

## Electrochemical Alloying-Dealloying in Ionic Liquids for Fabricating Nanoporous Microelectrodes

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Nanoporous microelectrodes with high surface area and open pore network are of current research topics due to their potential applications in electrocatalysis, neuroscience, electrochemical analysis, sensors, micro-to-nano fabrications, mapping and microscopy [1]. Therefore their fabrication has received much attention. Template approaches have been successfully used for the preparation of a range of nanostructured precious metal or alloy microelectrodes. The limitation of the template approaches is associated with the need of high-quality templates and subsequent template removal. Several groups prepared array microelectrodes by dispersing metallic nanoparticles on a conductive substrate. Well dispersion of individual nanoparticles is however challenging. Other reported techniques include physical or chemical deposition of nanoparticles on inert substrates, lithography, nano-imprint, etc.. These generally require complicated processing, are time-consuming and sometimes suffer from poor reproducibility. It is therefore interesting to develop convenient approaches to prepare nanoporous microelectrodes.

Dealloying has studied as a promising technique for the preparation of free-standing nanoporous metallic films from alloy precursors [2]. The obvious advantage of the dealloying over template approaches is no need of a high-quality template and subsequent template removal. However, the demand of alloy precursors imposes different challenges. This can be avoided by using one-pot electrochemical alloying/dealloying technique. During electrochemical alloying, highly reactive metal component such as Zn is introduced via electrodeposition to interact with the substrate to form alloy phase. During subsequent electrochemical dealloying, the reactive component is selectively removed from the alloy layer leading to the formation of initial nanoporous layer. The nanoporous layer can be developed by repeating the electrochemical alloying-dealloying processes. The most obvious advantage of this approach over others is that no net chemical is consumed. It offers a green chemistry method. Large nanoporous metallic electrodes with high surface area prepared in this manner have been used in several electroanalytical and electrocatalytic studies. Microelectrodes are more preferable for these studies because of their advantages such as fast responses, high signal-to-noise ratio, and ability to be miniaturized. We have studied the electrochemical alloying/dealloying method to fabricate nanoporous Au microelectrodes in an electrolyte bath of  $\text{ZnCl}_2$  in benzyl alcohol [3]. Because elevated temperature is needed to drive the alloying/dealloying processes, a greener electrolyte medium with vapor pressure much lower than that of benzyl alcohol would be ideal. Ionic liquids are a novel class of electrolyte themselves and electrolyte media with very low vapor pressure. They have been used for a wide range of electrochemical studies. Moreover, they have the ability of dissolving several kinds of metal salts. It is therefore expected that operating electrochemical

alloying/dealloying in ionic liquids at elevated temperature will enable the preparation of a range of nanoporous metallic microelectrodes.

We have successfully fabricated a range of nanoporous microelectrodes of both noble and base metals by applying modulated potential to their corresponding disk microelectrodes in an ionic liquid electrolyte bath comprising of  $\text{ZnCl}_2$  and 1-ethyl-3-methylimidazolium chloride. The resulted microelectrodes have high surface area and retain diffusional properties typical of a regular microelectrode. Figure 1 show SEM images of nanoporous microelectrodes of Au (A) and Pd (B). Both of them exhibit regular nanopores and ligament spacings. We have studied the applications of nanoporous microelectrodes to electrocatalytic and electroanalytical studies. Figure 2 shows that voltammetric limiting currents and steady-state chronoamperometric currents on a nanoporous gold microelectrode are obviously higher than those on a Au-disk microelectrode with the same geometric diameter for electrochemical nitrite reduction under similar conditions.

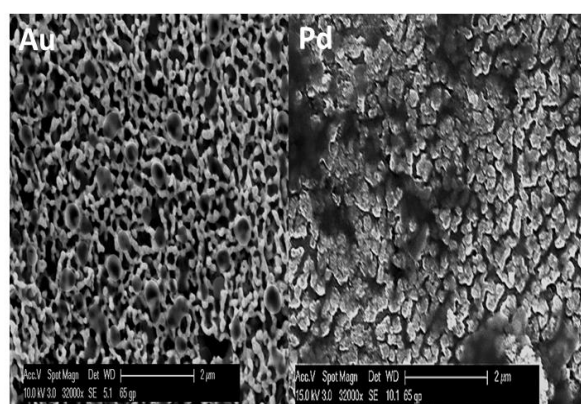


Figure 1 SEM images for nanoporous Au and Pd.

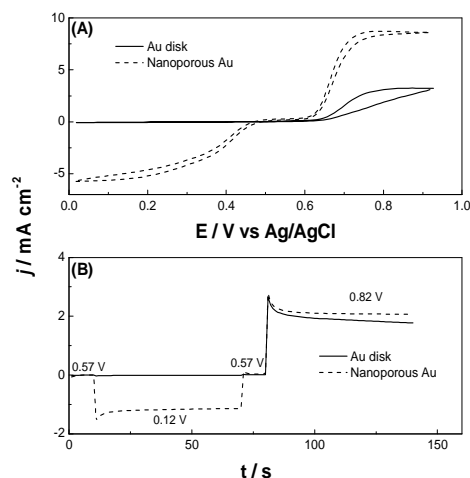


Figure 2 Steady-state voltammograms measured at  $5 \text{ mV s}^{-1}$  (A) and chronoamperograms (B) for Au-disk (solid) and nanoporous Au (dash) microelectrodes in  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  containing  $0.02 \text{ mol dm}^{-3} \text{ KNO}_2$  solution.

### References

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2. J. Erlebacher, M. Aziz, A. Karma, N. Dimitrov, K. Sieradzki, Nature, **410**, 450 (2001).
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