

Abstract

The synthesis and characterization of Ni-MnO₂ and Cu-MnO₂ nanowires has been investigated to determine their potential to effectively catalyze the oxygen reduction reaction (ORR) in alkaline media. Efficient ORR is crucial in the fields of electrochemical energy storage and conversion; new catalysts could potentially be incorporated into the cathode of metal-air batteries, thereby increasing their efficiency. Nanowire α-MnO₂, in addition to being a low-cost alternative for existing catalysts based on noble metals, has been shown to be the most catalytically active size, morphology, and phase for manganese dioxide.¹ Doping α-MnO₂ with Cu or Ni improves its catalytic function, attaining steady state currents significantly higher than un-doped MnO₂. In an attempt to further increase conductivity, these nanowires were blended with newly developed graphene-like polycrystalline nanocarbon scaffolds.² We demonstrate that the combination of the nanocarbon graphene-like material with Ni-MnO₂ provides for a catalyst blend that achieves steady-state currents approaching that of the commercial benchmark catalyst, Pt/C. We have characterized these materials by powder x-ray diffraction (PXRD), surface area analysis (BET), and scanning electron microscopy (SEM). In addition, these catalyst materials have been evaluated on kinetic parameters pertaining to the oxygen reduction reaction, including n-value, onset potential, and terminal current density.

Introduction

Devices such as fuel cells and metal-air batteries, require electro-catalysts for the oxygen reduction reaction (ORR), as this reaction plays a critical role in the performance of the system. The oxygen reduction reaction can proceed through two possible mechanisms: (i) a direct four electron process, or (ii) a less efficient two-step, two electron pathway that involves the formation of hydrogen peroxide ions as an intermediate.¹

ORR electro-catalysts, found at the air cathode of electrochemical systems, must be durable and highly active. Noble metals such as platinum and its alloys have commonly been investigated for these applications; however, the high price of these materials prevents them from being widely utilized, thereby preventing the broad implementation of electric and hybrid vehicle technologies, and the optimization of mobile electronic devices.^{5,6} Therefore, many research efforts are focused on developing an economically viable alternative that will improve the electrochemical capabilities of batteries and fuel cells so new technologies can be realized. Recently, manganese oxides (MnO_x) have been demonstrated to be abundant, low cost, environmentally compatible, active materials for potential application in ORR catalysis.^{1,3-4}

We demonstrate a modified synthetic route that yields α-MnO₂ nanowires that have been doped with Ni and Cu, thereby enhancing the catalytic activity previously observed for un-doped α-MnO₂.

Goals

- Demonstrate synthesis of Ni and Cu doped α-MnO₂ nanowires.
- Characterize the synthesized materials.
- Evaluate the electrochemical properties of the newly synthesized materials for applications in electrocatalysis.

References

1. Cheng, F.; Su, Y.; Liang, J.; Tao, Z.; Chen, J. *Chem. Mater.* **2009**, *22*, 898-9-5.
2. Jin, Z.; Sun, Z.; Simpson, L.J.; O'Neill, K.; Panilla, P.; Li, Y.; Stadie, N.; Ahn, C.; Kittrell, C.; Tour, J. *J. Am. Chem. Soc.* **2010**, *132*, 15246-15251.
3. Roche, I.; Chalnet, E.; Châtenet, M.; Vondrák, J. *J. Phys. Chem. C* **2009**, *113*, 1434-1443.
4. Roche, I.; Chalnet, E.; Châtenet, M.; Vondrák, J. *J. Appl. Electrochem.* **2008**, *38*, 1195-1201.
5. Garsany, Y.; Batrinia, O.; Swider-Lyons, K.E.; Kocha, S. *Anal. Chem.* **2010**, *82*, 6321-6328.
6. Kumar, A.; Cluzet, F.; Morozovska, A.; Katin, S.; Jesse, S. *Nat. Chem.* **2011**, *3*, 707-713.
7. Pine Research Instrumentation. "Hydrodynamic Voltammetry Theory." http://voltammetry.net/pine/rotating_electrode/theory

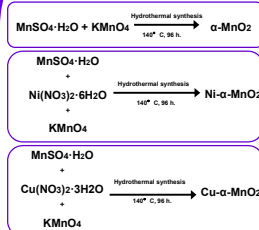
Acknowledgments

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

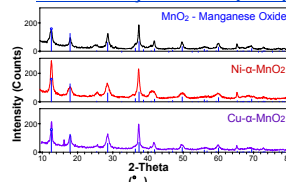
The authors would like to acknowledge Wei Lu and Professor James Tour of Rice University for providing us with novel nanocarbon materials.



Synthetic Route and Characterization Methods



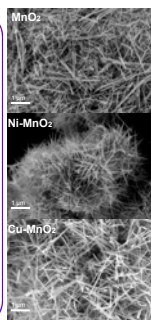
Powder X-Ray Diffraction (PXRD)



Sample	Reactant Ratio	BET Surface Area (m ² /g)
MnO ₂	NA	73.5686
NiMnO ₂	Mn:Ni = 1:1	54.1266
CuMnO ₂	Mn:Cu = 1:1	43.6917

The synthesis of α-MnO₂, doped Ni-α-MnO₂, and doped Cu-α-MnO₂ was achieved through a modified literature procedure.¹ In our hands, much longer reaction times (96 h) than initially reported (12 h)¹ were required in order to obtain nanowire structures as the predominant morphology.

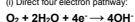
The presence of Ni and Cu was confirmed by Energy Dispersive Spectroscopy (EDS) and X-Ray Photoelectron Spectroscopy (XPS); data is not shown.



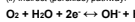
Catalysis of the Oxygen Reduction Reaction

Oxygen Reduction Reaction (ORR) Scheme¹

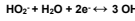
(i) Direct four electron pathway:



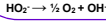
(ii) Indirect (peroxide) pathway:



followed by either (a) the further reduction of peroxide:



or (b) the catalytic peroxide decomposition:



Solutions of the activated catalyst in isopropanol with 5% Nafion were prepared and sonicated to achieve dispersion.¹ A known volume of the material was deposited on a 5 mm diameter glassy carbon rotating disk electrode and allowed to dry, forming a thin film.

Catalyst testing was performed in 0.1M KOH solution that had been purged with oxygen. Current levels were monitored at various electrode rotation rates. Rotating Disk Electrode (RDE) studies were performed using a VoltaLab potentiostat for preliminary screenings. Rotating Ring Disk Electrode (RRDE) studies were performed using a Gamry bipotentiostat. Data was processed and plotted using Kaleidagraph software.

The kinetic parameters that were evaluated to determine catalytic activity included the following:

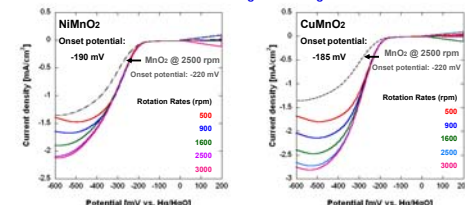
n-value: The number of electrons involved in the reduction (optimum value = 4e⁻).

terminal current density: The current density reached at -600 mV.

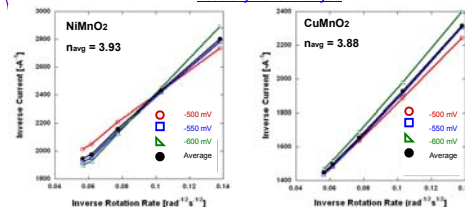
onset potential: The potential at which the current begins to fall below zero, indicating reduction.

peroxide generation/oxidation: The current densities in the positive direction, indicating oxidation of peroxide at the ring electrode.

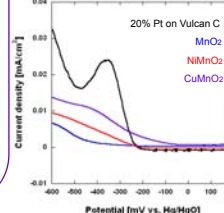
Linear Scanning Voltammograms



Koutecky-Levich Analysis



Peroxide Oxidation Currents



Monitoring Peroxide Oxidation

In Rotating Ring Disk Electrode (RRDE) studies, a ring electrode surrounds the disk electrode. The potential of the disk is scanned while the potential of the ring is held constant. The axial flow pattern brings O₂ molecules to the disk electrode, where they are reduced. The subsequent outward radial flow carries a fraction of reduction intermediates (peroxide) away from the disk electrode and past the surface of the ring electrode.⁷ This pattern allows the products generated upstream at the disk electrode to be detected as they are swept past the ring electrode downstream.⁷

Nanowires and Novel Nanocarbons

Linear Scanning Voltammograms

Activity of Graphene-Like Nanocarbon

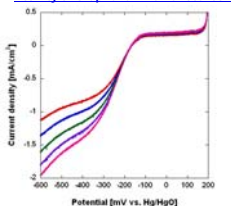
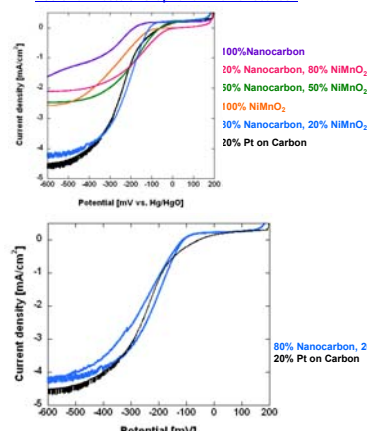


Figure A demonstrates the catalytic activity of the graphene-like nanocarbon. While the steady-state current plateaus do not demonstrate ideal behavior, the attained current densities are near those of undoped MnO₂. $n_{\text{avg}} = 1.8$

Figure B demonstrates the additive effect of the nanocarbon when blended with NiMnO₂. The optimum blend was determined to be 80 wt. % Nanocarbon, 20 wt. % NiMnO₂. The attained current density is near that of 20% Pt on Vulcan Carbon, which is the commercial benchmark material.

Figure C demonstrates the reproducibility of the data when the blend of 80% Nanocarbon, 20% NiMnO₂ is tested for its catalytic activity. Further investigations of reaction kinetics, as well as attempts to optimize blending, are underway.

Additive Effects of Graphene-Like Nanocarbon



Conclusions

We have demonstrated the synthesis of nanowire Ni-α-MnO₂ and Cu-α-MnO₂ as improved, highly-active, non-precious metal catalysts for the oxygen reduction reaction.

Preliminary catalysis results are encouraging; when blended with novel nanocarbon scaffolds, these materials can attain terminal current densities near those of 20% Pt on Vulcan Carbon, the benchmark catalyst. Not only are these materials catalytically active, but they hold promise as an economically viable alternative to Pt-based catalysts.

Future Work

- Investigate the doping mechanism and determine where the dopant cations are located in the α-MnO₂ lattice.
- Gain a more comprehensive understanding of the role of the α-MnO₂ lattice in the oxygen reduction mechanism.
- Continue to optimize blending of nanocarbon with NiMnO₂.
- Perform RRDE studies for nanocarbon/NiMnO₂ blends and evaluate peroxide generation and subsequent oxidation.
- Spray-deposit catalyst blends onto gas diffusion electrodes and fabricate air cathodes for implementation into experimental coin cells.
- Develop procedure that allows doped-MnO₂ nanowires to be synthesized on a nanocarbon scaffold support.