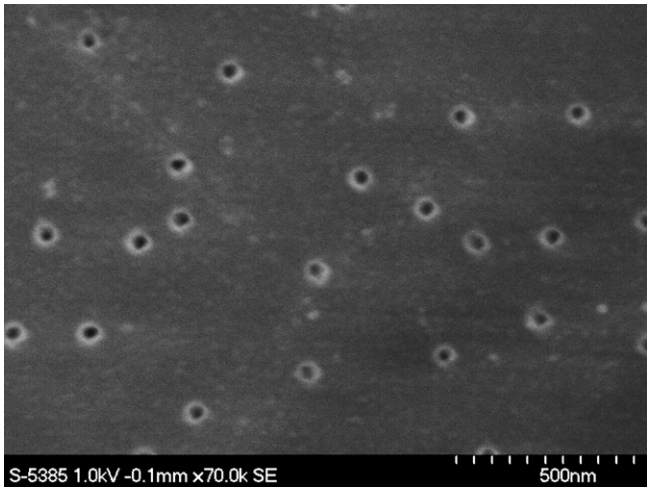

Fig. 2. SEM image showing the spacial distribution and uniformity in size of the nanopores within the track-etched polycarbonate membranes.