**Porous Ag/P/C Composite Electrodes: A new approach for metal air batteries**

This project has encompassed the design, preparation, characterization, and electrochemical study of novel composite electrodes for use in metal air batteries. Metal air batteries offer the potential for unprecedented high energy density relative to batteries in common use today. Improvement of cathode oxygen reduction activity will increase current capability and power output of metal air batteries, facilitating development of small, lightweight, long-life power sources for deployment in currently inaccessible locations.

**Subject Terms**: metal air battery, oxygen reduction reaction, multifunctional composite
Final Performance Report

1. Cover Sheet:

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2. Objectives:
   I. Design and demonstrate new composite electrode based on carbon-conductive polymer-silver (C-cp-Ag) composite.
   II. Evaluate composite oxygen reduction activity.
   III. Interrogate the oxygen reduction mechanism in nonaqueous electrolyte
   IV. Assess roles of composite components.
   V. Develop and investigate three dimensional (3D) carbon-conductive polymer-silver (C-cp-Ag) composite.

3. Status of effort:
This study encompassed design, preparation, and electrochemical evaluation of a novel composite cathode for metal air batteries prepared via stepwise electrochemical deposition processes. At the conclusion of this project, all objectives have been realized:
   I. Prepared a new composite electrode based on carbon-conductive polymer-silver (C-cp-Ag) composite.
   II. Composite oxygen reduction activity exceeds that of current state of the art.
   III. The oxygen reduction data is consistent with a first order mechanism.
   IV. The silver (Ag) catalyst significantly improves oxygen reduction activity, and the conductive polymer (cp) significantly improves the physical strength of the composite and mitigates the impact of the substrate on the oxygen reduction activity.
   V. Three dimensional (3D) carbon-conductive polymer-silver (C-cp-Ag) composites yield 4x the oxygen reduction activity of their planar counterpart.
4. Accomplishments/New Findings:

Background

Metal air batteries can provide significant energy density improvements over conventional batteries because the electroactive cathode material (O$_2$) is provided by ambient air. Since the electroactive cathode material (O$_2$) is provided by air, the metal air batteries house only electroactive anode, resulting in significantly smaller, lighter batteries relative to the current state of the art in energy storage. While aqueous metal air batteries have been successfully deployed in consumer and defense related applications, development of practical non-aqueous metal air batteries remains elusive. Investigation of non-aqueous metal air batteries has received increased attention recently as a research focus area.

Slow oxygen reduction kinetics at the air electrode has been a significant challenge to the development of practical metal-air batteries. The slow kinetics results in high cathode polarization, causing substantial voltage drop on load. To address this issue, the search for new oxygen reduction catalysts has been an area of research interest. The primary focus to date has been metal oxide catalysts.

This project encompassed the design, preparation, characterization, and electrochemical study of novel composite electrodes for use in metal air batteries. Accomplishments and new findings are discussed in detail below in the context of the four project objectives.

Objective I: Design and demonstrate new composite electrode based on carbon-conductive polymer-silver (C-cp-Ag) composite.

IA. Composite concept

A new carbon-conductive polymer-silver (C-cp-Ag) composite electrode was developed under this project. The utility of each component is described below.

substrate (C): Carbon is relevant to battery applications as a low cost, environmentally sustainable, light weight, low resistivity (10$^{-5}$ - 10$^{-2}$ Ω·cm) material, with a wealth of carbon substrates of differing geometry and porosity available.

conducting polymer (cp): Polypyrrole was selected as the conducting polymer for the project. Like conventional binders, conducting polymers promote good physical contact, but in contrast to conventional binders, conducting polymers also promote good electrical contact throughout the composite.

catalyst (Ag): Silver metal has been shown to function effectively as an oxygen reduction catalyst in aqueous alkaline electrolyte, but was unexplored for non-aqueous use prior to this project. In addition, polycrystalline silver and deposited silver particles have shown feasibility as aqueous gas diffusion electrodes for fuel cells and metal-air batteries in basic aqueous electrolyte. Silver was identified therefore as an attractive catalyst for this project.

IB. Methods used for composite preparation

Potentiostats were used for the deposition experiments. Glassy carbon and silver working electrodes were polished prior to use. Pyrrole was purified prior to use. Tetrabutylammonium hexafluorophosphate was precipitated from tetrabutylammonium bromide and potassium
tetrafluorophosphate. Other reagent grade chemicals were used as received, including silver nitrate, acetonitrile, sodium nitrate, nitric acid, and sodium hydroxide.

An inductively coupled plasma-optical emission spectrophotometer was used for silver analysis. Scanning electron microscopy (SEM) images were recorded.

Temperature was maintained at 25°C throughout all electrochemical experiments. A three electrode setup was utilized with a glassy carbon or polypyrrole coated-glassy carbon working electrode, aqueous silver-silver chloride reference electrode, and platinum auxiliary electrode. Polypyrrole was deposited using a three electrode setup was utilized with a glassy carbon working electrode, aqueous silver-silver chloride reference electrode, and platinum auxiliary electrode. Silver was then deposited on the electrode surface.

IC. Results of composite preparation

Polypyrrole was deposited on glassy carbon electrodes (Figure 1). Pyrrole polymerizes oxidatively at +0.6 V. A semi-reversible reduction-oxidation couple appeared with the oxidative peak potential at +0.4 V and the reductive peak potential at -0.25 V, where both waves grew in magnitude and the reduction peak broadened as the deposition progressed. This couple is attributed to switching of the polypyrrole film between oxidized (PPy⁺) and neutral (PPy) forms. A broader reduction peak with a narrower oxidation peak has been observed for other polypyrrole films.

Silver (Ag) was electrochemically deposited on conductive polymer coated carbon (C-cp) electrodes. Masses of silver deposited were calculated from total cumulative charge using Faraday’s law, assuming one electron reduction per formula unit for \( \text{Ag}^+ \rightarrow \text{Ag}^0 \). In order to independently quantify the amount of silver deposited, a series of C-cp-Ag composite electrodes was analyzed using inductively coupled plasma optical emission spectroscopy. The calculated and measured silver showed excellent correspondence (Figure 2).

Scanning electron micrographs showed a regular arrangement of Ag nanoparticles deposited on the smooth PPy surface (Figure 3). Notably, the Ag coating adhered well to the cp substrate, without noticeable Ag loss during bending of the cp-Ag composite for preparation of the SEM sample.
Objective II: Evaluate composite oxygen reduction activity.

IIA. Methods used for electrochemical evaluation

Oxygen reduction was measured using a three electrode setup with a glassy carbon, silver, or composite working electrode, a platinum wire auxiliary electrode, and a non-aqueous silver-silver nitrate reference electrode. Electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in acetonitrile (CH₃CN).

IIB. Results of electrochemical evaluation

Oxygen reduction was evaluated for the carbon-conductive polymer-silver (C-cp-Ag) composite electrode and compared with a silver-free (C-cp) electrode, an uncoated carbon (C) substrate electrode and a solid platinum (Pt) disk electrode. Evaluation under pure oxygen atmosphere with the four electrode types is shown (Figure 4). Reductive waves appeared at peak potentials near -1.7 V, -1.3 V, and -1.4 V for the Ag, GC, and C-cp-Ag electrodes, respectively. Consistent with our hypothesis, the silver electrode showed higher peak Coulomb flux (mA/cm²) than the glassy carbon electrode. Most notably, the peak Coulomb flux (mA/cm²) for the C-cp-Ag composite electrode was higher than the other two electrodes, demonstrating activity 2.6X greater than C and 1.4X higher than platinum.

AC impedance measurements were taken to assess the conductivity of the C-cp-Ag composite electrode near open circuit potential (-0.5 V) and at a potential appropriate for oxygen reduction (-1.6 V). The diameter of the semicircle in the Nyquist plot was approximately 100 ohms in both cases, and did not change significantly at the lower potential (Figure 5). This data verified that the C-cp-Ag composite electrode maintained its conductivity at a negative potential appropriate for oxygen reduction.

A C-cp-Ag composite electrode was subjected to 20 consecutive reduction-oxidation cycles in ambient air at 100 mV/sec (Figure 6). The composite electrode showed quasi-reversible behavior, retaining high oxygen reduction activity over all 20 cycles.
Objective III: Interrogate the oxygen reduction mechanism in nonaqueous electrolyte.

IIIA. Methods used for mechanistic investigation
Oxygen reduction was measured using a three electrode setup with a glassy carbon, silver, or composite working electrode, a platinum wire auxiliary electrode, and a non-aqueous silver-silver nitrate reference electrode. Electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) in acetonitrile (CH$_3$CN). Nitrogen:oxygen gas ratios were controlled using Matheson Trigas flowmeters.

IIIB. Results of mechanistic investigation
The oxygen reduction activity of the three electrode types was assessed at different oxygen concentrations, ranging from 1 – 9 mM. The mechanism was investigated based on oxygen concentration dependence, where the peak Coulomb flux of oxygen reduction increased linearly with oxygen concentration, consistent with a first order mechanism for oxygen reduction (Figure 7). Notably, the C-cp-Ag composite electrode showed higher activity at all concentrations.

![Figure 7. Cycling of carbon-conductive polymer-silver (C-cp-Ag) electrode](image)

Objective IV: Assess roles of composite components.

IVA. Methods used for composite assessment studies
Composite preparation and electrochemical evaluation methods were consistent with those described in sections I and II above, respectively. Some composite electrodes were prepared using gold (Au) as substrate instead of carbon (C), thus gold-conductive polymer (Au-cp) and gold-conductive polymer-silver (Au-cp-Ag) composite electrodes were fabricated. For the electrode durability test, coated electrodes were horizontally dragged a distance of 5.6 cm, while exerting a 4 N downward force. Optical images were acquired for the coated electrodes before and after the electrode durability test.

IVB. Results of composite assessment studies

IVBi. Substrate functionality assessment
Carbon (C) was selected as a current collector substrate for our composite electrode since it is an inexpensive, lightweight, high conductivity material. In order to assess the contribution of the current collector substrate toward the overall activity of the current collector-conductive polymer-silver (cc-cp-Ag) composite, comparative electrodes were prepared and tested using a gold (Au) disk electrode as a current collector substrate in place of the carbon (C) electrode, where the resulting composites were identified as Au-cp-Ag and C-cp-Ag, respectively.
Uncoated carbon (C) (Figure 8) and gold (Au) disk (Figure 9) electrodes were tested. The peak reduction potentials were different for the two electrode types. The Au electrode (Figure 9) showed significantly higher activity, by a factor of 2.5X in air and 1.9X in pure oxygen.

![Figure 8. Oxygen reduction behavior of carbon (C)](image8)

![Figure 9. Oxygen reduction behavior of gold (Au)](image9)

The carbon (C) and gold disk (Au) electrodes were each coated with a conductive polymer (cp) layer using a previously described and subjected to the same oxygen reduction tests. Notably, both types of polymer coated electrodes showed quasi-reversible oxygen reduction behavior at the same potentials and similar magnitude, regardless of the substrate used (Figure 10). Next, the C-cp and Au-cp polymer coated electrodes were each coated with silver (Ag), at similar low 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 electrodes were measured (Figure 11).

![Figure 10. Oxygen reduction behavior of gold-conductive polymer (Au-cp) and carbon –conductive polymer (C-cp) electrodes](image10)

![Figure 11. Oxygen reduction behavior of gold-conductive polymer-silver (Au-cp-Ag) and carbon –conductive polymer-silver (C-cp-Ag) electrodes](image11)

As with the silver-free polymer coated electrodes, both types of silver-polymer coated electrodes showed quasi-reversible oxygen reduction behavior at the same potentials and similar magnitude, regardless of the substrate used. *This data established for the first time that the oxygen reduction activity of the composite electrodes is dictated by the conductive polymer and not the*
underlying substrate, opening the possibility for the use for diverse types of current collector substrates for silver-polymer composite electrodes in the future.

Also notably, the oxygen reduction activity of the C-cp-Ag composite electrode was comparable to that 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.

IVB. Results of composite assessment studies

IVBii. Conductive polymer functionality assessment

Polypyrrole was selected as a conductive polymer (cp) for the composite electrode to promote good physical and electrical contact between the current collector and silver deposit. A durability test was designed to assess the structural role of the polymer in improving physical strength of the composite electrode. Carbon-silver (C-Ag) composite electrodes were prepared with and without conductive polymer (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 12). 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 (Figure 13). 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%.

To assess the Ag retention capability of the conducting polymer (cp) on a microscopic level, a cp-Ag coating with an Ag loading of 1.6 mg/cm² was removed from a planar substrate and placed into a scanning electron microscope (SEM). Images were acquired at varying magnifications (Figure 14). No evidence of Ag loss was observed after flexing the cp-Ag composite. This SEM experiment verified that there was strong adhesion between the cp and
Ag, and that it should be possible to prepare non-planar cp-Ag electrodes. Based on this result, it should be possible to prepare a composite free-standing cp-Ag electrode in the future.

**In summary, the durability tests demonstrated that the polymer layer plays an important role in improving the robustness of the composite electrode. They also established that it should be possible to prepare a free-standing (substrate-free) cp-Ag electrode in the future.**

IVB. Results of composite assessment studies

IVBiii. Silver functionality assessment

Since silver metal (Ag) is the most expensive component of the carbon-conductive polymer-silver (C-cp-Ag) composite electrode, it was important to determine the minimum amount of Ag needed. In order to determine the minimum Ag loading required for increased oxygen reduction activity, a series of C-cp-Ag composite electrodes was prepared with differing Ag content. The oxygen reduction activity of the C-cp-Ag composite electrodes was measured in nonaqueous electrolyte. Comparative data was collected with uncoated carbon (C), an uncoated solid silver disk (Ag), and silver-free conductive polymer coated glassy carbon (C-cp) electrodes. Since oxygen partial pressure can significantly affect performance of the air electrode, measurements were made under both air (Figure 15) and pure oxygen (Figure 16). The relative activities of the various electrodes were consistent in both gases. The measured activity in air was 20 - 40% of the activity in pure oxygen.

The C-cp electrodes and uncoated C electrodes showed very similar activity, consistent with the results discussed above. The Ag disk electrodes showed 3X higher activity in air (Figure 14) and 2X higher activity in oxygen (Figure 15) 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. Thus, this study demonstrated that a low silver loading of 0.08 mg/cm\(^2\) was required to optimize the oxygen reduction activity of the C-cp-Ag composite.

Objective V: Develop and investigate a three dimensional (3D) carbon-conductive polymer-silver (C-cp-Ag) composite.

VA. Methods used for three dimensional (3D) composite preparation, characterization, and electrochemical evaluation

Deposition procedures for deposition of conductive polymer (cp) and silver (Ag) coatings were consistent with the above descriptions. To prepare the nonplanar three dimensional (3D) composite electrodes, carbon felt or reticulated vitreous carbon from were used as the current collector substrates. Methods used for evaluation of oxygen reduction activity were consistent with those described above.

VB. Results of three dimensional (3D) composite preparation and characterization

In order to prepare three-dimensionally structured composite electrodes, carbon felt and reticulated vitreous carbon (RVC) were employed as current collector substrates. To verify that the polypyrrole deposition process was not impacted by the current collector morphology, a series of current collector-conducting polymer (cc-cp) composites was prepared with different amounts of polypyrrole coating utilizing both 2D (planar)
and 3D (non-planar) carbon based current collectors as substrates. Specifically, a planar glassy carbon substrate, a moderate surface area reticulated vitreous carbon (RVC) substrate, and a high surface area carbon felt substrate were used. 

Regardless of the current collector type used, a consistent mass-charge relationship was observed (Figure 17), verifying that the conducting polymer deposition was a well controlled process which was not sensitive to the geometry of the current collector substrate.

Optical microscope images (Figure 18) and scanning electron microscope (SEM) images (Figures 19 and 20) were acquired at varying magnifications. The Cfelt-cp-Ag composite electrode showed a range of Ag morphologies, ranging from nanosized to micron sized deposits. It was evident that the majority of the Ag deposit resided on the exterior of the Cfelt-cp-Ag composite electrode. Thus, there is opportunity for further refinement of the Ag deposition conditions to improve the Cfelt-cp-Ag composite homogeneity.

VB. Results of three dimensional (3D) composite electrochemical evaluation

Oxygen reduction activity of the 3D Cfelt-cp-Ag electrode was evaluated, using methodology consistent with that used for the 2D composite electrodes described above. The 3D Cfelt-cp-Ag composite exhibited ~4X enhancement in oxygen reduction activity over the planar C-cp-Ag electrode (Figure 21). This data highlights the significant opportunity that transitioning to a 3D architecture can provide for metal air batteries.
5. Personnel:

**PI**
Amy C. Marschilok

**Undergraduate students**
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Patrick T. Saitta  
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**Ph.D students**
Shu Han Lee  
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**Masters students**
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6. Publications:


Marschilok, Amy C.; Lee, Shu Han; Milleville, Christopher C.; Chen, Peiwen; Takeuchi, Esther S.; Takeuchi, Kenneth J. “Three dimensional carbon-conductive polymer-silver (C-cp-Ag) composite electrodes for metal-air batteries.” Submitted for publication.

Marschilok, Amy C.; Lee, Shu Han; Takeuchi, Kenneth J.; Takeuchi, Esther S. “Mechanistic investigation of the oxygen reduction reaction on carbon-conductive polymer-silver composites.” In preparation.

7. Interactions/Transitions:


Participation/presentations at meetings


11. **S. H. Lee, K. J. Takeuchi, E. S. Takeuchi, A. C. Marschilok.**


8. **New discoveries, inventions, or patent disclosures**


9. **Honors/Awards:**

   **Electrochemical Society Early Career Faculty Travel Grant.** Recipient 2010. The Battery Division has established the Early Career Faculty Travel Grants program to recognize promising faculty members at colleges and universities who are in the first five years of their appointments and engaged in research in the science and engineering of electrochemical energy storage and conversion.

   **Woman of Distinction Award.** Education Category Recipient 2011. This regional award is given annually by the Girl Scouts of Western New York in recognition of excellence in education, leadership, role modeling, and the mentoring of women.