Final Technical Report

to

U.S. Department of Energy ARPA-E

Batteries for Electrical Energy Storage in Transportation (BEEST) Program
DE-FOA-0000207

High Performance Cathodes for Li-Air Batteries

Award No. DE-AR0000066

Lead Recipient: University of Missouri

Principal Investigator: Yangchuan Xing

Date of Report: August 22, 2013

Project Period: August 1, 2010 – January 16, 2013

Subcontractors: Brookhaven National Laboratory, MaxPower, Inc. and NanoLab, Inc.

Executive Summary

The overall objective of this project was to develop and fabricate a multifunctional cathode with high activities in acidic electrolytes for the oxygen reduction and evolution reactions for Li-air batteries. It should enable the development of Li-air batteries that operate on hybrid electrolytes, with acidic catholytes in particular. The use of hybrid electrolytes eliminates the problems of lithium reaction with water and of lithium oxide deposition in the cathode with sole organic electrolytes. The use of acid electrolytes can eliminate carbonate formation inside the cathode, making air breathing Li-air batteries viable. The tasks of the project were focused on developing hierarchical cathode structures and bifunctional catalysts. Development and testing of a prototype hybrid Li-air battery were also conducted.

We succeeded in developing a hierarchical cathode structure and an effective bifunctional catalyst. We accomplished integrating the cathode with existing anode technologies and made a pouch prototype Li-air battery using sulfuric acid as catholyte. The battery cathodes contain a nanoscale multilayer structure made with carbon nanotubes and nanofibers. The structure was demonstrated to improve battery performance substantially. The bifunctional catalyst developed contains a conductive oxide support with ultra-low loading of platinum and iridium oxides. The work performed in this project has been documented in seven peer reviewed journal publications, five conference presentations, and filing of two U.S. patents. Technical details have been documented in the quarterly reports to DOE during the course of the project.

Acknowledgement

This report is based upon work supported by the U.S. Department of Energy under Award No. DE-AR0000066.

Disclaimer

Any opinions, findings, and conclusions/recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the Department of Energy.

Introduction

For the past two years and five and a half months, we have performed work supported by the ARPA-E BEEST program in developing technologies for Li-air batteries, in particular, related to aqueous catholytes. The project was proposed to circumvent some technical roadblocks encountered in using organic electrolytes. Research tasks include developing new materials and technologies for the cathodes of hybrid electrolyte Li-air batteries – in which the anode side has organic electrolytes, the cathode has aqueous electrolytes, and they are separated by a Li ion conducting ceramic membrane.

Work performed includes (1) cathode development and (2) prototype battery development. The first was performed at the University of Missouri (PI-Yangchuan Xing), NanoLab, Inc. (David Carnahan), and Brookhaven National Laboratory (Radoslav Adzic); the second was performed at the MaxPower, Inc. (Mark Salomon) and the University of Missouri.

The following provides a summary of achievements. For more technical details, readers are referred to the quarterly reports and journal publications by the performing team.

Cathode Development Achievements

1. Conductive TiO₂ as catalyst support

The goal of this task was to develop a conductive oxide to replace carbon as catalyst support. Carbon can be easily oxidized at high potentials, especially during recharge. An oxide support is needed to resist oxidation during recharge. To accomplish this, we have explored several ways to make TiO₂ conductive and a catalyst support. The following two approaches have been successful.

(a) TiO₂ nanocoating on carbon nanotubes (CNTs)

To make the nanocoating, CNTs were treated with 3:1 H₂SO₄:HNO₃ (volume ratio) in ultrasonic bath at 60 °C for 2 hrs, followed by filtration and thorough washing with deionized water. The treated CNTs were dispersed in a solution containing ethanol/benzyl alcohol plus excess water, with the aid of ultrasonication and stirring. Desired amount of titanium isopropoxide was dissolved in ethanol and slowly dropped into the CNT suspension. After 2hrs of stirring, the final suspension was vacuum-filtered, washed in ethanol, and dried in 80 °C in vacuum-oven overnight. Fig. 1 shows the TiO₂ coated CNTs (TiO₂/CNTs) with different TiO₂ loading. Fig. 2 shows a sample of the Pt catalyst deposited on the TiO₂/CNTs support that has a TiO₂ coating less than 10 nm. The TiO₂/CNTs hybrids were thermally doped with carbon under 10% acetylene C₂H₂ in N₂ at 500 °C or 700 °C for 20 min, designated as c-TiO₂/CNTs.

Fig. 1 TiO_2 by sol-gel coating has been achieved with different coating thicknesses (10~50nm). From left with 50, 70 and 85 wt% TiO_2 .

Fig. 2. A typical TEM image showing a TiO_2 nanocoating on CNTs with a thickness of ~9nm, which also has Pt nanoparticles (black dots) deposited on the support.

Electrochemical measurement was first performed to find if the c- TiO_2/CNTs is conductive. To do this, catalyst Pt was deposited on the support c- TiO_2/CNTs . Pt was also deposited on undoped TiO_2/CNTs . The test results are shown in Fig. 3.

From Fig. 3, we can see that Pt nanoparticles supported on c- TiO_2/CNTs exhibit much higher electrochemical activity, and Pt on TiO_2/CNTs shows negligible catalytic activity due to the low conductivity of the undoped support TiO_2 . These

Fig. 3. CV comparison of Pt/c- TiO_2/CNTs -500 with Pt/ TiO_2/CNTs . Electrolyte: N_2 purged 1.0 M H_2SO_4 , scan rate: 50 mV/s.

results demonstrate that carbon doping can significantly increase the electrical conductivity in TiO_2 due to suboxide formation as confirmed by XPS and XAS studies.

After the catalyst was made into a cathode in the buckypaper form, the resistance of buckypaper was measured using polarization curves by scanning the paper at varying currents. The resistance was thus obtained through the Ohm's law. Based on the measurements (Fig. 4), we can see that the resistance is very small for the doped sample ($\sim 46.66 \text{ Ohm}$), but it is significantly larger for undoped sample ($\sim 4689 \text{ Ohm}$), indicative of the larger conductivity of the carbon doped TiO_2 and consistent with what we observed from the electrochemical measurements.

The resistance was further converted to resistivity of the buckypaper since the dimensions of the paper are known. Since the buckypaper is porous, a further correction was done using the porosity. We used the CNT's density of 2.1 g/cm^3 , and the porosity of the vacuum filtered buckypaper estimated at 84.1%. This yielded a compact (no pores) resistivity to $2.13 \times 10^{-3} \text{ ohm-cm}$, which is less than that of the Magneli phase. So the task target is achieved. The undoped have a resistivity of $2.14 \times 10^{-1} \text{ ohm-cm}$, which are two orders of magnitude higher, indicative of that the conductivity improvement in c-doped TiO_2 has been accomplished.

Fig. 4. I-V curves of the measured buckypaper with carbon doped on CNTs. Inset: the configuration of measurement.

(b) Carbon-doped nanoscale sized TiO_2

Commercial TiO_2 (Degussa P25) were used for making a conductive substrates. The P25 has a structure similar to carbon black (common electrocatalyst support). The idea was that if we can make this TiO_2 conductive, then we would have a cheap material while achieving the project goal. Enlightened by our carbon doping, we sought to dope the P25 with carbon. We eventually

found that we may coat the P25 with a nanoscale thick layer and then in situ dope the P25 using the coating as a carbon source. We have succeeded in this regard, because we found not only the carbon layer prevented the sintering of the nanosized TiO_2 particles and keeping them at the nanosize, we can dope the P25 at a relative low temperature to make them conductive.

We found that this carbothermal reduction process converted semiconducting TiO_2 into highly conductive titanium oxy carbide (TiO_xC_y). At low temperatures (e.g., 700°C), carbon only substitutes part of the oxide and distorts the TiO_2 lattice to form $\text{TiO}_{2-x}\text{C}_x$ with only substitutional carbon. When the carbon doped TiO_2 is annealed at a higher temperature (1100°C), XRD and XPS results showed that TiO_xC_y , a solid solution of TiO and TiC , was formed, which displays different diffraction peaks and binding energies. It was shown that TiO_xC_y has much better electrocatalyst support than TiO_2 or $\text{TiO}_{2-x}\text{C}_x$.

Fig. 5 (a)-(f) show the morphologies of P25 untreated and thermally treated at different temperatures. After carbon coating process at 700°C , the amorphous TiO_2 crystallized and the mean size grows from the original 22 nm to about 35 nm (see Fig. 1(b)). Further annealing up to 1000°C , the particles only yield tiny growth

and are still in a range of 30–40 nm; no obvious sintering was detected and the shape of particles still appears spherical, shown in Figs. 5 (c) and 5 (d). When the annealing temperature was increased to 1100°C , some particles agglomerated and their sizes increased to about 55 nm, see

Fig. 5 SEM images of titanium oxide nanopowders obtained under different thermal treatments. (a) P25: original TiO_2 , (b) P25-700: P25 carbon coated at 700°C , (c) P25-700-900h: P25 carbon coated at 700°C and further annealed at 900°C , (d) P25-700-1000h: P25 carbon coated at 700°C and further annealed at 1000°C , (e) P25-700-1100h: P25 carbon coated at 700°C and further annealed at 1100°C , and (f) P25 annealed in air at 800°C . Annealing time was 4 hours for all samples.

Fig. 5(e). A sample of P25 was directly annealed in air at 800 °C for the same duration, resulting in a substantial growth of particle size (up 300 nm), as can be seen from Fig. 5(f). It is clearly shown that the carbon nanocoating is necessary to prevent severe sintering in the TiO₂ nanoparticles.

Electrochemical tests of thermally treated P25 TiO₂ were performed to investigate the electrochemical activity of different nanopowders, results of which are shown in Fig. 6. The anodic peak at 0.65 V and cathodic peak at 0.58 V in Fig. 6 (a) are associated with the oxidation and reduction of the surface oxide groups. The bigger double layer capacity in P25-700-1000h (carbon doping at 700 °C and annealing at 1000 °C), and -1100h can be attributed to the formation of TiO_xC_y since surface carbon coating is consumed during annealing. Oxygen evolution reaction (OER) was carried out to investigate the catalyst activity towards oxidation of water to generate molecular oxygen in acidic electrolyte medium, $2\text{H}_2\text{O} = 4\text{e}^- + 4\text{H}^+ + \text{O}_2$, and the onset potential for this reaction is a basic criterion to evaluate the efficiency of the catalyst.

Based on previous studies, the presence of defects at TiO₂ surface, *e.g.*, oxygen vacancies, is essential for water splitting. Undoped TiO₂ showed the worst OER activity, as can be seen in Fig. 6 (b). The sample has the highest onset potential and lowest current, which could be attributed to its low surface defects. Introducing carbon doping and further annealing can create oxygen vacancies as predominant defects, as confirmed by the formation of reduced Ti. Annealed at 1100 °C, the

Fig. 6 Electrochemical characterization: (a) cyclic voltammograms of undoped and doped TiO₂ in N₂ saturated 1.0 M H₂SO₄ with scanning rate at 50 mV/s, (b) OER results of the corresponding nanopowders in N₂ saturated 1.0 M H₂SO₄ with scanning rate at 5 mV/s. (c) Typical ORR results of TiO_xC_y nanopowders in O₂ saturated 1.0 M H₂SO₄ with scanning rate at 5 mV/s, with or without Pt electrocatalyst.

carbon coated TiO_2 has almost completed the transformation from TiO_2 to TiO_xC_y , which has the most oxygen vacancies. As a result, the catalyst showed the best OER catalytic activity, with the lowest OER onset potential at 1.45 V. The TiO_xC_y (curve 5) in Fig. 6 (b) yielded a *ca.* 5 mA/mg_{catal.} current density at 1.6 V, therefore having a comparable OER activity to the perovskites (would not be stable) previously reported and further demonstrating the substantial OER activity of the titanium oxy carbide.

However, none of the materials exhibit oxygen reduction reaction (ORR) activity, as shown in Fig. 6 (c), in which large overpotentials and negligible currents were observed. To obtain ORR activity, Pt was deposited on the TiO_xC_y and typical ORR curves were obtained (Fig. 6(c)). An onset potential at *ca.* 0.85 V shows that the TiO_xC_y support is an excellent alternative support to the high surface area carbon black. Altogether, the catalyst Pt/ TiO_xC_y has both OER and ORR activities, demonstrating an effective bifunctional catalyst.

2. Ultra-low Pt loading on the support

The goal of this task was to develop a low loading but active Pt catalyst on carbon support. Pt is an expensive catalyst. To lower its loading is necessary to make the batteries competitive. Toward this goal we have worked on 1% weight loading and achieved the activity targets.

Two samples of catalysts of Pt/c- TiO_2 /CNTs were analyzed by a third party company, Luvak, Inc. for Pt content in the catalysts. In addition, a commercial sample from Sigma-Aldrich labeled as 1% Pt on activated carbon (catalog #205923) was also analyzed by Luvak. The catalysts were also tested for their electrochemical activity on the reduction of oxygen.

The results are listed in Table 1. All three samples have Pt loading less than 1wt%. The catalysts were tested for ORR in the electrolyte with 1M H_2SO_4 and 3M Li^+ at room temperature. The ORR activities at 0.75V are also given in the following Table. The activity of both catalysts reached or exceeded the target activity of 0.2 mA/cm²_{-Pt}.

Table 1 Pt weight loading and ORR activity

Pt catalysts	Pt loading (wt %)	ORR Activity (mA/cm ² _{-Pt})
Sample 1: Pt/c- TiO_2 /CNTs	0.85	0.20
Sample 2: Pt/c- TiO_2 /CNTs	0.90	0.21
Sample 3 (Sigma-Aldrich): Pt/C	0.95	-

The catalyst activity towards oxygen reduction and water oxidation is shown in Fig. 7 The catalyst showed an OER activity that reached the target. In this case, it is suspected that the oxide substrate played a role improving water oxidation on Pt.

Fig. 7. The results for Pt/C-TiO₂/CNT with 1wt.% Pt loading evaluated in 1.0M H₂SO₄ + 3M Li⁺, (a) the Tafel plots showing ORR activity of 0.2 mA/cm₂_{Pt} at 0.75V and (b) the linear polarization curve for OER with a 1.51V on-set potential on the same catalyst.

3. Bifunctional Pt/IrO₂ on support CNTs

The goal of this task was to develop a bifunctional catalyst for the aqueous electrolyte Li-Air battery. While Pt has OER activity, the surface oxidation makes it inefficient, especially at high potentials. Iridium oxide (IrO₂) has been found to be an active and stable OER catalyst at high current densities. Pt/IrO₂ as a bifunctional oxygen catalyst has been used in regenerative fuel cells, in which Pt serve for ORR and IrO₂ for OER. But such catalysts are often composed of large of IrO₂ particles (e.g., microns). We developed a unique thermal oxidation technique that can prepare the bifunctional oxygen catalysts with nanoscale size (see Fig. 8). More importantly, the bifunctional oxygen catalysts showed excellent performances. In addition, carbon black is often used as support that is easily oxidized. Therefore, it is also of interest to support the catalysts on c-TiO₂/CNTs.

With the thermal oxidation technique, we obtained nanosized IrO₂, measured to be 3.6±0.5 nm from image analysis. A high magnification image in Fig. 8(A) shows lattice spacing of the graphitic layers of CNTs and rutile IrO₂ at 0.34 and 0.26 nm, respectively. After deposition of Pt on IrO₂/CNTs, the morphology of IrO₂ does not show changes, as can be gauged from Fig. 8(B). XRD patterns showed that Pt now appears in the catalyst. Carefully examining the surface of the catalyst Pt/IrO₂/CNTs, there exist many round, darker black nanoparticles. These nanoparticles are believed to be Pt since stronger lattice diffraction occurs in metals than in oxides, giving the contrast. These nanoparticles are measured to have a size of 2.3±0.2 nm.

The prepared catalysts were put under electrochemical tests in a three-electrode cell. The CV plots of catalysts Pt/CNTs, IrO₂/CNTs and Pt/IrO₂/CNTs were presented in Fig. 9(A). The anodic peak at 0.66 V and cathodic peak at 0.58 V were associated with the redox reactions of surface oxide groups, which have been found in acid-treated CNTs. The anodic current occurred

beyond 1.4 V (*vs.* RHE) was assigned to water oxidation currents. IrO₂ was found to be electrochemical inert in the potential range 0-1.4V and have negligible contribution to the electrochemical surface area (ESA), while Pt/IrO₂/CNTs exhibits the typical peaks belonging to hydrogen ad/de-sorption on Pt surface. The ESA of Pt in the catalyst was obtained using the methods commonly accepted. The ESA in Pt/IrO₂/CNTs was obtained to be 905.7 cm²/mg Pt, close to the 996.2 cm²/mg Pt obtained for Pt/CNTs, indicating that Pt active surface area is large in both catalysts.

Fig. 8. TEM images of: (A) IrO₂/CNT, shown are a low and a high magnification images. The numbers on the right image are lattice spacing (in nanometers), with 0.34 nm for graphite and 0.26 nm corresponding to rutile IrO₂ crystalline plane (101). (B) Pt/IrO₂/CNTs, showing the round dark black dots as Pt nanoparticles (e.g., those indicated by arrows); no obvious morphological changes of the IrO₂ particles were observed.

The ORR activities of IrO₂/CNT, Pt/CNT and Pt/IrO₂/CNTs were plotted in Fig. 9(B). IrO₂/CNTs exhibits negligible catalytic activity and has no contribution towards ORR. Meanwhile, Pt/IrO₂/CNTs showed a similar ORR performance as Pt/CNTs with the same Pt loading, suggesting that IrO₂ has not affected Pt for catalyzing ORR. Linear sweep voltammetry (LSV) was conducted to record the OER performances of the three different catalysts. As shown in Fig. 9(C), Pt has some catalytic activity towards OER (all OER currents were capacitance-corrected), but is significantly lower when compared to that from IrO₂. The mass activity of IrO₂/CNTs at overpotential $\eta = 0.25$ V can reach 6 A/g IrO₂ without Ohmic correction, which are comparable or better than the 5 A/g IrO₂ and 3 A/g IrO₂ most recently reported in the literature. We found that by incorporating Pt with IrO₂/CNTs, a significantly higher current density can be

achieved than IrO₂/CNTs alone (96 mA/mg_{catal.} vs. 56 mA/mg_{catal.} at 1.6 V), which is also higher than the sum of IrO₂/CNTs and Pt/CNTs, indicative of that there may be a possible synergistic effect between Pt and the oxide IrO₂ for OER. It was argued that the downshift of *d*-band center of Pt on Pt/IrO₂ weakened the O_{ads} bound to the catalytic surface, favoring water dissociation to form oxygen. It decreases the coverage of O₂/O_{ads} on the catalyst surface and thus, increases the available active sites.

Fig. 9. Electrochemical characterizations of catalysts. (A) cyclic voltammograms of Pt/CNTs, IrO₂/CNTs and Pt/IrO₂/CNTs; (B) polarization curves of ORR on Pt/CNTs, IrO₂/CNTs and Pt/IrO₂/CNTs; (C) polarization curves of OER on Pt/CNTs, IrO₂/CNTs and Pt/IrO₂/CNTs.

Fig. 10. Electrochemical characterizations of catalyst Pt/IrO₂/CNTs before and after 1000 cycles. (A) Cyclic voltammograms; (B) Polarization curves of ORR; (C) OER activities.

Accelerated cycling test was performed by applying 1000 potential cycles from 0.6-1.5 V (vs. RHE) in N₂-bubbled 1.0 M H₂SO₄. As shown in Fig. 10(A), Pt in this catalyst only suffered very small surface area loss, verified by negligible change in H ad/de-sorption region of 0.05-0.4 V before and after the potential cycling tests. In contrast, ESA of Pt/CNTs suffered a much larger loss after 1000 cycles, from 996 to 230 cm²/mg_{Pt}, leading to a severe degradation of ORR performances. Fig. 10(B) showed that the ORR half-wave potential shifted 40 mV negatively,

indicative of an ORR activity loss, but it's much smaller than that of the Pt/CNT catalyst (*ca.* 300 mV shift). We attributed the loss of the Pt to its easy degradation on carbon support due to weak interaction between the metal and carbon. We have previously shown that Pt severely degrades on carbon black (Vulcan-XC72) in sulfuric acid, but it can be significantly improved by supporting the Pt on a conducting titanium suboxide coated on the CNTs. The fact that oxide IrO_2 is involved may have similarly improved the stability of Pt, although perhaps to lesser degree since iridium oxide in this case is a not a continuous film and some Pt is in contact with carbon. Decrease in ORR activity is also attributed to the formation of a thin Pt-oxide layer at high potentials.

In the OER region (1.4-1.6 V), the CVs showed changes of the catalyst $\text{Pt/IrO}_2/\text{CNTs}$ after cycling. It was determined that the OER current density decreased from 105 to 86 $\text{mA/mg}_{\text{catal.}}$ at 1.6 V (see Fig. 10(C)). Oxygen is split off from water on IrO_3 with Ir in the hexavalent state, which was formed by two consecutive deprotonation steps from $\text{IrO}(\text{OH})_2$. Meanwhile, IrO_3 may corrode into electrolyte as IrO_4^{2-} ion and lead to direct OER activity loss. Formation of poorly conductive and catalytically inactive Pt oxide species may also contribute to the loss of OER activity. Nevertheless, the results showed a relatively stable performance of the bifunctional catalyst in sulfuric acid electrolyte.

The 1 wt%Pt catalysts with the IrO_2 were also tested in H_2SO_4 with Li ions present. The results are shown in Fig. 11. Both the ORR and OER activities reached the technical targets.

Fig. 11 The series result for $\text{Pt/IrO}_2/\text{C-TiO}_2/\text{CNT}$ with 1wt% Pt loading evaluated in 1M H_2SO_4 + 3.0M Li ions, the Tafel plots for ORR and the linear polarization curve for OER.

4. Carbon nanotube array for cathodes

The goal of this task was to develop a hierarchical array electrode that can improve mass transfer of different species and electronic conduction. The task was focused on growing aligned CNT

arrays (CNTAs) on a carbon backing paper. By developing an electroplating technique, we were able to deposit Ni nanocatalyst on the carbon fibers in carbon paper. A follow-on plasma assisted chemical vapor deposition process was used to grow aligned CNTAs.

The carbon fiber paper was sputter coated with 50 nm thick Cr to improve electrodeposition of Ni catalyst. It was then fixed in a plating frame and immersed in an electroplating bath. The bath contained 5 mM NiSO_4 and H_3BO_3 solution as electrolyte. Based on the plating area (5.06 cm^2), a constant current was set between 5.06 and 32 mA, and applied for 15 to 20 seconds. As a result, Ni nanoparticles were deposited on Cr coated carbon paper.

The CNTAs were grown using a PECVD process. The carbon paper substrates were loaded into a PECVD system equipped with parallel filaments to heat the substrate and assist plasma generation. During PECVD growth, a DC power supply provided a total of 12.0 A current for the filaments. At the same time, another power supply (Advanced Energy, MDX1100) maintains an electric field (800~900 V at 0.4~0.5 A) between the anode and the sample stage (cathode). The PECVD process begins with pumping down the system to a base pressure of 10^{-6} Torr using a turbo pump backed by a mechanical pump. The chamber is then backfilled to 40~50 Torr of ammonia and acetylene. Flow rates for the backfilling process are 60 ml/min NH_3 and 23 ml/min C_2H_2 at standard conditions. The PECVD growth conditions were maintained for 15 minutes at a temperature of 600~650°C.

SEM images (Fig. 12) were recorded to characterize the CNTAs. The site density, diameter, and tube length were obtained for each CNTA. It was found that, depending on deposition conditions, the CNTAs can be grown to 25 microns, which were the target for the current application. The site density can be controlled to 10^7 to 10^9 / cm^2 . The lower density was preferred because one aim was to increase species mass transfer in the electrode. At low density, there is more space between the CNTs and thus it provides room for easy movement of species.

Fig. 12 Selected EM images from 6 nanotube arrays. The image 892-4 shows top view of nanotubes, allowing calculating nanotube site density. The image 886-3 presents nanotube diameter, and the images 886-2, 888-2, 891-2, and 893-2 present nanotube length and morphology.

Battery Development Achievements

1. Hierarchical layered buckypaper cathodes

We have developed a multi-layer cathode with materials of different length scales, from a few nanometers to tens of microns. The air cathode consists of an active catalyst layer, a transition layer and the backing layer of Toray[®] carbon paper, which are laminated together (Fig. 13). The preparation of Pt/CNT catalysts (CNTs from NanoLab, 50 ± 15 nm) includes depositing Pt nanoparticles (~ 3 nm) on the CNTs. The air-breathing cathodes were prepared as follows. 10 mg carbon nanofibers (CNF ~ 150 nm in diameter and ~ 10 μ m long, Pyrograf, PR-24-Xt-LHT) and 10 mg Pt/CNT catalysts (5wt.% Pt) were dispersed under sonication in *ca.* 8 mL ethanol in two separated beakers. First, the CNF ethanol dispersion was vacuum filtered through a 0.4 μ m Millipore ISOPORE[®] membrane (47 mm diameter). Then filtration of the 10 mg Pt/CNT ethanol dispersion was done on the same Millipore membrane covered with the CNF layer.

Fig. 13. SEM images of (A) a cross-section of Pt/CNT buckypaper layer on a CNF transition layer, (B) surface morphology of (A), (C) a cross-section of Pt/CB on a CNF transition layer, and (D) surface morphology of (C).

This produced a buckypaper of catalyst layer based on the Pt/CNTs. The resulted total thickness of this buckypaper layer is *ca.* 60 μm . This buckypaper was laminated onto a Toray carbon paper (Fuel Cell Store, TGP-H-030) at 140 $^{\circ}\text{C}$ and a pressure of 2 atm, with the CNF side on the Toray paper. For performance testing comparison, repeating the same process using 5 wt.% Pt/C E-TEK catalysts produced the catalyst layer with the carbon black (CB) structure. Again, the transition layer is CNF. We found that the transition CNF layer can serve well to support both the Pt/CNT and the Pt/CB catalyst layers. The whole cathode thickness after hot press was at *ca.* 150 μm . A photo of the original cathode is shown in Fig. 14.

Fig. 14. Cathode showing the Toray paper and the laminated catalyst layer (buckypaper).

Performance test were conducted for the cathodes assembled with a protected Li anode from MaxPower. The battery has sulfuric acid as the catholyte and a large active electrode area at 10 cm^2 . It is demonstrated that sulfuric acid can achieve high discharging current densities while maintaining relatively high cell potentials. The cell with Pt/CNTs showed a much better performance than with Pt/CB at high current densities. The Li-air battery with Pt/CNTs achieved a discharging capacity of 306 mAh/g and a cell voltage of 3.15 V at 0.2 mA/cm^2 . The corresponding specific energy is 1067 Wh/kg based on the total weight of the sulfuric acid. Slow decrease in performance was observed, but it can be recovered by refilling the cell with new electrolyte after continuous discharging of more than 75 hours. A charge-discharge experiment at 0.2 mA/cm^2 showed that the cell was rechargeable with a capacity of more than 300 mAh/g, Fig. 15.

Fig. 15. Battery performance Left: Discharge curves at different discharge current densities in 1.0 M H_2SO_4 . Middle: Discharge with the buckypaper cathode showing capacity. Right cycling at 0.2 mA/cm^2 at 25 $^{\circ}\text{C}$ and in ambient air, using dilute H_2SO_4 (10 mM) as catholyte.

2. CNT array cathodes

The CNT array cathodes are made with the CNTAs. These cathodes feature a sparse layer of aligned CNTs on the carbon fibers on the surface of the supporting carbon paper. As a result, there is no hot pressing needed, i.e., the CNTAs and the carbon paper backing has already made together (see Fig. 16). It can be clearly seen that the CNTAs grew on each of the fibers exposed on the surface of the carbon paper. The fibers deep inside the carbon paper were found to have no obvious CNTs grown on them. This is important because only the CNTAs at the surface will take effect for electrochemical reactions.

The total thickness of the cathode (CNTAs + carbon paper) is at about 120 microns, which combines with 100 microns of the backing carbon paper and 20 micron length of CNTAs. The carbon paper has a porosity of 80% percent, with carbon fibers of about 10 microns in diameter on average. With a population density of $10^8/\text{cm}^2$ and diameter of 100 nm, the CNTs would only cover 1.77% fibers in terms of areas. Consequently, the total porosity is 99.65% in term of the geometric cathode areas in the active layer (CNTAs). This highly porous nanostructure should significantly enhance the transport of reactant species to the reaction sites.

Performance tests were conducted in LiOH electrolyte with ambient air (Fig. 17). The sparse CNTAs not only provide effective pathways for reacting species, but also show significantly high catalytic activity, which was found to be comparable to that of supported Pt electrocatalyst. That means the battery does need Pt as a catalyst. The high activity of the CNTAs is attributed to the rich graphene edges exposed on the CNT surface and nitrogen doping. Hybrid Li-air batteries with such cathode have shown a consistent discharging capacity of 710 mAh/g and a specific energy of 2057 Wh/kg at $0.5 \text{ mA}/\text{cm}^2$. Stable charge-discharge cycling at $0.5 \text{ mA}/\text{cm}^2$ showed an average potential difference of 1.35 V, indicative of relatively small overpotential and high round trip efficiency (71%).

Fig. 16 CNTA cathodes showing the arrays as catalyst layer and the carbon paper backing (partial view in (B)).

Fig. 17 Top: Battery cycling performance at 0.5 mA/cm². The voltage difference increased from 1.35 V to 1.58 V after 63 hours, showing relatively small overpotential and high round trip efficiency. Bottom: Performance of discharge at different current densities, with inset showing small Ohmic drop.

3. Pouch prototype Li-Air battery

A schematic diagram of the cell can be seen from Fig. 18. The pouch cell has protected (sealed) anode that was fabricated at MaxPower, interfacing with the cathode through an Ohara ceramic membrane for Li ion conduction. The air cathode was made at Missouri. MaxPower developed and designed procedures for integrating the anode and into a pouch cell. The cell can be described by the following:

MaxPower's Protected Anode	0.5 M Li ₂ SO ₄ 3 M H ₂ SO ₄	Missouri S&T's Air cathodes
-------------------------------	---	--------------------------------

Fig. 18 Schematic diagram of the Li-air battery with sulfuric acid catholyte. Sealed anode contains a Li foil, an aprotic buffer, and the top ceramic membrane.

Figs. 19 and 20 show the pouch cells fabricated by combining the protected anode fixture with an air cathode in a heat sealed pouch. The anode and cathode were separated by a Whatman glass fiber filter saturated with 0.5 M Li_2SO_4 in 3 M H_2SO_4 . Stability was first determined by measuring the OCV with the results given below.

Fig. 19. Front and back of the Li-air cell.

Fig. 20. Three Li-air cells built for testing.

- The OCV of a single cell was 4.02 V.
- For two cells in series, the OCV was 7.84 V.
- For three cells in series, the OCV was 10.02 V.
- For three cells in parallel, the OCV was 3.76 V.

The pouch Li-air cells were tested as a power source for a few electronic devices, including a toy car driving (Fig. 21) and cell phone charging. The batteries work as they were supposed to and further development is needed to make them large capacity and closer to commercial applications.

Fig. 21. Three Li-air cells in parallel used to power a remotely operated toy car.

Products resulted from the project

Patents

1. Xing, Y., Huang, K. and Li, Y.F., “Cathodes for Lithium-Air Battery Cells with Acid Electrolytes”, US Patent Application Number 13949875. July 2013.
2. Provisional patent: Ceramic membrane stabilization with Li_2SO_4 added to the H_2SO_4 electrolyte, filed by MaxPower, 2012
3. Non-disclosure: Modifying the surface of ceramic Li ion conducting membranes for aqueous Li-Air batteries. University of Missouri, 2013.

Journal publications

1. Li, Y., Huang, Z-P, Huang, K., Carnahan, D., and Xing, Y.*, “Hybrid Li-Air Battery Cathode with Sparse Carbon Nanotube Arrays Directly Grown on Carbon Fiber Paper”, Energy & Environmental Science, published online 2013. DOI: 10.1039/C3EE41116H
2. Huang, K., Li, Y. and Xing, Y.*, “Increasing Round Trip Efficiency of Hybrid Li-air Battery with Bifunctional Catalysts”, Electrochimica Acta, 103, 44-49, 2013.
3. Xing, Y.*, “Hybrid Li-Air Batteries”, Preprints - American Chemical Society, Division of Energy & Fuels, 58(1), 563-564, 2013.
4. Huang, K., Li, Y. and Xing, Y.*, “Carbothermal Synthesis of Titanium Oxy Carbide as Electrocatalyst Support with High Oxygen Evolution Reaction Activity”, Journal of Materials Research, 28, 454-460, 2013.
5. Li, Y., Huang, K. and Xing, Y.*, “A Hybrid Li-air Battery with Buckypaper Air Cathode and Sulfuric Acid Electrolyte”, Electrochimica Acta, 81, 20–24, 2012.
6. Huang, K., Sasaki, K., Adzic R.R., and Xing, Y.*, “Increasing Pt oxygen reduction reaction activity and durability with a carbon-doped TiO_2 nanocoating catalyst support”, Journal of Materials Chemistry, 22, 16824-16832, 2012.
7. Liu, H. and Xing, Y.*, “Influence of Li ions on the oxygen reduction reaction of platinum electrocatalyst”, Electrochemistry Communications 13, 646-649, 2011.

Journal papers to be submitted

8. Owen Crowther, Yunfeng Li, Fausto Croce, Mark Salomon, Yangchuan Xing, “Stability of the Glass Ceramic Membrane in H_2SO_4 Solutions for Li-Air Batteries”, to be resubmitted, 2013.
9. Yangchuan Xing and Mark Salomon, “Sulfuric Acid as an Electrolyte for Hybrid Li-Air Battery”, to be submitted, 2013.
10. Yunfeng Li, Kan Huang, Litao Yan, Yangchuan Xing, “Catholyte Acidity on the Performance of Aqueous Li-air Batteries”, to be submitted, 2013.
11. Kan Huang, Yunfeng Li, Litao Yan, Yangchuan Xing, “Platinum-niobium oxide-carbon nanotubes as electrocatalyst for the oxygen reduction reaction”, to be submitted, 2013.

Conferences

1. Xing, Y., “Hybrid Li-Air Batteries”, 245th ACS National Meeting and Exposition April 7-11, 2013, New Orleans, Louisiana.
2. Li, Y., Huang, K. and Xing, Y., “Hybrid Li-Air Battery with Sulfuric Acid Electrolyte and Buckypaper Air Cathode”, AIChE 2012 Annual Meeting, Pittsburg, PA, Oct. 28-Nov. 2, 2012.
3. Huang, K., Li, Y. and Xing, Y., “Carbon-Doped TiO₂ Nanocoating As Durable Pt Electrocatalyst Support”, AIChE 2012 Annual Meeting, Pittsburg, PA, Oct. 28-Nov. 2, 2012.
4. Li, Y., Huang, K. and Xing, Y., “Hybrid Li-Air Battery with Sulfuric Acid Electrolyte and Buckypaper Air Cathode”, 222nd Electrochemical Society Meeting (PRiME2012), Honolulu, Hawaii, Oct. 11th, 2012.
5. Xing, Y., Li, Y., and Huang, K., “Rechargeable Dual-Electrolyte Hybrid Li-air Battery”, The 3rd International Conference on Applied Energy, Suzhou, China, July 5-8, 2012.