# Bi-Functional Oxygen Electrodes – Challenges and Prospects

*by S. R. Narayan, Aswin K. Manohar, and Sanjeev Mukerjee*

In rechargeable metal-air batteries and regenerative fuel cells, the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) both occur on the same electrode (usually the positive electrode) during the charge and discharge processes, respectively. Such an electrode is termed a "bi-functional" oxygen electrode. Bi-functional electrodes are used in aqueous and non-aqueous electrolytes. The reactions occurring at a bi-functional oxygen electrode during charge and discharge are listed in Fig. 1.

The materials used in the bi-functional oxygen electrode should be good electro-catalysts for both the oxidation and reduction reactions of oxygen and should be chemically stable over the wide range of potentials experienced during charge and discharge. Further, the electrodes should be sufficiently robust to resist the mechanical and compositional changes occurring during repeated cycling. In some cases, the products of the oxygen reduction reaction are solids that must be accommodated within the structure of the electrode. These solid products must remain accessible for further electrochemical reaction. In other cases, the soluble substances produced at the surface of the electrode need to be transported into the electrolyte phase during charge and discharge. Meeting such diverse and demanding requirements has been a formidable challenge. However, the realization of such electrodes presents immense potential in terms of designing power sources with specific energy densities that are several times larger than the state-of-art. Metal-air rechargeable batteries using zinc, iron, metal hydrides or lithium as the negative electrode have theoretical specific energy values ranging from 1000 to 11000 W-h/kg because the oxygen needed for the reaction can be drawn from the surroundings and does not add to the mass of the battery. However, these (potentially) high-energy battery systems remain elusive in practice because of the lack of suitable bi-functional oxygen electrodes. Regenerative hydrogen/oxygen fuel cells based on a polymer electrolyte membrane (PEM), although quite efficient, rely on expensive precious-metal-based catalysts to achieve bi-functional capability. The large-scale commercial deployment of regenerative fuel cells is presently predicated upon a significant reduction in the cost of the catalysts, which has again remained elusive. Current research on bi-functional oxygen electrodes is motivated by the above challenges.

## Voltage Losses from Charge Transfer at the Bi-functional Oxygen Electrode

A significant portion of the voltage losses during charge and discharge of metal-air batteries occurs on the bi-functional air electrode. In an iron-air battery developed by the Swedish National Development Company, about 70% of the total voltage loss was reported to occur on the bi-functional air electrode.[3] Rechargeable metal-air battery technologies have been limited by their low power-density and poor round-trip energy efficiency. Power densities based on the electrode area are usually about 50-60 mW/cm$^2$ at a round-trip efficiency of 70%.[4-6] In PEM regenerative fuel cells, while operating at a high power density of 500 mW/cm$^2$, the round trip energy efficiency can be less than 50%.[7] A major fraction of the voltage loss results from the sluggish kinetics of charge transfer during the OER and ORR. These reactions proceed step-wise through the sequential breaking and formation of strong chemical bonds such as the O-H bond, and the generation of adsorbed species on the surface of the electrode. Tailored electrocatalyst materials are necessary to lower the activation barriers and reduce overpotential, as the reaction pathways adopted are dependent on the electrocatalyst materials.

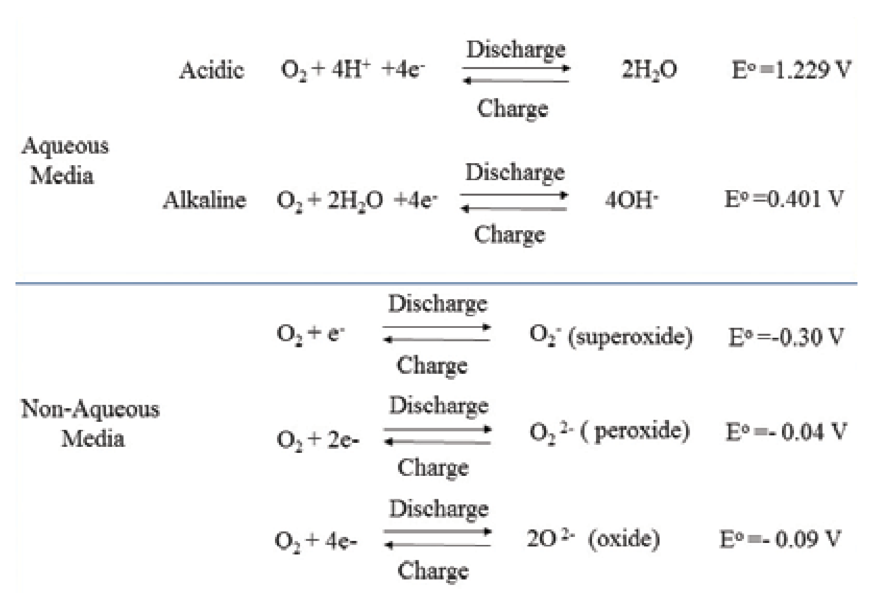

**Fig. 1.** *Reactions occurring at a bi-functional oxygen electrode. (Electrode potentials in non – aqueous media are from References: [1-2])*

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In aqueous media, the electrochemical reduction of oxygen occurs by three possible pathways: (1) direct four-electron reduction, (2) a series pathway with successive two-electron electrochemical steps through a peroxide intermediate, and (3) a two-electron reduction to peroxide followed by the chemical decomposition of peroxide. For platinum-based catalysts, the direct four-electron pathway is adopted in acidic media whereas a series pathway is more likely in alkaline media.[8-9] Carbon based catalysts (under acid and alkaline conditions) tend to support the two-electron reduction to peroxide followed by desorption of peroxide from the surface. Consequently, a peroxide decomposer such as silver or a transition metal oxide is needed in conjunction with carbon to achieve the four-electron reduction of oxygen. In non-aqueous media, oxygen reduction occurs through sequential outer-sphere reactions involving the formation of the superoxide, the peroxide and ultimately the oxide (Fig. 1).

The oxygen evolution reaction in aqueous media on transition metal oxides and noble metal oxides occurs via formation of the M-OH bond arising from the interaction with water or hydroxyl ions, followed by electrochemical transformation to M-O bonds, which lead to the desorption of the oxygen molecule by recombination of the surface oxo-species. Consequently, an oxide surface with optimal metal-oxygen bond strength is necessary for facile oxygen evolution. In acidic media, iridium oxide and ruthenium oxide are particularly active, while in alkaline media, nickel and cobalt oxides exhibit good electro-catalytic activity.

Oxygen reduction in non-aqueous media typically does not need a catalyst. However, the cations in the electrolyte strongly influence the reduction mechanism of oxygen. Electrolytes with larger cations such as tetrabutylammonium show a reversible $O_2/O_2^-$ redox couple, in contrast to those containing the smaller Li (and other alkali metal) cations, where an irreversible one-electron reduction of $O_2$ to $LiO_2$ occurs. This process is followed by the decomposition of $LiO_2$ to $Li_2O_2$ and further reduction to $Li_2O$. These metal oxides passivate the electrode surface, making the processes irreversible.[10-11] The product distribution is also influenced by the nature of the electrode surface. Electrodes with strong affinity for oxygen such as ruthenium tend to form oxide products, while gold tends to form the peroxide.[12] Electrolyte stability is a major issue in non-aqueous media. Conventional alkyl and cyclic carbonates used in lithium batteries are unstable during oxygen reduction, and lead to the formation of insoluble lithium carbonates. Consequently, dimethoxyethane and glymes are more suitable as solvents. The insulating nature of the products also increases the overpotential for the oxygen electrode reactions. Oxygen is evolved readily from lithium peroxide, but the oxidation of lithium oxide is irreversible and requires an electrocatalyst.[13] The mechanism of oxygen reduction and oxygen evolution in non-aqueous electrolytes is a topic of current research.

## Electrocatalyst Materials for Regenerative Fuel Cell Electrodes

In acidic media, or in contact with proton conducting electrolytes such as Nafion™, only platinum, gold, and iridium are stable under bi-functional operation. Therefore, unitized regenerative fuel cells (URFC) using proton exchange membrane electrolytes need to use noble metal catalysts at the positive and negative electrodes. Mixtures consisting of 40% platinum and 60% iridium oxide have been successfully used in unitized regenerative fuel cells with Nafion. This mixture combines the electrocatalytic activity of platinum for oxygen reduction with the extraordinary activity of iridium oxide for oxygen evolution. Usually, the precious metal blacks or oxides are used without any other support because carbon supports are readily oxidized during oxygen evolution.[14-15] The precious metal blacks are usually prepared by the Adam's method involving the nitrate fusion of the salts of the noble metals, followed by washing with water.[16]

In combinatorial studies on electrocatalysts, Mallouk *et al.* have investigated different compositions of Pt, Ru, Ir, Os, and Rh for bi-functional operation.[17-18] A catalyst rich in platinum and ruthenium, with the composition $Pt_{4.5}Ru_4Ir_{0.5}$ was found to have the best catalytic activity and stability (resistance to anodic dissolution).[18] The use of ruthenium oxide and iridium oxide mixtures has been found to be promising for improving oxygen evolution activity.[19] High durability and reduced precious-metal loadings can be achieved by using the nano-structured thin film configuration (NSTF) developed by 3M Corporation.[20] NSTF catalysts were found to perform better than the precious metal blacks for oxygen evolution and oxygen reduction for as long as 4600 hours without failure.[21] The NSTF based Pt-Ir and Pt-Co-Mn catalysts, when used at less than 10% of typical catalyst loadings, were reported to meet or exceed the performance of precious metal blacks. Reduced titanium oxides have also been reported to provide a stable catalyst support.[17,22-23] A Pt-Ru-Ir catalyst supported on niobium-doped titanium oxide, $Ti_{0.9}Nb_{0.1}O_2$, was found to have the highest level of stability and catalytic activity in a combinatorial study involving various metal catalysts and titanium supports.[17-18] Typically, the current collectors and separator plates in the URFC stack have to be made of platinized titanium or niobium sheets and foams to resist corrosion, resulting in high cost of URFCs. Consequently, achieving high current density combined with high efficiency is critical to reduce the overall cost of URFCs. While separate fuel cell and electrolyzers (termed "discrete" as opposed to the "unitized") allow for independent optimization and flexibility with the system design, the impact of this discrete configuration on reducing cost has not been significant for acidic systems. Recent advances in alkaline ion-exchange membranes suggest the prospect of regenerative fuel cells in which non-precious metal catalysts can be used.[24]

## Electrocatalysts for Metal-Air Batteries

Metal-air rechargeable batteries such as the zinc-air, iron-air, and metal hydride-air systems require bi-functional air electrodes to operate in concentrated potassium hydroxide electrolyte. Lithium-air rechargeable batteries using both aqueous and non-aqueous electrolytes are being developed. In aqueous alkaline media, the material options expand to the use of non-precious metals and metal oxides. For oxygen reduction, carbon combined with silver or manganese dioxide has been used in alkaline fuel cells for many years.[25] Similarly, carbon when mixed other transition metal oxides of the perovskite and spinel families has shown good electrocatalytic activity. In these catalysts, carbon is the primary catalyst that supports the reduction of oxygen to peroxide. The transition metal oxides and silver are by themselves very poor electrocatalysts for oxygen reduction, but are very effective in decomposing the peroxide generated on the carbon. Consequently, carbon in conjunction with silver or transition metal oxides serves as a viable electrocatalyst for oxygen reduction.[26-27]

Although carbon/metal oxide composites are useful in reducing the overpotential for oxygen reduction, these catalysts are unstable under the conditions of oxygen evolution because the oxidation of carbon occurs under these conditions (Eq. 1).[28]

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \qquad E^o = 0.207V \qquad (1)$$

Thus, a slow loss of electrode performance is to be expected during cycling, and this is usually followed by excessive electrolyte flooding of the air electrode. While high-surface area carbons are generally unstable under the conditions of oxygen evolution, graphitic carbons with lower surface area are found to be more resistant to oxidation.[29] Graphitized carbon supports have been shown to improve the stability of zinc-air battery electrodes.[30-31] While the graphitization treatment improves the stability characteristics during oxygen evolution, the decrease in the active area of the catalysts with graphitization leads to reduction in the catalyst activity for the ORR. For applications that exceed 300-500 hours, carbon materials must be avoided in the oxygen evolution layer. More recent results suggest that graphite is the preferred carbon additive for extending the life of the bi-functional electrode. It is not yet clear if the recent developments in nitrogen-doped carbons offer any advantage with respect to their oxidative stability.

Metal oxides of the perovskite, spinel, and pyrochlore structure have shown promise as stable catalysts in alkaline media. They not only serve to decompose peroxide during oxygen reduction, but are also catalytically active for the oxygen evolution reaction.[32-33]

The best-studied perovskites (general formula $ABO_3$) are the cobaltates, nickelates and manganates, which contain the rare-earth elements (lanthanum and neodymium) in the A site of the perovskite. To improve the conductivity of these perovskites, the A site is often substituted partially with calcium, barium or strontium. This doping results in a higher oxidation state for the transition metal in the B site or an increase in concentration of oxygen vacancies. Examples of typical compositions are $La_{0.6}Ca_{0.4}CoO_3$ and $La_{0.5}Sr_{0.5}CoO_3$. The strongly-bonded oxygen framework created by the rare earth elements, provides a stable host for the transition metal ions, and resists oxidative degradation. High-surface area materials in nano-crystalline form can be prepared by the auto-combustion of gels prepared (by sol-gel methods) from metal nitrates with citric acid. The oxide materials thus produced are subjected to further heat treatment in the temperature range of 400–700 °C. Alternately, thin films of desired composition can be prepared on a nickel substrate by direct thermal decomposition of the nitrates in air or by pulsed laser deposition. Mixed-metal perovskites of the type $AA'(BB')O_3$ (e.g., $La_{0.6}Ca_{0.4}Co_{1-x}Mn_xO_3$) present the opportunity to tune the activity for oxygen reduction and oxygen evolution by changing the composition of the metals.[32,34]

The onset potential for oxygen reduction on perovskite-carbon composites is in the range of 0.0 to −0.1 V vs. the mercury/mercuric oxide (MMO) electrode.[26] This range of potentials is 0.4 V negative to the standard reduction potential for the oxygen reduction reaction. Also, this low onset potential is close to the standard reduction potential for the oxygen/peroxide couple in alkaline media ($E^o = -0.065$ V), confirming the process of formation of peroxide on carbon as the primary reaction. Of the perovskite-carbon composite catalysts for oxygen reduction, the best activity is exhibited by the manganese rich materials with activity numbers of about 22 mA/mg at 0 V vs. the normal hydrogen electrode (NHE) in 1 M potassium hydroxide. The oxygen reduction activity of carbon-perovskite composites has been correlated with the ability of the perovskite to decompose peroxide.[35-36] In some perovskites, the direct electrochemical reduction of hydrogen peroxide has been studied.[37] Doped lanthanum nickelate (both $LaNiO_3$ and $La_2NiO_4$) and lanthanum cobaltate have shown excellent stability and activity towards oxygen reduction in the presence of carbon. Perovskite catalysts have also been employed as oxygen evolution catalysts. Typical oxygen evolution activity on perovskite catalysts is about 5 mA/mg at 750 mV vs. NHE.[32] Cobalt and nickel based materials are generally more active, while manganese tends to reduce oxygen evolution activity.

Transition metal oxides of the spinel structure containing nickel and cobalt are promising because of their low overpotentials for oxygen evolution and oxygen reduction (with carbon). $NiCo_2O_4$ is the most stable towards oxygen evolution and is one of the preferred catalysts for alkaline water electrolysis. Although $Co_3O_4$ has been widely studied, it is not as stable as $NiCo_2O_4$ under long-term oxygen evolution tests. Tseung *et al* have reported on the effect of preparative methods, electrode composition and crystal structure on the electrochemical properties of the Ni-Co-O catalysts. The optimal catalyst composition was observed to be 2Co:1Ni and the best ORR performance was obtained by synthesizing an oxide in spinel form by heat treating the catalyst in air at 400 °C.[38] We have observed about 15 mA/mg at 750 mV vs. NHE on nickel cobalt oxide spinel catalysts in 1 M potassium hydroxide.

Metal oxides with the pyrochlore structure have also shown good catalytic activity as bi-functional air electrodes.[39] However, these catalysts uniformly contain some precious metals. Shukla *et al* have reported the stable operation of an iron-air battery using air electrodes containing lead-iridium and lead-bismuth-ruthenium pyrochlore oxide catalysts. At 7.5 mA/cm$^2$, the overpotential for the OER and ORR on the lead-iridium oxide based air electrode was about 200 mV and 350 mV, respectively.[40-41] The electrode was operated using pure oxygen in the ORR mode and no electrode deterioration was observed in 120 cycles. Similar highly-active lead-iridium pyrochlore oxides were also reported by ten Kortenaar *et al*.[42] Bismuth ruthenate is among the most stable pyrochlore oxide material that has been reported.[43] Yeager *et al* have used ionically conducting polymers and anion exchange membrane layers to improve the stability of air electrodes using pyrochlore catalysts.[39,44] These layers inhibit the diffusion of metal ions from the air electrode into the electrolyte. Consequently, an increase in the oxygen evolution activity of a bi-functional lead-ruthenium pyrochlore catalyst with the protective layer has been observed.[39,44]

Recent developments in nitrogen-doped carbon materials have shown very promising oxygen reduction performance in acidic and alkaline media comparable to that of platinum.[45-48]

## Electrode Structure

The structure of a bi-functional air electrode must include two separate zones for oxygen reduction and oxygen evolution, as these reactions usually require different catalysts (Fig. 2).

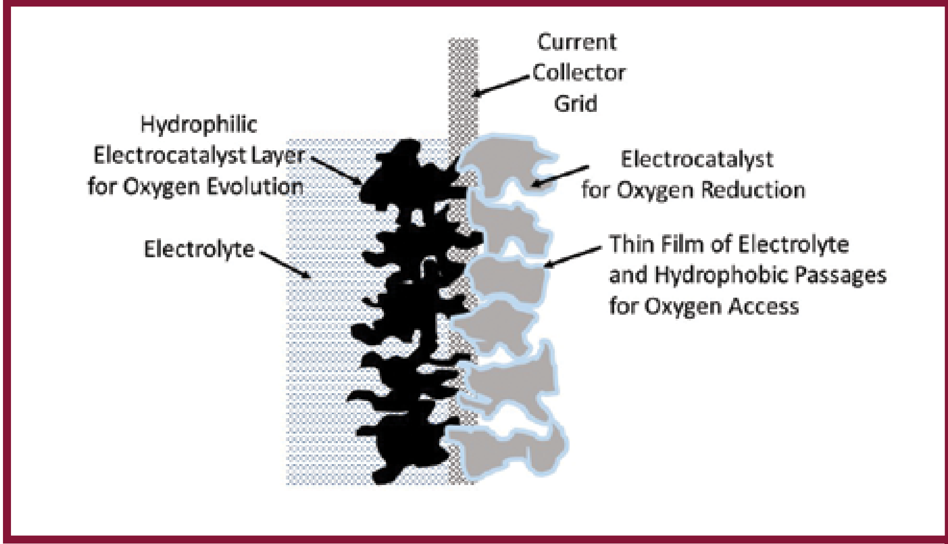

**Fig. 2.** *Layered structure of the bi-functional air electrode.*

These zones (or layers) also have different porosity and wetting characteristics. The zone supporting the oxygen reduction reaction must be semi-hydrophobic, highly porous (for oxygen to diffuse into the active layer), and have an extended layer of a thin film of electrolyte just like a fuel cell electrode. Hydrophobicity is achieved by the addition of Teflon™ to the extent of 15–30 weight percent. On the other hand, the zone that supports the oxygen evolution reaction must be hydrophilic and completely wetted by the electrolyte. The hydrophilicity prevents the sticking of gas bubbles and blockage of the surface to the electrolyte. The current collector is electrically connected to both zones and should be chemically stable under the conditions of the oxygen evolution reaction. The separation of the zones is also necessary so that the carbon based catalysts used for oxygen reduction are minimally impacted during the oxygen evolution process. These electrodes are fabricated by pressing on the active layers onto either side of the current collector, typically a nickel mesh. The layers are

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compressed under heat and pressure with binders to form an integrated structure with a low electrical resistance. Delamination of the layers can occur with oxygen evolution because of gas bubbles exerting pressure or causing erosion of the loosely bound particles. Some of the engineered structures described in various patents carry multiple layers, often with a gradient in wettability, or including additives that prevent the dissolution of the oxygen reduction catalysts. Often, an additional layer containing PTFE is bonded to the outside of the electrode structure to prevent electrolyte accumulation and blockage of pores on the exterior surface of the oxygen reduction zone.

In non-aqueous bi-functional electrodes such as those used in lithium-air batteries, hydrophilic and hydrophobic criteria do not apply. Solid products are generated from the electrochemical reduction of oxygen. The porosity of the electrode must be adjusted to accommodate the reaction products while still permitting access of oxygen into the electrodes. A combination of carbon black and polyvinylidene fluoride binder are impregnated on a nickel or aluminum foam substrate to form a positive electrode. Moisture access and loss of organic electrolyte must be prevented and hence most experiments on these cells are performed in controlled environments in a dry box, with oxygen instead of air. Thus, the design of a practical bi-functional electrode for non-aqueous electrolytes continues to be an interesting topic for research and development.

## Carbonation of the Electrolyte

When a bi-functional air electrode is operated using atmospheric air as the reactant, the carbon dioxide present in air reacts with the alkaline electrolyte, forming carbonate ions (Eq. 2).

$$CO_2 + 2OH^- \leftrightarrows CO_3^{2-} + H_2O \qquad (2)$$

The carbon dioxide can also be produced at the air electrode by the oxidation of any carbon component in the electrode (Eq. 1). The carbonate ions formed according to Eq. 2 either diffuse into the alkaline electrolyte or precipitate as potassium carbonate on the gas diffusion electrode. These precipitates of potassium carbonate block the pores in the air electrode, decrease the active surface area available, and reduce the access of oxygen to the electrocatalyst. The decrease in performance of metal-air batteries and fuel cells due to carbonation of the electrolyte has been shown in the literature.[49-51] Cnobloch *et al* have studied the influence of carbonation of the electrolyte on the performance of an iron-air battery. At 40 mA/cm$^2$, the discharge potential of the air electrode increased by 190 mV when the concentration of potassium carbonate in the electrolyte was increased from 0.06 N to 4.08 N.[51] When a truly bi-functional electrode is used, carbonate precipitation in the hydrophilic OER layer will lead to deterioration of performance during both OER and ORR reactions. To address this issue, regenerative carbon dioxide absorbers with sufficient specific capacity need to be part of the system design. Examples of such efficient absorbers are those that allow for regeneration using the oxygen evolved during charging as the sweep gas, concurrently using the waste heat from the system. Polyethyleneimine supported on silica has properties that are very attractive for this application.[52]

## Future Directions

Recent advances in the electrocatalysis of oxygen reduction using nitrogen doped carbons present opportunities to reduce the overpotential during oxygen reduction. Some of these materials can match the performance of platinum. However, the anodic stability of these carbon materials needs to be established. The use of nano-structured thin film catalysts based on 3M's NSTF substrate is a promising approach to reduction of the amount of precious metal used in regenerative fuel cells. As the research on alkaline ion-exchange membranes progresses, alkaline regenerative fuel cells that use non-precious metals and metal oxides could become an inexpensive alternative to today's regenerative fuel cells based on acidic Nafion membranes. The opportunity to tune the catalytic activity of perovskite and spinel oxides for oxygen evolution and peroxide decomposition by varying the mixture of metals and dopants presents new possibilities for the realization of efficient rechargeable metal-air batteries. Until stable electrode structures can be designed, the problems relating to electrode durability in metal-air batteries may have to be addressed through the use of separate electrodes for oxygen reduction and oxygen evolution. Such separated electrode structures will permit significant flexibility in the design and formulation of the electrodes, and also facilitate long lifetimes for the air electrodes. Electrode performance in non-aqueous electrolytes could be improved by the use of specific catalysts to promote both oxygen reduction and evolution, as the current density in lithium battery electrolytes are still too low for any practical application. Addressing the intrinsic problems of precipitation and passivation of the electrode surfaces in non-aqueous lithium battery electrolytes await innovative electrode designs that disperse the insoluble products in a form that precludes interference with the kinetics of the oxygen electrode reaction. ■

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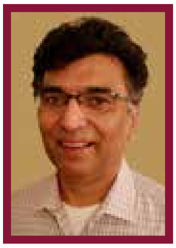
## About the Authors



**Sri Narayan** has over 30 years of experience in the fundamental and applied aspects of energy storage and conversion systems. During his 20-year tenure at the NASA-Jet Propulsion Laboratory, he pioneered the development of the Liquid-Fed Direct Methanol Fuel Cell that led to its commercialization. Prof. Narayan's current focus at the University of Southern California is on developing inexpensive, robust and sustainable energy storage systems for large-scale integration of the electricity from solar and wind based generation. In the last five years, under the sponsorship of ARPA-E, Prof. Narayan and his team have made notable innovations in the area of robust iron-based batteries and inexpensive aqueous organic redox flow batteries. Prof. Narayan was awarded the Exceptional Achievement Award from the NASA-Jet Propulsion Laboratory, and was recently elected as the Fellow of the Electrochemical Society. He may be reached at sri.narayan@usc.edu.

**Aswin Manohar** is a post–doctoral research associate working under the supervision of Prof. S.R. Narayanan at the University of Southern California (USC). His current research is focussed on the development of batteries for large-scale energy storage applications. He received his PhD degree in Materials Science from USC and his B.Tech degree in Chemical and Electrochemical Engineering from the Central Electrochemical Research Institute, Karaikudi, India. He may be reached at aswinkam@usc.edu.

**Sanjeev Mukerjee** is a Professor in the Department of Chemistry and Chemical Biology (Northeastern University); where he has been since September of 1998. He also heads the newly created center for Renewable Energy Technology at Northeastern University and its subset the Laboratory for Electrochemical Advanced Power (LEAP). He is the author of 130 peer reviewed publications and is a fellow of the Electrochemical Society. He has given numerous invited and keynote presentations in various national and international meetings and holds five US and international patents. He also serves on the scientific advisory boards of three companies. He may be reached at s.mukerjee@neu.edu.

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