

Silver and Silver-Manganese Cathode Catalysts for Alkaline Fuel Cells

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1. Introduction

Requirements for the commercialization of fuel cell technology are that devices are relatively inexpensive and that they will operate reliably over a wide range of power demands. Both of these requirements necessitate that active, stable, and cost effective electrocatalysts be developed to not only replace the expensive noble metals now used in alkaline fuel cell electrodes, but also reduce the requisite catalyst loading where the pertinent reactions of interest are O₂ reduction and H₂ oxidation. Much of the recent activity in both electrolysis and fuel cell technologies have centered on either proton exchange membrane (PEMFC/SPEWE) or in solid oxide electrolytes (SOFC/SOEC) because of the potential for high current/power densities and efficient packing. In spite of the great progress, PEM based technologies still suffer from the cost penalty associated with using precious metal catalysts and the reliability issues stemming from the polymer electrolyte membrane. Similarly, SOFC/SOEC technologies have been slow in bringing down their operating temperature due to electrode/electrolyte restraints. Alkaline fuel cells are examined in this study as a potential near-term fuel cell technology for applications such as stationary power generators or backup power sources in remote locations.

The cathode electrode was chosen as it is the main contributor to cell power losses in alkaline fuel cells (Figure 1) due to the complexity of the oxygen reduction reaction, the mechanisms of which are still not entirely understood to this day. Significantly higher overpotentials are found with the cathode to achieve equivalent current density performance to the anode. While platinum is still the standard and best performing catalyst in AFC systems, studies of replacement catalysts have shown that non-precious metal catalysts demonstrate comparable performance. In this work, alkaline fuel cells are investigated with the goal of enhancing cathode catalytic performance by creating two possible electrode structures: a synergistic bi-metallic alloy catalyst and a nano-structured catalyst supported on carbon nanofibers.

The bimetallic silver-manganese system was chosen as both silver [1-15] and manganese dioxide [2,13-14,16-21] show similar oxygen reduction catalytic activities to platinum in an alkaline electrolyte. A comparison of silver and platinum carbon electrodes adapted from Hacker et. al [1] (Figure 2) shows similar performance at low current densities, with an eventual tail-off at higher current densities.

The second cathode material, a carbon supported nano-structured system was chosen due to the inherent catalytic ability of carbon nanofibers to reduce oxygen on their own. By decreasing particle size, an increase in the surface area to volume ratio of the catalyst can greatly increase the effectiveness and activity of

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the catalyst per mass loading. By electrolessly depositing silver and manganese dioxide nano particles on carbon nanofibers, a distributed, highly active catalyst towards the oxygen reduction reaction can be synthesized. The conductive, graphitic carbon support structure would also be catalytically active and act as a current collector.

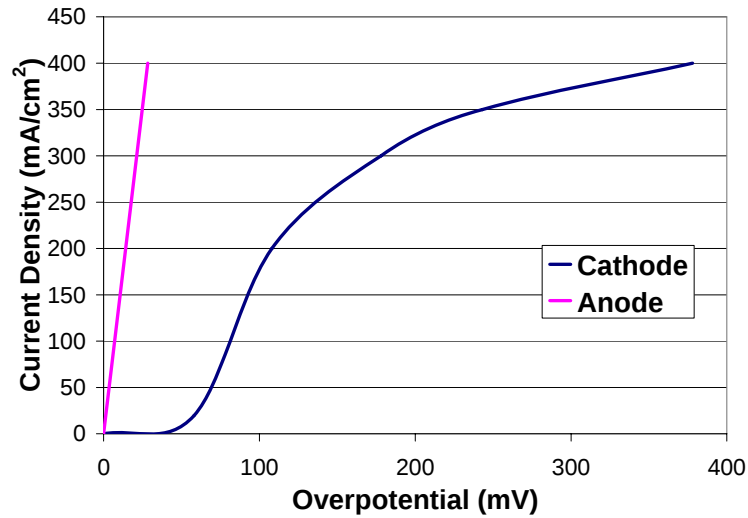


Figure 1 - Comparison of overpotential requirements for cathode and anode in an AFC (adapted from [22])

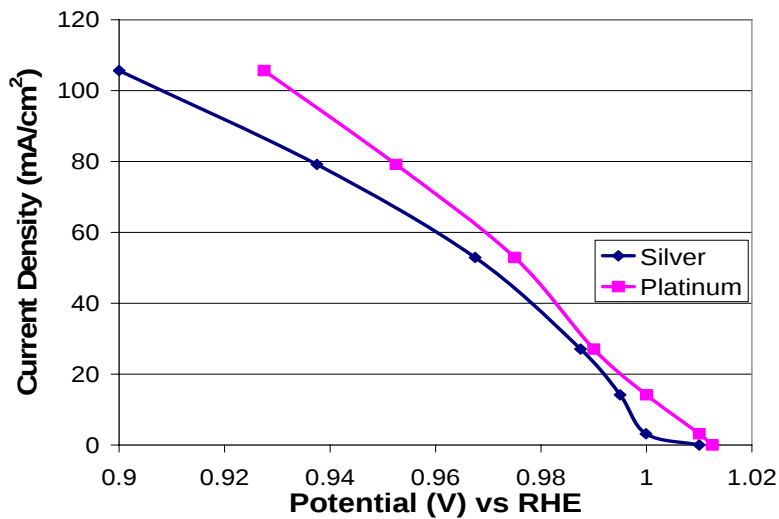


Figure 2 - Catalytic performance comparison of silver and platinum with respect to the oxygen reduction reaction in 9 M KOH at 80°C (adapted from [1])

2. Experimental

Bulk Alloy Production

Silver and manganese bi-metallic alloys were created by arc-melting compressed powders of silver (APS 4-7 micron, 99.9% - Alfa Aesar) and manganese (-325 mesh, 99.95% - Alfa Aesar). Three distinct alloy systems were made consisting of 5, 10 and 15 wt% manganese in bulk silver. The alloys were melted in an argon atmosphere and separate compressed compacts of pure manganese were melted immediately prior to the alloy melting in order to act as an oxygen getter and remove any residual oxygen from the system.

Nano-structured system production

Silver and manganese dioxide catalysts were electrolessly deposited on carbon nanofibers (CNFs) produced by ElectroVac. Three distinct catalyst systems were created: pure silver deposited on CNFs, silver and manganese dioxide deposited on CNFs and manganese dioxide deposited on CNFs. The deposition system for silver was adapted from Hacker et al [1] where the raw CNFs were first pre-treated in a nitric and sulphuric acid mixture to oxidize the surface of the fibers, rendering them more active for electroless deposition. Silver nitrate was utilized as the catalyst precursor; silver ions were complexed by ammonia and reduced/deposited on the fibers by glucose under refluxing conditions. The silver and manganese dioxide mixed catalyst system was electrolessly deposited based on a method devised by Zhang et al. [2]. The CNFs were acid-treated as before; silver permanganate was the catalyst precursor and was reduced on the carbon nanofibers with hydrazine as the reducing agent. To distinguish between the catalytic activity of pure silver and pure manganese dioxide, a third catalyst system was produced by applying a nitric acid treatment to the silver and manganese dioxide system, removing the silver and leaving only manganese dioxide.

Electrodes were prepared from pure CNFs, silver deposited on CNFs, manganese dioxide deposited on CNFs and silver with manganese dioxide deposited on CNFs. The electrode preparation procedure consisted of adding 30 wt% solid polytetrafluoroethylene (PTFE) from a PTFE emulsion to the CNFs and catalyst system, treating the mixture ultrasonically in excess isopropyl alcohol (IPA) and vaporizing the excess IPA. The resulting paste was passed through a stainless steel rolling press multiple times, each time decreasing the separation distance between the two rollers. After achieving the desired thickness, the CNF and catalyst sheets were pressed onto a thin nickel mesh (as a current collector) followed by a sintering treatment for 2 hours at 200°C.

Electrochemical Testing

The bi-metallic alloys along with pure silver were fashioned into electrodes to be tested by cyclic voltammetry (-200 mV to 900 mV at a sweep rate of 500 mV/min) and potential step and hold (100 to -350 mV in 10 mV increments) testing in the oxygen reduction region. A standard 3-electrode cell consisting of a platinum counter electrode, a mercury/mercury oxide reference electrode and the

respective alloy or pure silver as the working electrode was utilized for all electrochemical measurements. 0.1 M KOH (AnalaR, EMD – pre-electrolyzed for 5 days) was used as the electrolyte in all electrochemical experiments. The nano-structured catalyst electrodes were tested for their activity towards the oxygen reduction reaction in oxygen saturated 0.1 M KOH at 80°C with a potential step and hold test (100 to -350 mV in 10 mV increments).

Analytical Testing

The bi-metallic silver-manganese alloys were characterized by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX). X-ray photoelectron spectroscopy (XPS) was conducted on silver-manganese alloys and pure silver to examine their surface composition and determine if any change occurred in the electronic structure of the surface states of silver or manganese; Mg K α x-ray source was used for all measurements. Binding energies were normalized to the carbon 1s peak of 284.8 eV and the XPS software was calibrated to both the above mentioned carbon 1s peak and the silver 3d^{5/2} peak of 368.3 eV before and after each spectral measurement.

The electrolessly deposited nanosystem, pure CNFs and fabricated electrodes were characterized by scanning transmission electron microscopy (STEM), SEM and their chemical composition obtained and mapped by EDX.

3. Results and Discussion for Silver-Manganese Bi-Metallic Alloy System

The oxygen reduction activities of the silver and silver-manganese alloy catalysts were compared in 0.1 M KOH at 80°C. Results of the potential step and hold test can be seen in Figure 3.

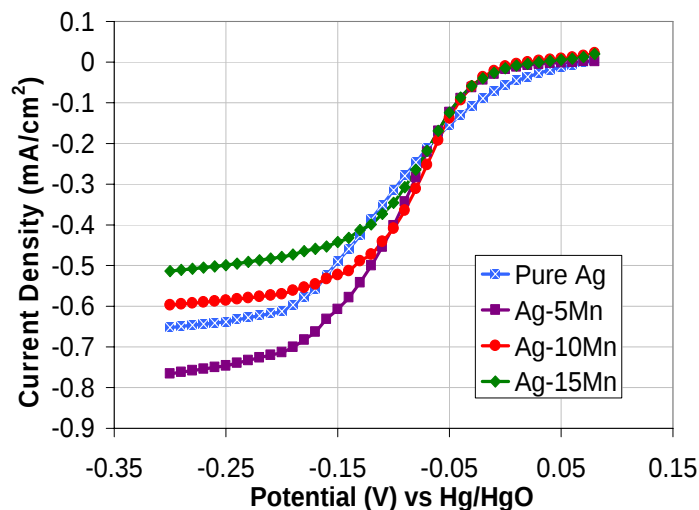


Figure 3 - Polarization curves for oxygen reduction on pure silver and silver with 5, 10 and 15 wt% manganese in oxygen saturated 0.1 M KOH at 80°C, 10 mV increments, held for 90 seconds at each increment.

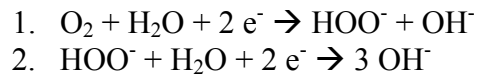
As seen in Figure 3, the oxygen reduction reaction initiates for pure silver at a potential of approximately 75 mV and reaches a maximum current density of 65 mA/cm². The manganese-silver alloys initiate the oxygen reduction reaction at a slightly lower potential (30-50 mV), but show a quicker increase in current density compared to pure silver. The silver-manganese alloys share relatively the same polarization curve shape initially and at lower potentials the maximum current density increases significantly with decreasing manganese content. The silver alloy containing 5 wt% manganese showed the highest activity among all alloys having an approximate 15 to 20% increase in maximum current density over that of pure silver. The polarization curves were plotted on a logarithmic current scale and Tafel slope data was extrapolated for all of the alloys. The results from the oxygen reduction reaction polarization experiments are summarized in Table 1.

Alloy	Maximum Current Density (mA/cm ²)	Onset of ORR (V vs Hg/HgO)	Tafel Slope (mV/dec)	Cathodic Transfer Coefficient
Pure Silver	65	+ 0.075	70 (small η) 140 (large η)	1 (small η) 0.5 (large η)
Ag-15wt%Mn	51	+ 0.030	60	1.16
Ag-10wt%Mn	60	+ 0.030	60	1.16
Ag-5wt%Mn	77	+ 0.050	60	1.16

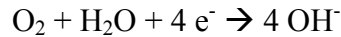
Table 1 - Summary of results for silver and silver-manganese alloy polarization tests for the oxygen reduction reaction

Pure silver shows two distinct Tafel regions, with a Tafel slope of 70 mV/decade at small overpotentials and 140 mV/decade at large overpotentials. The subsequent cathodic transfer coefficient calculations suggest that silver reduces oxygen by two different reaction mechanisms:

i) The 2 e⁻ hydroxide intermediate formation process at small overpotentials:



ii) The 4 e⁻ direct reduction process at large overpotentials:



The manganese alloys all show the same Tafel slopes and cathodic transfer coefficients, suggesting that the manganese containing alloys reduce oxygen by a mixed reaction process.

Cyclic voltammetry was performed on pure silver (Figure 4) and the bi-metallic silver-manganese alloy electrodes. The cyclic voltammogram for pure silver in Figure 4 shows the respective oxidation and reduction peaks of AgO and Ag₂O. Subsequent results will focus specifically on the Ag₂O reduction peak as

highlighted in Figure 4, for a direct comparison of the oxide reduction characteristics of pure silver and the silver-manganese alloys (seen in Figure 5).

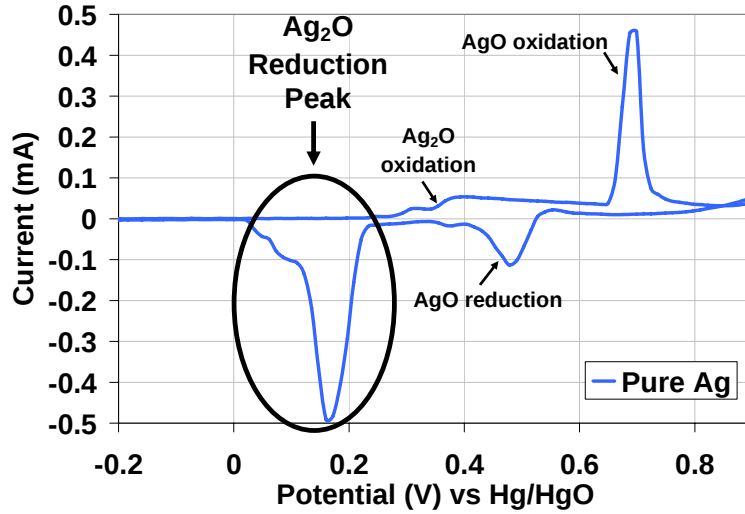


Figure 4 - Cyclic voltammetry results for pure silver in 0.1 M KOH in an argon saturated atmosphere. 500 mV/min sweep rate from -200 to 900 mV.

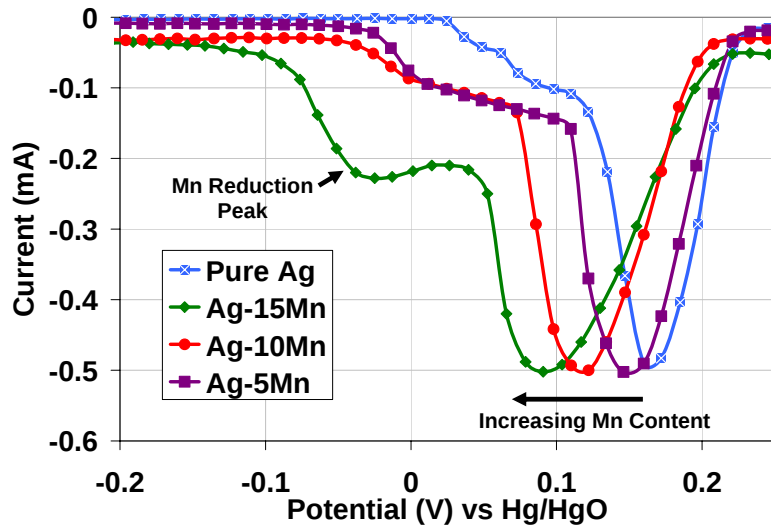


Figure 5 - Ag_2O reduction peak of pure silver and silver-manganese alloys in argon saturated 0.1 M KOH, 500 mV/min sweep rate from -200 to 900 mV.

With increasing manganese content, the Ag_2O reduction peak shifts to lower potentials, from 170 mV for pure silver to 90 mV for the silver-15wt% manganese alloy. This shift to lower potentials corresponds to an increase in the cathodic overpotential that is required to reduce Ag_2O from the silver or silver-manganese alloy surface. The cathodic overpotential increases with increasing manganese content, suggesting that alloying manganese to silver increases silver's affinity

towards surface oxygen bonding, requiring a greater applied driving force before oxygen can be removed from the surface.

XPS analysis was undertaken on pure silver and the silver-manganese alloys to examine the surface state and surface elemental concentration of the alloys. An entire spectra was obtained for all samples and the silver and manganese regions were examined in depth. The results for the silver spectra can be seen in Figure 6.

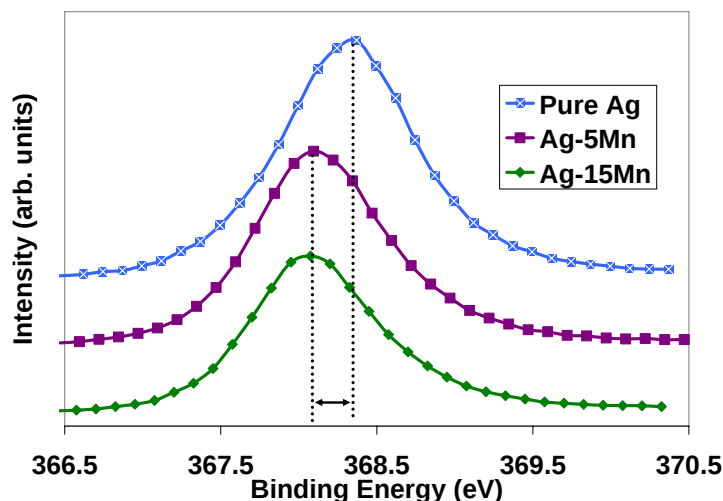


Figure 6 - XPS spectra of silver's 3d^{5/2} binding energy

The XPS analysis of pure silver shows a 3d^{5/2} binding energy of 368.3 eV, while the XPS analysis of the manganese containing alloys shows a binding energy of 368.1 eV; a decrease of 0.2 eV from that of pure silver. The decrease in silver's binding energy with manganese addition supports the earlier cyclic voltammetry results; it is hypothesized that the increased affinity for surface oxygen with increasing manganese content is due to a change in the electronic binding energy state for silver on the surface with the addition of manganese. The increased affinity for surface oxygen, increases the efficiency of the oxygen-oxygen bond cleavage, which increases the catalytic activity of the alloy. The XPS spectra for manganese was also examined to determine why the alloys containing high amounts (10 and 15 wt%) of manganese showed a decreased activity compared to that of pure silver, when it was expected they should be significantly more active. The manganese XPS spectra can be seen below in Figure 7.

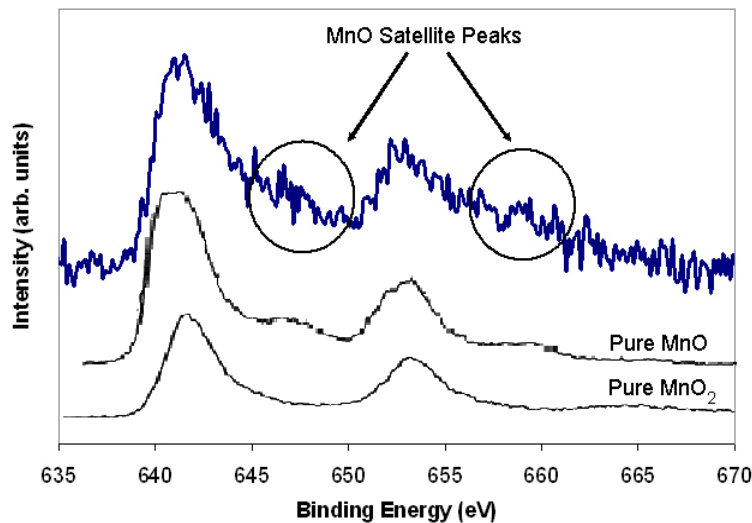


Figure 7 - Manganese XPS spectra in order from the top – Raw spectra of Ag-15%Mn alloy, pure MnO and pure MnO₂ (Pure MnO and pure MnO₂ spectra adapted from [23]).

The obtained manganese spectra from the silver-15wt% manganese alloy were compared to Oku et al.'s [23] XPS study of pure manganese oxides. The manganese in the silver-manganese alloys matched the XPS spectra of manganese oxide as opposed to the desired active manganese dioxide. The manganese peak from the silver-manganese alloy closely corresponds to the binding energies of pure manganese oxide and has corresponding satellite peaks that are unique to manganese oxide (of all the manganese oxide forms). Of the different forms of manganese oxides (MnO, Mn₂O₃, MnO₂, etc.) manganese oxide (MnO) is the least active [13]. The formation of manganese oxide on the surface of the high manganese containing alloys can explain the observed decreased activity. Non-active manganese oxide sites replaced highly active silver sites, which corresponded to the increase in catalytic activity with decreasing manganese content.

Manganese has limited solubility in silver and was expected to form second phase precipitated particles in the 10 and 15 wt% manganese-silver alloys. Image analysis by SEM on the silver-manganese alloys confirmed the degree of segregation of manganese oxide to the catalyst surface for the 15 wt% manganese alloy as seen in Figure 8. The 5 wt% manganese alloy appeared to solidify as a solid solution alloy and did not show significant second phase segregation.

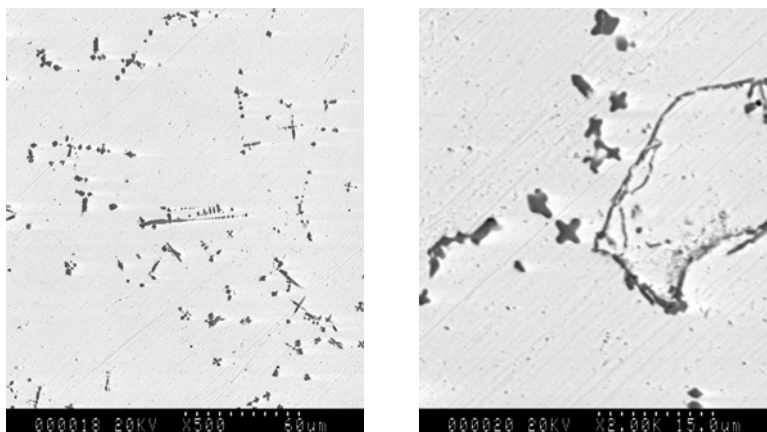


Figure 8 - Backscattered electron SEM images of Ag-15wt%Mn alloy showing manganese oxide surface segregation

Surface chemical composition was analyzed by XPS to determine accurate surface concentration values. XPS surface composition analysis showed a significant manganese surface depletion. The alloy of silver containing 15 wt% manganese had a surface concentration of 10.7 wt%, while the silver – 5wt% manganese alloy had a surface concentration of 0.5 wt%. The samples were ion sputtered for 1 hour, removing approximately 10 nm from the surface of the alloy. After sputtering the manganese concentrations returned to 15 wt% and 5 wt% respectively showing only the surface layer was depleted in manganese.

The oxygen reduction reactivity of the three silver-manganese alloys can be explained by a combination of the effect manganese has on silver's electronic structure and through the non-active manganese oxide formed on the catalyst surface. The 10 and 15 wt% manganese-silver alloys have a decreased activity due to the amount of manganese oxide on the surface, which depletes active silver sites. The 5 wt% manganese-silver alloy had a very limited amount of manganese oxide on the surface (~0.5 wt% manganese), so active surface sites were not significantly depleted. The results suggest that the addition of manganese to silver altered silver's electronic structure increasing its affinity towards oxygen atoms. This increased bond strength between silver and oxygen, increased the efficiency of the oxygen-oxygen bond cleavage and the overall efficiency of the oxygen reduction reaction which corresponded to an increased maximum current density. A visual representation of the silver-manganese alloy's surface structure is shown in Figure 9.

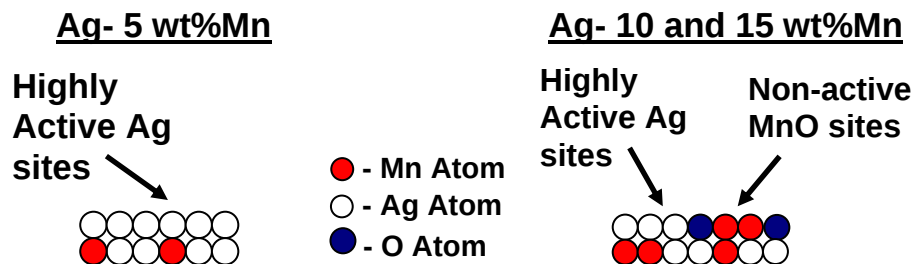


Figure 9 - Graphical representation of catalyst surface for Ag - 5, 10 and 15 wt% Mn alloys. Ag-5wt% Mn has a surface rich in active silver atoms, with manganese in solid solution in the bulk of the alloy. Ag-10 and 15wt% Mn forms second phase manganese precipitates as non-active manganese oxide (MnO) on the catalyst surface.

4. Nano-structured Catalyst System

The second system studied consisted of a base of carbon nano-fibers with an average diameter range of 50-150 nm. Images of the carbon nanofibers after acid treatment, but prior to deposition can be seen in Figure 10. Catalysts were electrolessly deposited on the carbon nanofibers, characterized visually and chemically, and prepared into electrodes which were then electrochemically tested. Two distinct systems were created: a pure silver deposited system and a mixed system of silver and manganese dioxide.

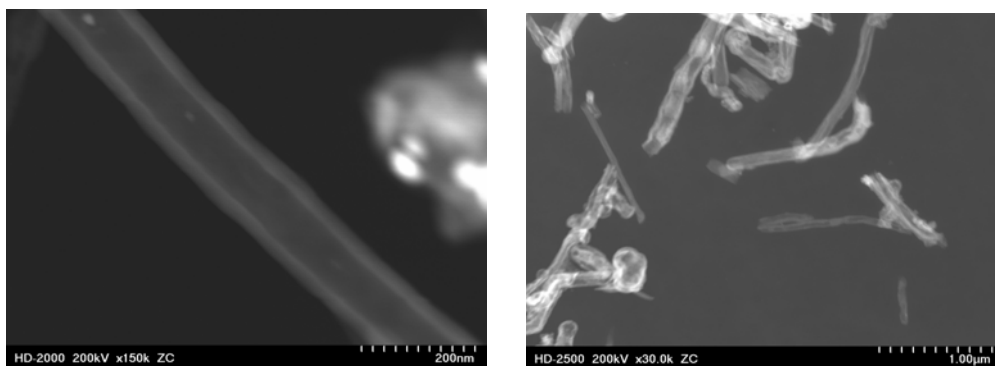


Figure 10 - TEM images of carbon nanofibers

Silver was deposited on CNFs by reduction of silver nitrate. The deposited silver particles appeared primarily as spherical deposits, demonstrating Volmer-Weber type growth. Image analysis performed on the silver deposits confirmed a size distribution of deposits ranging from below 10 nm to a maximum of 135 nm. Primarily, the silver deposits were in the range of 35-45 nm. TEM images of the deposited silver particles on CNFs and the catalyst size distribution can be seen in Figures 11 and 12.

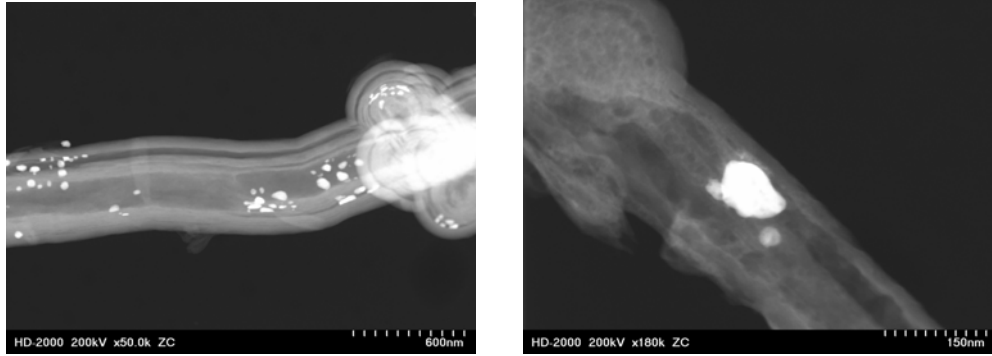


Figure 11 - TEM (Z-Contrast mode) images of CNFs with pure silver deposits. Silver deposits appear as spherical bright spots on tubular nanofibers.

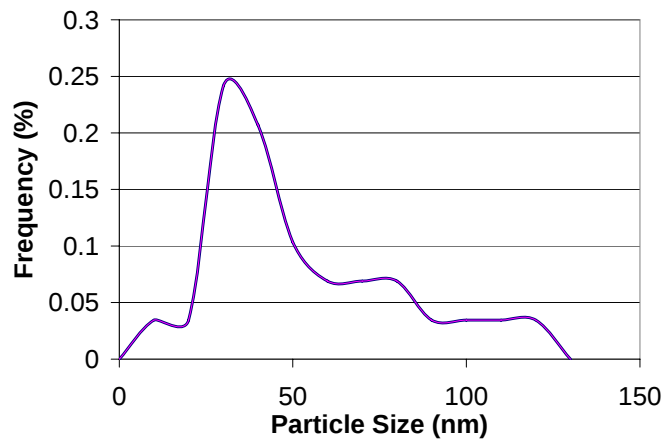


Figure 12 - Size distribution of deposited silver particles

Silver deposition was confirmed by EDX line scans across the carbon surface and silver deposits. An example of an EDX line scan is seen in Figure 13. The signal intensity for silver corresponds to the region directly on the expected location of the silver particle, while the carbon signal shows a standard intensity across the entire carbon nanofiber with its highest intensity at the edges of the tube. This was expected, since it is the thickest region of the nanofibers. Subsequent EDX analysis confirmed that silver was deposited in a 10 wt% ratio to the carbon nanofibers as intended.

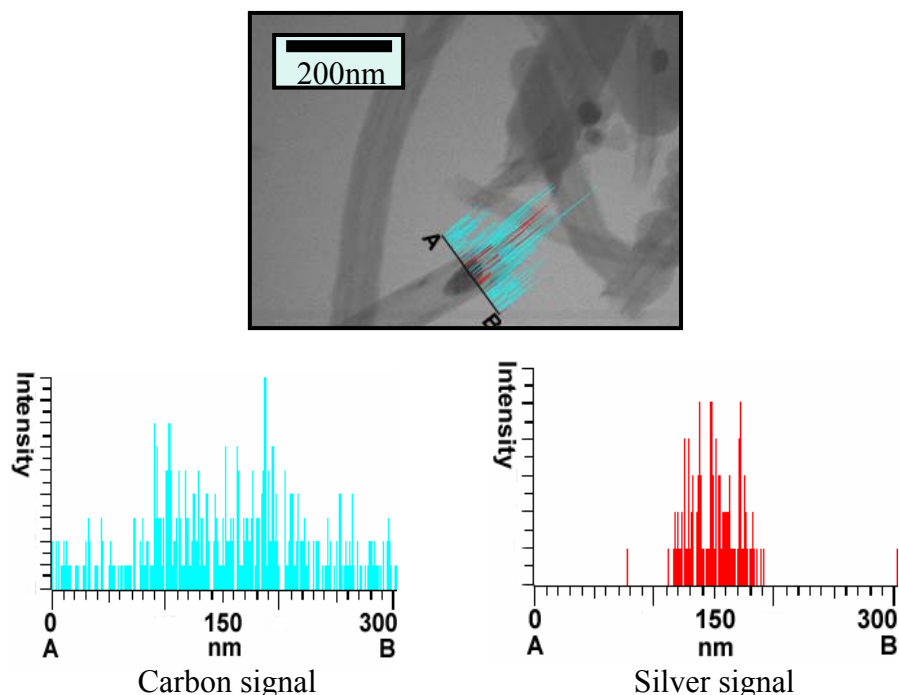


Figure 13 – EDX line scan of a silver particle deposited on a CNF

The second deposition system, consisting of silver and manganese dioxide was electrolessly deposited by reducing silver permanganate with hydrazine. Silver showed two distinct deposition mechanisms, a spherical growth and a dendritic based growth, both of which are seen in Figure 14.

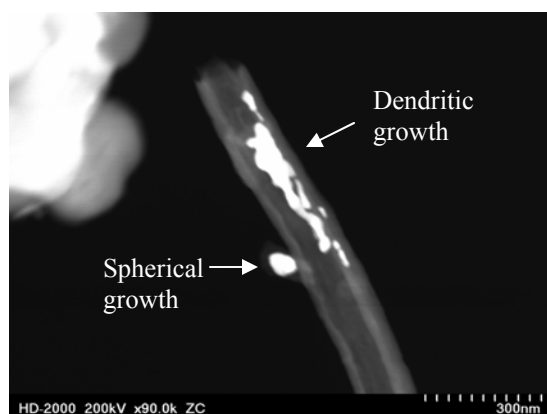


Figure 14 - Silver deposits on carbon nanofibers (silver and manganese dioxide system)

Manganese showed a distinctly different deposition scheme where it appeared to coat the entire carbon nanofiber with no significant agglomeration. This deposition process was confirmed by EDX mapping as seen in Figure 15.

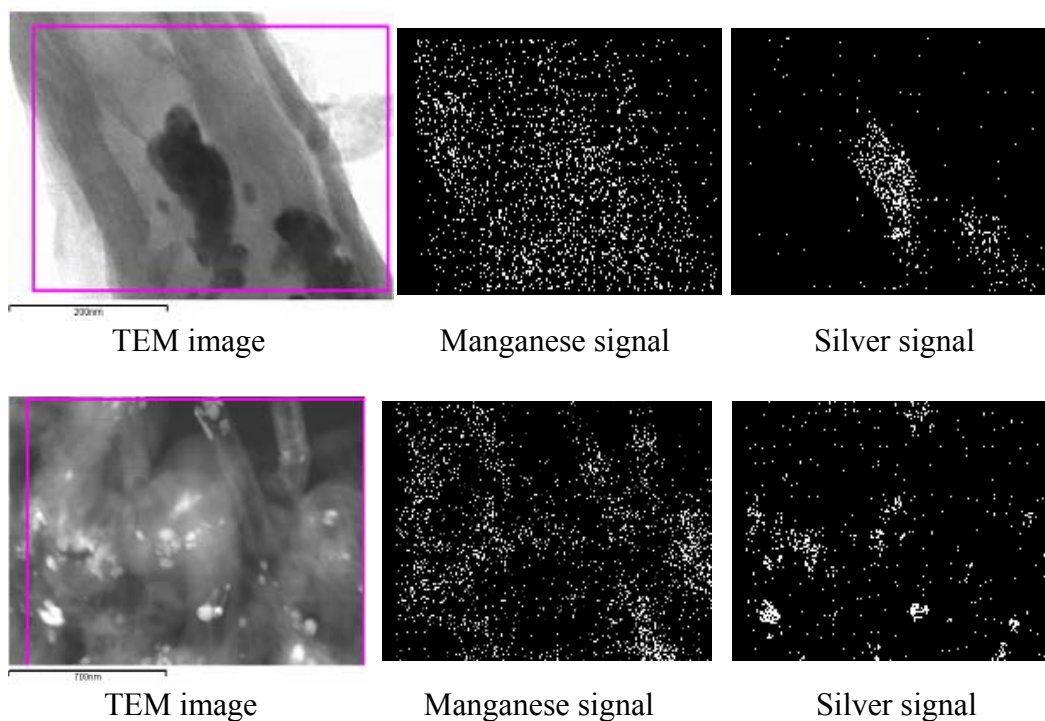


Figure 15 - EDX mapping of silver and manganese deposits

Electrodes consisting of CNFs with deposited catalyst, polytetrafluoroethylene as a binder and a thin nickel mesh as a current collector were fabricated for electrochemical testing. SEM images of prepared electrodes are shown in Figure 16.

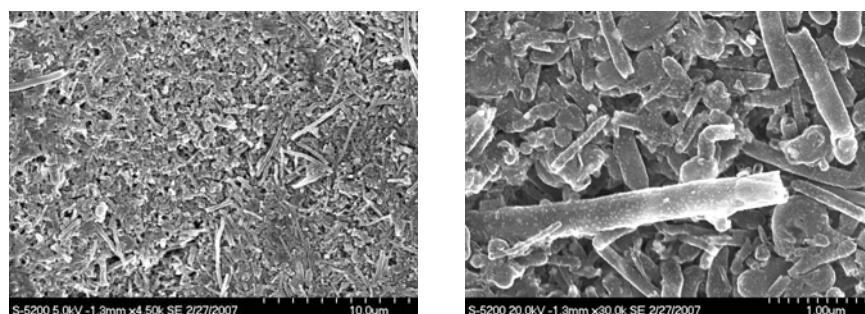


Figure 16 – SEM images of CNFs, catalyst and PTFE pressed electrodes

The electrodes were electrochemically investigated by step and hold voltammetry. A comparison of the catalytic activity with respect to the oxygen reduction reaction for electrodes consisting of just CNFs and PTFE, and CNFs with silver catalysts, manganese catalysts and silver with manganese catalysts is seen in Figure 17.

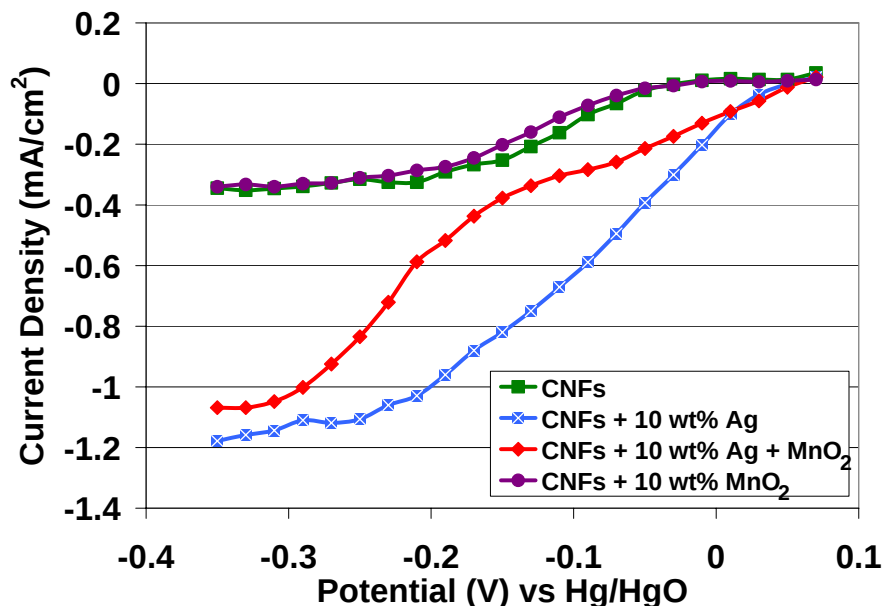


Figure 17 - Polarization curves for oxygen reduction on carbon nanofibers based electrodes in oxygen saturated 0.1 M KOH at 80°C, 20 mV increments, held for 90 seconds at each increment

Electrodes consisting of 10 wt% silver showed the highest catalytic performance, with the earliest onset of the oxygen reduction reaction and the highest maximum current density. Carbon nanofibers alone showed a slight activity towards reduction of oxygen in alkaline solution, although the reaction initiated at approximately 80 mV greater overpotential than that of the 10 wt% silver electrode and at a current density of approximately 3 times less. The manganese dioxide-based catalysts, which were created by stripping off deposited silver in the silver and manganese dioxide system, showed activity essentially equal to that of the carbon nanofibers. This suggests that the manganese dioxide as deposited was either non-active, or the acid treatment procedure may have altered the catalyst structure in such a way that it rendered the manganese dioxide inactive. The mixed catalyst system shows multiple distinct Tafel regions, suggesting that both silver and manganese dioxide catalysts are active in the mixed system. It is hypothesized that the acid treatment procedure actually renders the manganese dioxide catalysts to be non active post-treatment. While the nano-structured electrodes exhibited approximately the same magnitude of current density as compared to that of the solid polycrystalline alloy systems ($\sim 1 \text{ mA/cm}^2$), the actual mass loading of catalyst in the nano system was in the range of 1000 times less than that in the alloy system. This increase in catalytic activity with an extremely large difference in catalyst loading, is due to the resulting increased surface area by deposition of the nano-sized silver particle deposits.

5. Conclusions

The bi-metallic alloy of silver and 5 wt% manganese showed the highest catalytic activity of all the solid metallic catalysts tested, including a 15-20% increase in

maximum current density over pure silver. The activity increase was due to an electronic structure alteration effect resulting from silver alloying with manganese. The d-band of silver is altered such that the affinity for oxygen adsorption on silver's surface is increased, increasing the efficiency of the oxygen-oxygen bond cleave and increasing the overall efficiency of the oxygen reduction reaction.

For the nano-structured system, the carbon nanofiber-based electrodes all showed significant catalytic activities at significantly reduced catalyst loadings. Electrodes consisting of 10 wt% silver deposited on carbon nanofibers showed the highest catalytic activity, with the earliest onset potential of the oxygen reduction reaction and the highest maximum current density. The mixed catalyst system of silver and manganese dioxide deposited on CNFs also showed significant catalytic activity with a comparable maximum current density at high overpotentials.

6. Acknowledgements

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