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SAND2011-6937C

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 reduction 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.

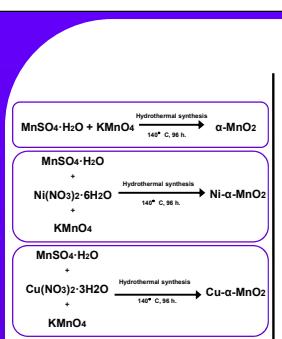
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Acknowledgments

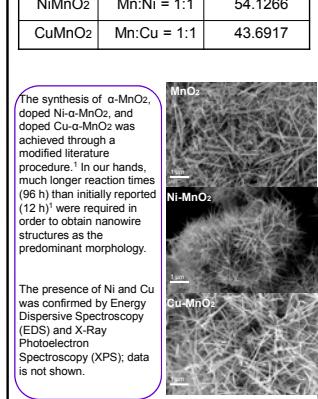
Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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

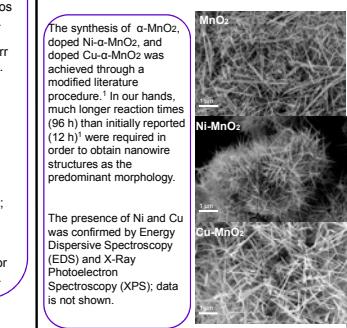


Utilizing a modified hydrothermal synthesis procedure,¹ doped α-MnO₂ nanowires were prepared by adding Ni(NO₃)₂ or Cu(NO₃)₂ salts into the reaction media at various molar ratios (Mn:dopant cation = 1:1, 1:1.5, 1:2). Reactants were dissolved in deionized water and heated in a Parr reaction vessel at 140° C for ~96 h. Upon completion, the reaction was allowed to cool, and the obtained solids were washed with deionized water and ethanol via repeated centrifugation.

All synthesized materials were evaluated for their catalytic function; a molar ratio of 1:1 (Mn:dopant cation) proved to be ideal, as the samples prepared at this ratio were the most catalytically active. Data for this experimental ratio is presented.

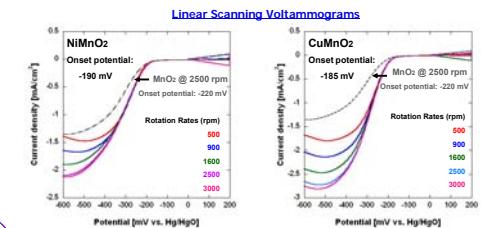


Sample	Reactant Ratio	BET Surface Area (m ² /g)
MnO ₂	NA	73.5686
NiMnO ₂	Mn:Ni = 1:1	54.1266
CuMnO ₂	Mn:Cu = 1:1	43.6917

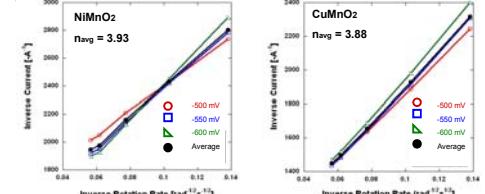


Synthetic Route and Characterization Methods

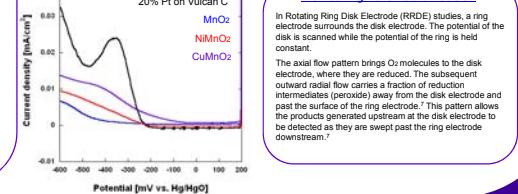
Catalysis of the Oxygen Reduction Reaction



Koutecky-Levich Analysis

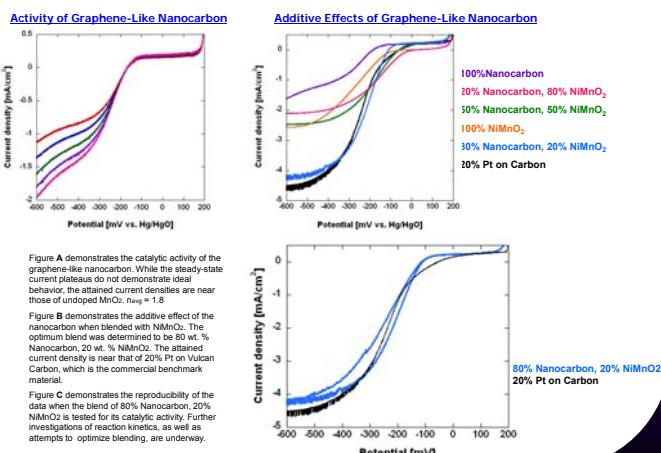


Monitoring Peroxide Oxidation



Nanowires and Novel Nanocarbons

Linear Scanning Voltammograms



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.

Novel Nanocarbons

Pristine carbon scaffolds were prepared by the Tour Group at Rice University using a novel bottom-up solution phase synthesis.² Data obtained to date suggests that a blend of 80 wt. % nanocarbon and 20 wt. % NiMnO₂ is capable of reaching current densities nearing those of the benchmark catalyst, 20% Pt on Vulcan Carbon.

Figure A demonstrates the catalytic activity of the graphene-like nanocarbon while the steady-state current density does not demonstrate ideal behavior, the attained current densities are near those of undoped MnO₂, $n_{av} = 1.8$.

Figure B demonstrates the additive effect of the nanocarbon when blended with NiMnO₂. The optimum weight was determined to be 80 wt. % Nanocarbon, 20 wt. % NiMnO₂, and 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.