

Electrodes for Nonaqueous Oxygen Reduction Based upon Conductive Polymer-Silver Composites

To cite this article: Amy C. Marschilok et al 2011 J. Electrochem. Soc. 158 A223

View the article online for updates and enhancements.

You may also like

- Progress toward Metal-Air Batteries: Mechanistic Investigation of the Effect of Water on the Oxygen Reduction Reaction at Carbon-Conductive Polymer-Silver Composite Air Electrodes Shu Han Lee, Rachel A. DeMayo, Kenneth J. Takeuchi et al.
- Preparation of micron-sized polystyrene/silver core-shell microspheres by ultrasonic assisted electroless plating Junhua Cheng, Guoyou Gan, Junpeng Li et al.
- Enhancement of the critical current density in Cu/Ag composite sheathed (Ba, K)Fe_AS2 tapes by pre-annealing process Liu Li, Xianping Zhang, Chao Yao et al.



This content was downloaded from IP address 18.119.131.72 on 01/05/2024 at 17:47



Electrodes for Nonaqueous Oxygen Reduction Based upon **Conductive Polymer-Silver Composites**

Amy C. Marschilok,^{a,b,z,*} Shali Zhu,^c Christopher C. Milleville,^c Shu Han Lee,^a Esther S. Takeuchi,^{a,b,c,d,*} and Kenneth J. Takeuchi^c

^aDepartment of Chemical and Biological Engineering, ^bDepartment of Electrical Engineering, ^cDepartment of Chemistry, and ^dDepartment of Biomedical Engineering, University at Buffalo (SUNY), Buffalo, New York 14260. USA

Progress toward the development of current collector-conductive polymer-silver (cc-cp-Ag) composite cathodes for nonaqueous metal air batteries is presented here, where the contribution of each component toward the overall oxygen reduction activity of the multifunctional cc-cp-Ag composite is studied. First, the effect of the chemical identity of the current collector (carbon versus gold) on the electrochemical reduction of oxygen is examined, accompanied by a conductive polymer deposition study. These two studies together demonstrate that a conductive polymer deposit can eliminate any competitive electrochemistry due to the current collector. Second, the role of the conductive polymer in improving physical strength of the composite electrode is evaluated using an electrode durability test. Third, a systematic study of the Ag loading effect is undertaken to determine the minimum silver loading required for significant enhancement in oxygen reduction activity. © 2010 The Electrochemical Society. [DOI: 10.1149/1.3527992] All rights reserved.

Manuscript submitted August 18, 2010; revised manuscript received October 22, 2010. Published December 29, 2010.

Metal air batteries are unusual because the only electroactive material contained within the metal air batteries is the anode, because the electroactive cathode material (O_2) is provided by ambient air. Even after accounting for the mass of the physical structure at the cathode and the mass gained at the cathode during the oxygen reduction process,^{1,2} lithium air batteries compare favorably to the existing battery technologies, offering the opportunity for significant improvements in energy density over current lithium-ion chemistries.^{3,4}

Slow oxygen reduction kinetics at the air electrode has been a significant challenge to the development of practical metal air batteries. The slow kinetics result in high cathode polarization, causing substantial voltage drop on load.⁵ To address this issue, the search for new oxygen reduction catalysts has been an area of research interest, in conjunction with investigations of the mechanism of catalyst activity. The primary focus to date has been metal oxide catalysts,⁶⁻⁹ with some studies involving metallic gold, platinum, and bimetallic gold–platinum catalysts.¹⁰⁻¹³ Although silver metal shows high oxygen reduction activity in aqueous alkaline electrolytes,^{5,14-18} it has been largely unexplored for nonaqueous oxygen reduction.

Recently, we introduced a new composite electrode concept for metal air batteries and reported for the first time on the preparation, characterization, and electrochemical activity of a carbon current collector-conductive polymer-silver (cc-cp-Ag) composite electrode.¹⁹ Enhanced oxygen reduction activity for our composite electrode was demonstrated relative to uncoated glassy carbon or silver disk electrodes, at a low silver loading of $< 0.3 \text{ mg cm}^{-2}$

This paper describes further progress toward the development of novel current cc-cp-Ag composite electrodes for nonaqueous metal air batteries. The contribution of each individual component toward the activity of the composite electrode is assessed. The role of the chemical identity of the current collector (cc) substrate is investigated by examining the behavior of carbon versus gold (C versus Au) toward the electrochemical reduction of oxygen, in conjunction with a conductive polymer (cp) deposition study. The structural role of the cp in improving the physical strength of the composite electrode is assessed. A systematic study of the Ag loading effect is undertaken to determine the minimum silver loading required for a significant enhancement in the oxygen reduction activity of the cccp-Ag composite. Improvement of oxygen reduction activity at the

^z E-mail: acm@buffalo.edu

air electrode will increase the current capability and the power output of the metal air battery, facilitating future development of small, lightweight, and long-life power sources.

Experimental

CH Instruments (Texas, USA) potentiostats and electrodes were used for the deposition and oxygen reduction experiments. Platinum auxiliary electrodes were used for all experiments. Reference electrodes were purchased from CH Instruments. For aqueous measurements, a silver/silver-chloride reference was used, while for nonaqueous measurements a silver-silver nitrate reference electrode was used. Potentials are reported versus the reference electrodes used. Glassy carbon and gold disk working electrodes obtained from CH Instruments were used as substrates for the depositions.

All electrochemical experiments were conducted at room temperature. Silver deposition was conducted using linear sweep voltammetry in a method consistent with that described by Batina and co-workers.²⁰ Potential windows for silver deposition and typical deposition voltammograms were previously reported.¹⁹ Polypyrrole was deposited using cyclic voltammetry with a methodology similar to that described by Wallace, Ralph, and co-workers.^{21,2} ² Potential windows for polypyrrole deposition and typical deposition voltammograms were provided in a previous publication.¹⁹ For some glassy carbon cc-cp-Ag composite electrodes, optical images of the cc-cp-Ag composite electrodes were acquired, and then the conductive polymer-and silver (cp-Ag) coatings were physically removed from the glassy carbon (C) substrate and subjected to scanning electron microscopy. Surface areas of the silver deposits were estimated using IMAGE-J software, after measurements of >100 particles per image. Increases in surface area upon Ag deposition were estimated assuming the surface area prior to Ag deposition was equivalent to the planar geometric area.

Oxygen reduction was measured using an electrolyte of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in acetonitrile (CH₃CN), at a scan rate of 100 mV s⁻¹. Acetonitrile was selected as it is an aprotic protophobic solvent with the same solvent classification as conventional lithium battery electrolytes,²³ which has also been used in other published studies relevant to lithium metal air batteries.²⁴ The oxygen reduction analysis was based on peak coulomb flux, based on the planar geometric area of the substrate of each electrode. Nitrogen:oxygen gas ratios were controlled using Matheson Trigas (Pennsylvania, USA) flowmeters. Oxygen concentration was calculated using Henry's law assuming an 8.1 mM oxygen solubility at the standard pressure^{25,26} and adjusted using local atmospheric pressures obtained from the National Oceanic and Atmospheric Administration's National Data Buoy Center.²⁷ For the

^{*} Electrochemical Society Active Member.



Figure 1. Oxygen reduction activity of C electrode in nitrogen, air, and oxygen.

electrode durability test, coated electrodes were horizontally dragged a distance of 5.6 cm over a Buehler polishing microcloth, while exerting a 4 N downward force.

Results and Discussion

Substrate functionality assessment.--- C was selected as a substrate for our composite electrode because it is an inexpensive, lightweight, and high conductivity material. In order to assess the contribution of the current collector substrate toward the overall activity of the cc-cp-Ag composite, comparative electrodes were prepared and tested using a Au disk electrode as a current collector substrate in place of the C electrode, where the resulting composites were identified as Au-cp-Ag and C-cp-Ag, respectively. Tests were typically conducted in a nanoqueous electrolyte of tetrabutylammonium hexafluorophosphate in acetonitrile over five reduction-oxidation cycles each in pure nitrogen, air, and pure oxygen atmospheres. Each electrode type showed consistent behavior over all five cycles. Representative data from the first cycle for each electrode type are shown below (Figs. 1-4). Similar and consistent activity was observed in oxygen reduction tests conducted in the tetrabutylammonium tetrafluoroborate based electrolyte.

Carbon shows adequate oxygen reduction activity in the absence of metal or metal oxide based catalysts,²⁸⁻³⁰ demonstrating revers-



Figure 2. Oxygen reduction activity of Au electrode in nitrogen, air, and oxygen.



Figure 3. Oxygen reduction activity of C-cp and gold-conductive polymer (Au-cp) composite electrodes in nitrogen, air, and oxygen.

ible behavior in some electrolyte systems.³¹ We tested the C electrode under pure nitrogen, air, and pure oxygen atmospheres and observed good activity and quasireversible behavior (Fig. 1). Au has been established to be a highly active metal catalyst for oxygen reduction;¹² however, it shows poor reversibility for the reverse oxidation process.¹¹ Our test of a Au disk electrode (Fig. 2) showed significantly higher reduction activity than the C electrode, by a factor of $2.5 \times$ in air and $1.9 \times$ in pure oxygen. Although the Au electrode showed repeatable behavior with no loss in activity over multiple cycling, no oxidation peak was visible, consistent with previous literature.¹² Notably, the peak reduction potentials were significantly different for the two electrode types, -1.3 V for C and -1.5 V for Au.

The C and Au disk electrodes were each coated with a thin polypyrrole cp layer using a previously described method.¹⁹ The carbonconductive polymer (C-cp) and gold-conductive polymer (Au-cp) electrodes were subjected to the same oxygen reduction tests. Notably, both types of polymer coated electrodes showed quasireversible oxygen reduction behavior at the same potentials and similar magnitude, regardless of the substrate used (Fig. 3). Next, the C-cp and Au-cp polymer coated electrodes were each coated with Ag, at similar loadings of 0.5 and 0.4 mg cm⁻², respectively. The oxygen reduction activities of the C-cp-Ag and Au-cp-Ag composite elec-



Figure 4. Oxygen reduction activity of C-cp-Ag and gold-conductive polymer silver (Au-cp-Ag) composite electrodes in nitrogen, air, and oxygen.



Figure 5. (Color online) Optical images of C-cp-Ag and polymer-free carbon–silver (C–Ag) composite electrodes before and after electrode durability tests.

trodes were measured (Fig. 4). As with the silver-free polymer coated electrodes, both types of silver-polymer coated electrodes showed quasireversible oxygen reduction behavior at the same potentials and similar magnitude, regardless of the substrate used. This indicates that the oxygen reduction activity of the composite electrodes is dictated by the conductive polymer and not by the underlying substrate, opening the possibility for use for diverse types of current collector substrates for silver-polymer composite electrodes in the future. Also notably, the oxygen reduction activity of the gold disk (Au) electrode, at a low Ag loading of 0.5 mg cm⁻². Our composite electrode concept shows a new pathway for the development of low cost, high functioning electrodes for metal air batteries.

Polymer functionality assessment: Electrode durability test.— Polypyrrole was selected as a cp for the composite electrode to promote good physical and electrical contact between the current collector and silver deposit. An electrode durability test was designed to assess the structural role of the polymer in improving the physical strength of the composite electrode. Carbon–silver (C–Ag) composite electrodes were prepared with and without cp coatings, and both types of electrodes were subjected to an aggressive physical abuse test. Optical images were acquired before and after the test



Figure 6. Oxygen reduction activity of C-cp-Ag composite electrode before and after electrode durability test.



Figure 7. Ag loading of C-cp-Ag electrodes as a function of scan rate.

(Fig. 5). The C-Ag electrode showed virtually complete Ag loss, while the C-cp-Ag composite showed good Ag retention.

To quantify the activity retained, three C-cp-Ag composite electrodes were prepared, and the oxygen reduction activity of each was assessed before and after durability testing. A representative data set is shown (Fig. 6). The C-cp-Ag composite consistently retained >70% of its original activity. For the 12 measurements, the average activity retained was 72.5%, the median activity retained was 71.9%, and the standard deviation was 8.7%. In contrast, for the polymer-free electrode, typical activity retained was 50%. This demonstrates that the polymer layer plays an important role in improving the robustness of the composite electrode.

Catalyst functionality assessment: Silver loading test.— Silver was selected as a catalyst to promote the oxygen reduction reaction. Our previous study demonstrated enhanced oxygen reduction activity for an C-cp-Ag composite electrode relative to the uncoated glassy carbon or silver disk electrodes, with a low Ag loading of $< 0.3 \text{ mg cm}^{-2}$.¹⁹ In order to determine the minimum Ag loading required for significantly increased activity, a series of C-cp-Ag composite electrodes was prepared with differing Ag content. Ag was deposited using linear sweep voltammetry, in a consistent potential window. Masses of silver deposited were calculated from the total cumulative charge using Faraday's law, assuming one electron reduction per formula unit for Ag⁺ \rightarrow Ag⁰. Using a range of scan rates for the depositions provided a well controlled, highly tunable process (Fig. 7).

The oxygen reduction activity of the C-cp-Ag composite electrodes was measured in nonaqueous electrolyte. Comparative data was collected with uncoated C, an uncoated solid silver disk (Ag), and silver-free conductive polymer coated glassy carbon (C-cp) electrodes. Because oxygen partial pressure can significantly affect the performance of the air electrode,³² measurements were made under both air (Fig. 8) and pure oxygen (Fig. 9). The relative activities of the various electrodes were consistent in both gases. The measured activity in air was 20–40% of the measured activity in pure oxygen. The C-cp electrodes and uncoated C electrodes showed very similar activity, consistent with our previous results.¹⁹ The Ag disk electrodes showed 3× higher activity in air (Fig. 8) and 2× higher activity in oxygen (Fig. 9) relative to the C-cp and C electrodes. Notably, the activity of the C-cp-Ag composite electrodes with high silver loading was typically slightly higher than that of a solid Ag disk electrode.

For the C-cp-Ag composite electrodes with lower silver loading (< 0.08 mg cm⁻²), a strong dependence was observed where oxygen reduction activity increased linearly with Ag loading. With higher silver loading (> 0.08 mg cm⁻²), the oxygen reduction activity remained relatively constant, showing no consistent increase with increased Ag loading. Using the density of silver metal



Figure 8. Oxygen reduction activity of C-cp-Ag composite electrodes in air as a function of Ag loading, with representative Ag, C-cp, and C electrode data shown as reference.

 (10.5 g cm^{-3}) and assuming an even Ag distribution, these data suggest that 0.08 µm is the minimum Ag thickness required to maximize oxygen reduction activity.

Scanning electron micrographs were acquired and analyzed for several cp-Ag coatings, including electrodes with Ag loadings ranging from 0.07 to 0.4 mg cm⁻². The corresponding increases in surface area upon Ag deposition were estimated to range from 70 to 300%, where surface area increased with increasing mass loading. Thus, the contribution of effective electrode surface area is likely a factor in the increased current observed for oxygen reduction for the electrodes with silver loading.

Summary

Progress toward the development of novel cc-cp-Ag composite electrodes for nonaqueous metal air batteries was presented herein. The contribution of each individual component toward the activity of the multifunctional composite was assessed. First, the role of the chemical identity of the cc substrate was investigated, demonstrating that a conductive polymer deposit can eliminate any competitive electrochemistry due to the current collector. Stepwise preparation and electrochemical characterization of C-cp-Ag and goldconductive polymer-silver (Au-cp-Ag) electrodes demonstrated that under the appropriate conditions, the oxygen reduction activity could be determined predominantly by the cp layer or conductive polymer-silver (cc-Ag) layers, independent of the Au or C cc. Sec-



Figure 9. Oxygen reduction activity of C-cp-Ag composite electrodes in pure oxygen as a function of Ag loading, with representative Ag, C-cp, and C electrode data shown as reference.

ond, the structural role of the cp in improving the physical strength of the composite electrode was assessed, where a conductive polymer containing cc-cp-Ag composite was found to provide favorable robustness compared to that of a polymer-free cc-Ag electrode. Finally, a systematic study of the Ag loading effect was undertaken, where a silver loading of 0.08 mg $\rm cm^{-2}$ (equivalent thickness of 0.08 µm) was determined to be the minimum silver loading required for a significant enhancement in the oxygen reduction activity of the cc-cp-Ag composite. Improvement of oxygen reduction activity at the air electrode will increase current capability and power output of the metal air battery, facilitating future development of small, lightweight, and long-life power sources.

Acknowledgment

This project was supported by the Air Force Office of Scientific Research under award no. FA9550-09-1-0334. The authors thank Chia-Ying Lee for assistance with scanning electron microscopy.

University at Buffalo, State University of New York assisted in meeting the publication costs of this article.

References

- S. S. Sandhu, J. P. Fellner, and G. W. Brutchen, J. Power Sources, 164, 365 (2007).
- S. S. Sandhu, G. W. Brutchen, and J. P. Fellner, *J. Power Sources*, **170**, 196 (2007). K. M. Abraham and Z. Jiang, *J. Electrochem. Soc.*, **143**, 1 (1996). 2.
- 3.
- M. Armand and J. M. Tarascon, Nature, 451, 652 (2008)
- K. Kinoshita, Electrochemical Oxygen Technology, John Wiley & Sons, New York 5. (1992)
- 6. J. K. Ngala, S. Alia, A. Dobley, V. M. B. Crisostomo, and S. L. Suib, Chem. Mater. 19, 229 (2007).
- J. Read, J. Electrochem. Soc., 149, A1 190 (2002).
- T. Ogasawara, A. Debart, M. Holzapfel, P. Novak, and P. G. Bruce, J. Am. Chem. 8. Soc., 128, 1390 (2006).
- 9 A. Debart, A. J. Paterson, J. Bao, and P. G. Bruce, Angew. Chem., Int. Ed., 47, 4521 (2008)
- 10. M. Moshkovich, Y. Gofer, and D. Aurbach, J. Electrochem. Soc., 148, E155 (2001).
- Y.-C. Lu, H. A. Gasteiger, M. Parent, C. V. Chiloyan, and Y. Shao-Horn, Electrochem. Solid-State Lett., 13, A69 (2010). 12. Y.-C. Lu, H. A. Gasteiger, E. Crumlin, J. R. McGuire, and Y. Shao-Horn, J. Elec-
- trochem. Soc., 157, A1016 (2010)
- Y.-C. Lu, Z. Xu, H. A. Gasteiger, S. Chen, K. Hamad-Schifferli, and Y. Shao-Horn, J. Am. Chem. Soc. 132, 12170 (2010).
- S. Gamburzev, K. Petrov, and A. J. Appleby, J. Appl. Electrochem., 32, 805 14. (2002).15.
- M. Chatenet, L. Genies-Bultel, M. Aurousseau, R. Durand, and F. Andolfatto, J. Appl. Electrochem., 32, 1131 (2002).
- L. Carlsson and L. Oejefors, J. Electrochem. Soc., 127, 525 (1980).
- C.-Y. Wu, P.-W. Wu, P. Lin, Y.-Y. Li, and Y.-M. Lin, J. Electrochem. Soc., 154, 17. B1059 (2007).
- 18 J. S. Spendelow and A. Wieckowski, Phys. Chem. Chem. Phys., 9, 2654 (2007) S. Lee, S. Zhu, C. C. Milleville, C.-Y. Lee, P. Chen, K. J. Takeuchi, E. S. Takeuchi, 19.
- and A. C. Marschilok, Electrochem. Solid-State Lett., 13, A162 (2010). 20. M. Palomar-Pardave, M. Miranda-Hernandez, I. Gonzalez, and N. Batina, Surf.
- Sci., 399, 80 (1998). J. Ding, W. E. Price, S. F. Ralph, and G. G. Wallace, Polym. Int., 53, 681 (2004). 21.
- R. Dimeska, P. S. Murray, S. F. Ralph, and G. G. Wallace, Polymer, 47, 4520 22. (2006)23
- G. E. Blomgren, in Nonaqueous Electrochemistry, D. Aurbach, Editor, Marcel Dekker, Inc., New York (1999).
- 24. C. O. Laoire, S. Mukerjee, K. M. Abraham, E. J. Plichta, and M. A. Hendrickson, J. Phys. Chem. C, 113, 20127 (2009). 25
- S. Horstmann, A. Grybat, and R. Kato, J. Chem. Thermodyn., 36, 1015 (2004). D. T. Sawyer, G. Chiericato, C. T. Angelis, E. J. Nanni, and T. Tsuchiya, Anal. 26. Chem 54 1720 (1982)
- 27. NOAA, National Oceanic and Atmospheric Administration's National Data Buoy Center, http://www.ndbc.noaa.gov, last accessed September 2010.
- 28 J. Xiao, D. Wang, W. Xu, D. Wang, R. E. Williford, J. Liu, and J.-G. Zhang, J. Electrochem. Soc., 157, A487 (2010)
- S. D. Beattie, D. M. Manolescu, and S. L. Blair, J. Electrochem. Soc., 156, A44 29. (2009)30.
- M. Hayashi, H. Minowa, M. Takahashi, and T. Shodai, Electrochemistry (Tokyo, Jpn.), 78, 325 (2010). 31. C. O. Laoire, S. Mukerjee, K. M. Abraham, E. J. Plichta, and M. A. Hendrickson,
- J. Phys. Chem. C, 114, 9178 (2010). 32. J. Read, K. Mutolo, M. Ervin, W. Behl, J. Wolfenstine, A. Driedger, and D. Foster,
- J. Electrochem. Soc., 150, A1351 (2003).