Brief Biography of Annamalai Karthikeyan, Ph.D.

Dr. Annamalai Karthikeyan is the founder and technical lead of the Microionic Systems LLC (MiST). He is responsible for developing and contributing to manufacturing methods, R&D projects related to advanced concepts in materials processing, device configurations and energy storage applications. He graduated in 1995 with Ph.D. Applied Materials Physics for developing solid state batteries based on novel silver electrolyte materials. Since then he worked as the technical lead in various successful projects in the field of nanomaterials, characterization, activated carbon, ultracapacitors, solid state batteries, hydrogen separation, fuel cells, electrolyzer cells and atomistic simulation. He has 25 years of full-time research expertise in various world class institutions including Harvard University, Boston University, Iowa State, CNRS-France, and the Indian Institute of Science. He has worked with agencies including the European Commission, US-Navy, NSF, US-DOE, etc. He has 8 patents, ~50 publications and ~50 presentations. He has mentored graduates, undergraduates, graduates, high school students and postdocs.

Recent employments:

2008– 2013, Senior Scientist University of Wisconsin System

Oshkosh Campus

- Started the electrochemical energy storage R & D work at Oshkosh Campus in 2008. Provided training to a University research professor and undergraduate students.
- Studied transition metal oxide nanomaterials and electrode architectures for pseudocapacitor devices.
- Hydrothermal processing of carbon microbeads and ceramic separators for ultracapacitors (These works currently licensed to Shamrock Energy Corporation).
- Developed new concept on energy storage using nanoionic MIEC materials using space-charge re-dox.
- Founded **Microionic Systems LLC** (2011) to commercialize a novel ultrafast method to prepare carbon and to develop hybrid batteries based on MIEC nanoionic storage concept.

Platteville Campus

- Developed a new and ultrafast method to carbonize cellulostic materials to manufacture high quality char, super high surface area and low impurity carbon (WiSCAP, Small company advancement program).
- Trained undergraduate students.

2006 – 2008, Research Associate, Harvard University, Cambridge, MA

- Developed unique laboratory tools for nanoionic research (with Dr. Shriram Ramanthan).
- Probe design, fabrication and evaluation of ultra thin films (5 nm to 100 nm at 300 K to 2000K).
- Discovered size dependent electrochemical properties in electrode and electrolyte materials.
- Start-up "Hydrophen", **Finalist** in 2006 Ignite Clean Energy (ICE) business competition, MIT, Cambridge.
- Findings published as 10+ papers and 2 patents.

2004 – 2006, Research Faculty, Boston University, Boston, MA

- Developed a novel composite mixed conductor (MIEC) with high ambipolar conductivity.
- Used electrical conductivity relaxation to characterize catalyst for the first time.
- Successfully separated hydrogen from water with record-high flux using the MIEC membrane.
- Solid Oxide Electrolyzer Cell (SOEC) development for hydrogen production technology.
- Work resulted in 5 publications, 2 patents and licensing by CTP Hydrogen.

Education:

1995- Ph.D., Solid State Physics, Pondicherry Univ., India. (Silver solid-state Batteries)
1988- M. S., Physics, University of Madras, Madras, India (With Electronics, Report: Black Holes).
1986 - B. S., Physics, University of Madras, Madras, India (Chemistry Minor).

Patents:

(1) Karthikeyan, A. (2013): All ceramic and all nanoionic components for hybrid capacitor and fabrication method therof (under development).
(2) Karthikeyan, A. (2012): An ultrafast process for patterned carbonization and method of making activated carbon thereof (provisional application); WiSys T130012US01.
(3) Gibson, C. and Karthikeyan, A. (2010): Carbon microbeads with hierarchical structure WO 2011/011579 PCT/US2010/042863
(4) Karthikeyan, A. and Gibson, C. (2010): High performance electrochemical redox capacitors using materials with non-stoichiometry and defect equilibrium; WO 2010/096527 PCT/US2010/024539.
(5) Gibson, C. and Karthikeyan, A. (2009): High dielectric ceramic separator components for ultracapacitors, US Patent 8,139,343.
(6) Gopalan, S., Pal, U.B., Karthikeyan, A. and Cui, H. (2006): Composite mixed ionic and electronic conductors for hydrogen separation. US Patent 8,588,626.
(7) Gopalan, S., Pal, U.B., Karthikeyan, A. and Cui, H. (2007): Surface exchange electrocatalysts for ceramic membranes, PCT Int. Appl. (2007), 41pp. 2007086949 dated 20070802.
(8) Ramanathan, S., and Karthikeyan, A. (2007): Nanoscale gas separation device utilizing thin films for hydrogen production for fuel cell. WO 2007/118237. PCT/US2007/066253.
(9) Ramanathan, S., and Karthikeyan, A. (2008): Photo activation of oxide fuel cells and gas separation devices. WO 2008/083224. PCT/US2007/088952.

Skills:

Materials preparation: Transition metal oxides, ceramics and glasses. Nanopowders, nanocomposites and nanofilms. Precipitation, energetic routes, thin-films by sol-gel and sputtering. Thick films by coating. Electrolytes (H^+, O^{2-}, Ag^+, Li^+), and electrodes (C, Ni, Co, Mn, MIECs).
Characterization: XRD, SEM/TEM/AFM, TG/DTA/DSC, IR,/Raman/NMR. Surface area and porosity.
Transport and electrochemical properties: Impedance spectroscopy, DC and AC conductivity, and conductivity relaxation methods. Electrochemical circuit elements.
Solid State Batteries: Design, fabrication of primary (silver) and secondary (lithium) batteries; Supercapacitors and hybrids. Fabrication and performance test using electrochemical systems.
Fuel Cells and related: SOFCs, SOECs, gas permeation devices. Design, fabrication and testing.
Others: Start-up and laboratory development. Design & fabrication of test and measure probes, electrochemical cells and reactors. Some experience in handling toxic and flammable gases.
Computer simulation: Structural and ion dynamics by molecular dynamics; Fortran.

Publications:

A. Hydrogen Production Technology

(1) Karthikeyan, A., and Ramanathan, S. (2007), Effect of photon irradiation on conductivity of nanoscale yttria-doped zirconia thin films, App. Phys. Lett., 90(9), 093107.
(2) Karthikeyan, A., Cui,H., Gopalan, S., and Pal, U.B. (2006): Oxygen flux and process analysis of hydrogen separation from water through mixed conducting membranes, MRS Symposium Proceedings Vol. 885, page 285-290.
(3) Cui,H., Karthikeyan, A., Gopalan,S. and Pal,U.B. (2006): Use of conductivity relaxation experiments to evaluate surface exchange catalysts. Electrochem. and Solid-state Lett., 9(3) A179-A181.
(4) Cui, H., Karthikeyan, A., Gopalan, S., and Pal, U.B. (2005): GDC-YSTA Composite Mixed Conductor for Hydrogen Separation. J. Electrochem. Soc. , 152, A1726-A1932.
(5) Karthikeyan, A., Cui,H., Gopalan, S., and Pal, U.B. (2005): Chemical Diffusion And Hydrogen Separation Properties of Lanthanum Ferrite And Doped Ceria Composite. Ceramic Engineering and Science Proceedings, 26(4) 91-98.
(6) Karthikeyan, A., Cui,H., Gopalan, S., and Pal, U.B. (2005): New MIEC Membranes for Hydrogen Separation. Proceedings of the SOFC Symposium, 207th ECS Meeting, Quebec, Canada.

B. Solid Oxide Fuel Cell (SOFC) Technology

(10) Ramanathan, S., Karthikeyan, A., Govindarajan, S. A., and Kirsch, P.D., (2008), Effect of rare-earth doping and nitrogen passivation treatments on properties of ultra thin hafnia films, ECS Transactions, 16(5), 497.
(11) Karthikeyan, A., and Ramanathan, S. (2008), Temperature dependant interfacial carrier transport in low dimensional oxide using ionic conductor-insulator (YDZ-SiO2) superlattices, Journal of Applied Physics, 104, 124314.
(12) Karthikeyan, A., Tsuchiya, M., and Ramanathan, S. (2008), Apatite phase synthesis from inter-diffusion in GDC-SiO2 thin-film superlattices and in-situ conductivity studies, Electrochemical Solid State. Lett. 11(11), K101.
(13) Ramanathan, S., Karthikeyan, A., Govindarajan, S. A., and Kirsch, P.D., (2008), Synthesis of nitrogen passivated rare-earth doped hafnia thin films and high temperature electrochemical conduction studies, J. Vac. Sci. Tech. 26(4), L33.
(14) Chengun H Ko, Karthikeyan, A., and Ramanathan, S. (2010), Oxygen surface exchange in titania films, Solid State Ionics (to be communiated).
(15) Karthikeyan, A., and Ramanathan, S. (2008), Surface exchange process in gadolina doped ceria nano-films, App. Phys. Lett. 92(24), 243109.
(16) Karthikeyan, A., Tsuchiya, M., and Ramanathan, S. (2008), Studies on structure-electrical conduction relationships in nanoscale zirconia films, Solid State Ionics 179(21-26), 1234.
(17) Ginestra,C.N., Sreenivasan,R., Karthikeyan,A., Ramanathan,S. & McIntyre,P.C., Atomic Layer Deposition of Y2O3/ZrO2 Nano-laminates, Electrochem. & Solid-State Lett.(2007), 10, B161-B165.
(18) Karthikeyan, A., Tsuchiya, M., Chang, C., and Ramanathan, S. (2007), Tunable electrical conductivity in nanoscale Gd-doped ceria thin films, App. Phys. Lett. 90(26), 263108.
(19) Karthikeyan, A., Chang, C. and Ramanathan. S. (2006), High temp. conductivity studies on nano-scale yttria-doped zirconia thin films and size effects, Appl. Phys. Lett. 89(18) 183116.

C. Proton Exchange Membrane (PEM) Technology

(20) Martindale, Chad A., Karthikeyan, A., Böhmer, Roland, and Martin, S. W. (2006), Synthesis and Characterization of Ge/Sn (II) Iodide Doped Thioborate Anhydrous Proton Conductors, Solid State Ionics, 177, 2865.
(21) Karthikeyan, A., Martindale Chad A. and Martin S. W. (2003): New Protonated Thioborate Glasses in the $x\ H_2S + (1-x)\ B_2S_3$ Series. J. Phys. Chem. B 107, 3384-3389.
(22) Karthikeyan, A., Martindale Chad A. and Martin S. W. (2003): New anhydrous proton conducting materials based on thioborates. Phys. Chem. Glasses 44(2), 143-146.

(23) Martin, S.W., Karthikeyan, A. and Martindale Chad A. (2002): Glass used in high-performance fuel cell development. The Glass Researcher 12(1) (2003) 10-11.

(24) Karthikeyan, A., Martin S. W. and Martindale Chad A. (2004): Preparation and characterization new proton conduction chalcogenide glasses. J. Non-Cryst. Solids, 139, 215-222.

(25) Karthikeyan, A., Martindale Chad A. and Martin S. W. (2004): Proton conductivity in a new class of H_2S modified thioborate based glasses and ceramics. Solid State Ionics 175, 655-659.

(26) Karthikeyan, A., Martindale Chad A. and Martin S. W. (2002): A new method to prepare polycrystalline meta-thioboric acid, $(HBS_2)_3$. Inorganic Chemistry Comm. 41, 622-624.

D. Lithium Battery and Capacitor Technology

(27) A. Karthikyean, and C. Gibson, Synthesis and development of supercapacitors using mixed metal oxide (Co-Ni) nanomaterials (to be submitted).

(28) A. Karthikeyan, and C. Gibson, Synthesis of high surface area carbon-metal nano-composites and potential use electrode materials in supercapacitors (to be submitted)

(29) Karthikeyan, A., Vinatier, P. and Levasseur. A. (2000): Impedance study of lithium glassy electrolyte interface with different electrodes. Bull. of Mat. Sci. 23, 179-183.

(30) Karthikeyan, A., Vinatier, P., Levasseur, A. and Rao, K. J. (1999): The molecular dynamics study of lithium ion conduction in phosphate glasses and the role of non-bridging oxygen. J. Phys. Chem. B 103, 6185-6192.

(31) Rao, K. J., Baskaran, N., Ramakrishnan, P.A., Ravi, B.G. and Karthikeyan, A. (1998): Structural and ion transport properties of sol-gel prepared lithium silicophosphate glasses. Chemistry of Materials 10, 3109-3123.

(32) Karthikeyan, A., Ravi, B.G., Baskaran, N. and Rao, K. J. (1998): Lithium lead phosphate glasses: Structure and Conductivity studies. Comm. of the Eur. Comm., INCO-DC: 950-400, 30-43.

E. Silver Battery Technology

(33) Satyanarayana, N., Karthikeyan, A., Venkateswarlu, M. and Rambabu, B. (2001): Structural characterization and transport studies of AgI-Ag_2O-$(MoO_3+As_2O_5)$ Glasses. Physics and Chemistry of Glasses 42(1), 67-73.

(34) Karthikeyan, A., Satyanarayana, N. and Venkateswarlu. M. (1996): AC conductivity studies on the silver molybdo-arsenate glasses. J. Mat. Sci. 31, 5471-5477.

(35) Karthikeyan, A. and Satyanarayana, N. (1994): Solid state batteries using silver based fast ionic conducting glassy electrolytes. J. Power Sources 51, 457-462.

(36) Karthikeyan, A., Govindaraj, G., Satyanarayana, N. and Venketeswarlu, M. (1992): Study of dopant salt concentration in silver molybdoarsenate glasses. J. Mat. Sci. Eng. B13, 295-298.

(37) Govindaraj, G., Satyanarayana, N. and Karthikeyan, A. (1990): Preparation and ion conductivity studies of silver based molybdoarsenate glasses. J.Mat. Sci. Lett. 9, 1123-1125.

(38) Satyanarayana, N., Govindaraj, G. and Karthikeyan, A. (1991): Effects of network modifier (Ag_2O) to network formers $(MoO_3+V_2O_5)$ and dopant salt (AgI)in silver based conducting glasses. J. Non. Cryst. Solids. 136, 219-226.

(39) Satyanarayana, N., Govindaraj, G., Karthikeyan, A. and Srinivasa Rao, A. (1991): Study of AgI-Ag_2O-$(MoO_3+V_2O_5)$ and AgI-Ag_2O-$(MoO_3+As_2O_5)$ quaternary glassy systems for solid state batteries. Proc. of the Int. workshop on Solid State Materials, Univ. of Malaysia, Malaysia, August 1991.

(40) Govindaraj, G., Satyanarayana, N., Karthikeyan, A. and Srinivasa Rao, A. (1991): An understanding of high ionic conductivity in glasses. Proc. Int. workshop on Solid State Mat., Univ. of Malaysia, Malaysia, August 1991.

(41) Karthikeyan, A., Govindaraj, G. and Satyanarayana, N. (1992): A study of pre-exponential factor and ionic conductivity mechanism in glassy electrolytes. Proc. of the III Asian conference on Solid State Ionics, World Scientific, L26-30.

(42) Satyanarayana, N., Govindaraj, G. and Karthikeyan, A. (1992): Silver based fast ionic conducting glassy systems: Transport and battery applications. Proc. of the V Asia Pacific Physics Conf., Malaysia, August 1992, 915-18.

(43) Karthikeyan, A. and Satyanarayana, N. (1993): Ionic conduction in glassy electrolytes a Monte Carlo study. Proc. of the Solid State Physics Sym. (India), 36C, 253.

F. Theoretical Research on Electrolytes used in Batteries

(44) Karthikeyan, A., and Ramanathan, S.(2010), Uncorrelated oxygen ion hopping in oxide nano-ceramics, (To be communicated).

(45) Karthikeyan, A. and Rao, K. J. (1997): Structure and silver ion transport in AgI-Ag_2MoO_4 glass: A molecular dynamics study. J. Phys. Chem. B 101, 3105-3114.

(46) Satyanarayana, N., Karthikeyan, A. and Vankateswarlu, M. (1997): Monte Carlo simulation of ion conduction in silver based glassy electrolytes. Mat. Sci. Eng. B 47, 210-217.

(47) Karthikeyan, A. and Almeida, Rui M. (2001): Structural anomaly in sodium germanates glass by molecular dynamics simulation. J. Non-Cryst. Solids, 281, 152-161.

G. Photo Electrochemistry, & Other areas

(48) Synthesis and variable temperature electrical conductivity studies of highly ordered TiO2 nanotubes (2009), Azmatulu, R., Karthikeyan, A., Bell, D.C., Ramanathan, S., Aziz, M.J., J. Mat. Science, 44, 4613.

(49) Karthikeyan, A., and Ramanathan, S. (2007), Effect of photon irradiation on conductivity of nanoscale yttria-doped zirconia thin films, App. Phys. Lett., 90(9), 093107.

(50) Martin S. W., Wallleser, J., Karthikeyan, A. and Sorderlet, D. (2004): Enthalpy relaxation studies of the metallic glass transition. J. Non-Cryst. Solids, 139, 347-354.

(51) Karthikeyan, A. and Almeida, Rui M. (2001): Phase Separation in SiO_2-TiO_2 gel and glassy films studied by AFM and TEM. J. Mat. Res. 16(6), 1626-1631.

(52) Karthikeyan, A. and Almeida, Rui M. (2000): Crystallization properties of TiO_2-SiO_2 thin films studied by Atomic Force Microscopy. J. Non-Cryst. Solids, 274, 169-174.

Some Recent Presentations – (Total presentations ~50).

(1) A. Karthikyean, (June 6, 2013), A rapid synthesis and a new opportunity to manufacture specialty activated carbon, American Chemical Society, Great Lakes Regional Meeting, Lacrosse, WI.

(2) A. Karthikyean, (July 28-29, 2011), Activated Carbon from Cellulose – A rapid synthesis and a new opportunity. 4th Annual Wisconsin Sci. & Tech. Symposium, White Water, WI.

(3) A. Karthikeyan, (April 15, 2008), Oxide Ceramics for Energy and Fuel Production – Prospects for 2nd and 3rd Generation Devices, Metal. and Mat. Eng., Colorado School of Mines, Golden, CO.

(4) A. Karthikeyan, H. Cui, S. Gopalan and U. Pal (January, 25, 2005): Ambipolar oxygen migration in La-Ferrite and doped ceria – $SrTiO_3$ dual phase composites for hydrogen separation, 29th Int. Conf. on Advanced Ceramics and Composites, Cocoa Beach, FL.