

Electrochemical Fuel Oxidation with a Novel Iron-Nickel Nanoparticle Catalyst

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Introduction

Electrochemical oxidation of small molecule fuels holds tremendous promise as the development of polymer electrolyte fuel cells continues, and hydrogen-powered proton exchange membrane fuel cell vehicles will be commercially available in the coming years. The advancement of catalyst design to include nanoparticle morphology and core-shell multi-metal structure has allowed the tuning of catalyst performance. The explosion of research on nanoparticle-based catalysis has demonstrated new synthesis strategies and has allowed the field to gain a better understanding of the connection between nanoparticle design and catalyst performance. However, key challenges remain, including nanoparticle durability and the reduction and elimination of precious metals. Here, we focus on the latter challenge with the development of a completely non-precious metal nanoparticle catalyst that is able to successfully catalyze the electrooxidation of small molecule fuels, such as methanol and ethanol, in alkaline solution.

Methods

Core-shell iron-nickel nanoparticles were synthesized using a solution-based synthesis technique. Briefly, the synthesis was performed in two sequential steps, where the iron core nanoparticles were first synthesized through chemical reduction with sodium borohydride. Once iron core nanoparticles were formed, the nickel shell was added in a second step by electroless deposition. Nanoparticles were separated from the synthesis solution through centrifugation and resuspended in ethanol for storage and analysis. Nanoparticles were characterized with electron microscopy, powder x-ray diffraction, and x-ray photoelectron spectroscopy, and performance was evaluated with cyclic voltammetry. Core-shell iron-nickel nanoparticles were compared with iron-only and nickel-only nanoparticles synthesized with the same general solution-based synthesis method.

Results

Iron-nickel core-shell nanoparticles were successfully synthesized through solution chemistry. The nanoparticles were approximately 150 nm in diameter, with a relatively large particle size distribution (Figure 1). The observed nanoparticle population had a heterogeneous morphology, where a portion of the nanoparticles had a visible core-shell structure (Figure 1b), while a portion of the nanoparticles did not show a core-shell structure in bright-field imaging (Figure 1a).

Dark-field imaging (Figure 1c), diffraction analysis (Figure 1d), and powder x-ray diffraction (not shown) analysis indicate that the nanoparticles are polycrystalline, with a crystal grain size of approximately 2 nm.

Therefore, even though the nanoparticles are quite large in comparison to other relevant nanoparticle catalysts, the nanocrystallinity and polycrystalline nature, in addition to the core-shell structure, may impart unique or enhanced catalytic behavior.

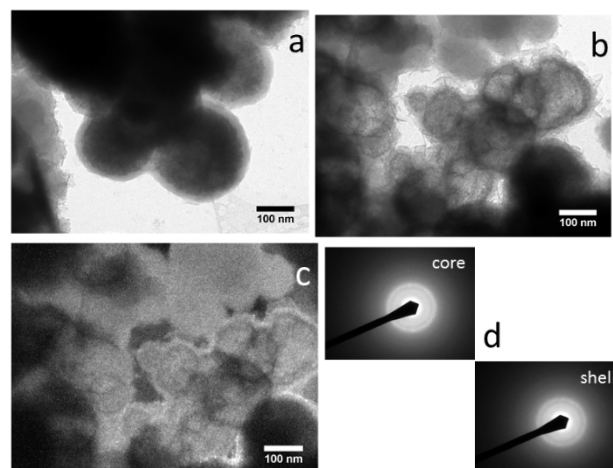


Figure 1. TEM images of iron-nickel core-shell internal morphologies including (a) nanoparticles with high contrast and a shell, (b) nanoparticles with lower contrast and no shell, and (b) nanoparticles with a low contrast core, high contrast shell, and a second, low-contrast shell. Dark-field imaging (c) of iron-nickel nanoparticles and (d) absence of diffraction patterns suggest nano-crystallinity.

Cyclic voltammetry experiments performed in alkaline solution with one of several small molecule fuels (e.g., ethanol or methanol) resulted in significant current densities in comparison with nickel-only nanoparticles. Current densities on the order of 100 mA/cm² and 50 mA/cm² were obtained, respectively, for methanol and ethanol when the iron-nickel core-shell nanoparticles were used as the catalyst. Nickel-only nanoparticles resulted in current densities of approximately 1.2 mA/cm² and 0.2 mA/cm², respectively, for methanol and ethanol. As expected, iron-only nanoparticles were not stable during electrooxidation and oxidized quickly once electrical potential was applied. The durability of the iron-nickel nanoparticles appears to be promising, as the same nanoparticle sample was successfully used in repeat experiments, and samples as old as four months remained stable and catalytically active.

Conclusions

We have successfully synthesized a novel nanoparticle catalyst composed completely of the non-precious metals iron and nickel. This core-shell nanoparticle catalyst can be used to electrochemically oxidize small molecule fuels such as methanol and ethanol. Given the catalytic performance obtained on this un-optimized heterogeneous material, this nanoparticle catalyst is quite promising as a precious-metal replacement in alkaline environments. Future work on nanoparticle optimization and development will likely result in further advances in material performance and lifetime.

Acknowledgements

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