Template Synthesis of Ni nanowire array electrodes for Urea Electrochemical Decomposition

Wei Yan, Dan Wang, Gerardine G. Botte*
Center for Electrochemical Engineering Research,
Chemical and Biomolecular Engineering Department,
Ohio University, Athens, OH 45701

Human/animal urine and industrial synthesis processes of urea generate a large amount of urea-rich wastewater every day. Natural decomposition of urea results in nitrate contamination of water, air emissions, and therefore causes people severe health problems [1-4]. Urea electrolysis as an effective wastewater treatment technology has become a topic of attention [1, 3, 5-8]. In the urea electrolysis process, urea is oxidized directly into nitrogen, and carbon dioxide, while producing hydrogen as a byproduct [1]. In addition, the hydrogen generated by urea electrolysis is theoretically 70% cheaper than one from water electrolysis [1].

However, low-efficient electrode materials for urea oxidation directly inhibit the commercialization of urea electrolysis. Although nickel foil as a catalyst has greatly reduced the cost and shown the better catalytic activity compared to Platinum group metals, there is still room to improve the reaction rate of urea electrooxidation. An ideal electrode of less cost, higher electrochemical activity and longer life-time for urea electrooxidation is still imperative. Electrochemical properties of electrode highly depend on the surface area, morphology, and grain size. Nanostructure materials have been widely used as electrode materials due to their high conductivity, large surface area, corrosion resistance, and high stability. Porous anodic aluminum oxide membrane (P-AAO) is regarded as an excellent template to synthesize nanoscale materials. The AAO template has excellent physical properties, such as regular and highly oriented porous structure, high thermal stability and hydrophilic surface. Within this context, this work aims to synthesize highly ordered and high surface-area nickel nanowires by using porous anodic alumina oxide (AAO) template and determine the effects of the electrodes on the electrooxidation of urea.

In this work, AAO membrane is fabricated by a two-step electrochemical oxidation of aluminum [9, 10] and nickel nanowires are formed by electrodeposition in AAO template in a nickel ionic liquid. The advantages of the method are that the Ni nanowires can be directly attached to the substrate without any bonding layer and their thickness, mass, length, and component can be well-controlled by adjusting the electrodeposition time, temperature, and bath composition.

Electrochemical measurements, such as cyclic voltammetry, chronoamperometry and chronopotentiometry are used to evaluate the electrodes electrochemical properties toward urea electrooxidation.

Figure 1 shows Scanning Electron Microscope (SEM) images of the AAO template (top-view), anodized in 0.3 M oxalic acid solution under an anodization voltage of 40 V. As can be seen from the figure, the shape, size and distribution of pores are uniform and the AAO template is highly ordered. The enlarged SEM image (inset) shows the hexagonally arranged pores located in the center of each cell with a pore diameter of ca. 80 nm.

The Atomic Force Microscope (AFM) image (see Figure 2) further indicates that the diameters and inter-pore distances are ca. 80 and 130 nm, respectively, which is in agreement with the SEM results.

Additional results, including the electrochemical tests will be presented at the meeting.

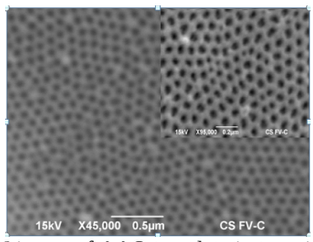

Figure 1. SEM image of AAO template in top-view, inset is the enlarged SEM image.

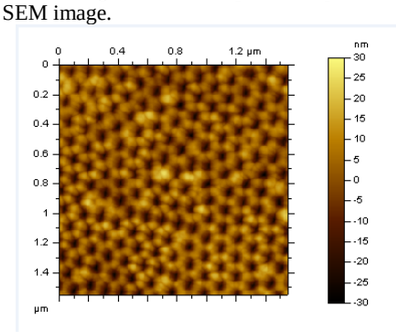

Figure 2 AFM image of the AAO template

References:

1. Boggs, B.K., R.L. King, and G.G. Botte, *Urea electrolysis: Direct hydrogen production from urine.* Chem. Commun. , 2009(32): p. 4859-4861.
2. Simka, W., J. Piotrowski, and G. Nawrat, *Influence of anode material on electrochemical decomposition of urea.* Electrochim. Acta, 2007. **52**(18): p. 5696-5703.
3. King, R.L. and G.G. Botte, *Investigation of multi-metal catalysts for stable hydrogen production via urea electrolysis.* J. Power Sources, 2011. **196**(22): p. 9579-9584.
4. Rahimpour, M.R., H.R. Mottaghi, and M.M. Barmaki, *Hydrogen production from urea wastewater using a combination of urea thermal hydrolyser-desorber loop and a hydrogen-permselective membrane reactor.* Fuel Process. Technol., 2010. **91**(6): p. 600-612.
5. Wang, D., et al., *Enhanced electrocatalytic oxidation of urea based on nickel hydroxide nanoribbons.* J. Power Sources, 2012. **217**: p. 498-502.
6. Yan, W., D. Wang, and G.G. Botte, *Nickel and cobalt bimetallic hydroxide catalysts for urea electro-oxidation.* Electrochim. Acta, 2012. **61**: p. 25-30.
7. Yan, W., D. Wang, and G.G. Botte, *Electrochemical decomposition of urea with Ni-based catalysts.* Appl. Catal., B, 2012. **127**: p. 221-226.
8. Wang, D., W. Yan, and G.G. Botte, *Exfoliated nickel hydroxide nanosheets for urea electrolysis.* Electrochem. Commun., 2011. **13**(10): p. 1135-1138.
9. Masuda, H. and K. Fukuda, *Ordered metal nanohole arrays made by a two-step replication of honeycomb structures of anodic alumina.* Science (Washington, D. C.), 1995. **268**(5216): p. 1466-68.
10. Hou, P.-X., et al., *Template synthesis of ultra-thin and short carbon nanotubes with two open ends.* J. Mater. Chem. **22**(30): p. 15221-15226.