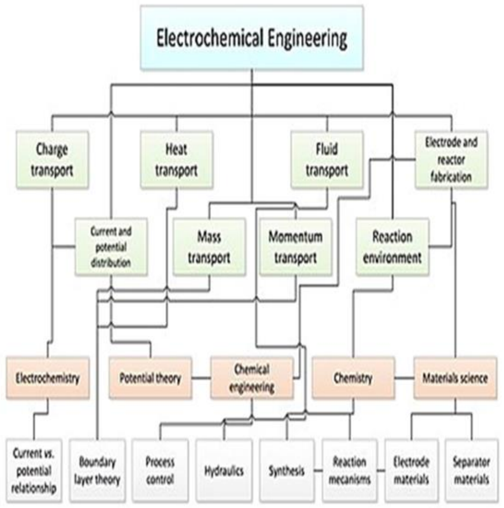
Electrochemical Energy Storage, Conversion & Environmental Technologies: Material Challenges, Opportunities, and Scope for Interdisciplinary Degree Program

Rambabu Bobba
Southern University and A&M College
Baton Rouge, Louisiana-70813



Relationship between electrochemical engineering and other disciplines.
After F.C. Walsh, 1993.

Electrochemical Technologies

- Hydrogen production technologies
- Low and High temperature water electrolysis
- Carbon assisted hydrogen production
- Energy storage & Conversion
- Rechargeable metal air batteries
- Flow batteries and their hybrids
- Storage integration into electric grids
- Membrane separation technologies
- Waste to fuel added projects
- Conversion of CO_2
- Ammonia Production

Environmental Technologies

- Waste-water treatment
- Recycling and waste management
- Self-sufficient buildings
- Waste-to-energy
- Generation of energy from the valves
- Vehicles that do not emit gases
- Harnessing solar energy
- Vertical gardens and farms
- Natural gas burners

In general, the degree program in **Electrochemical Engineering** integrates skill sets in fundamentals of chemistry, physics, mathematics, thermodynamics, mechanical, electrical, and civil engineering disciplines and electrochemical engineering applications (batteries, solar, flow and fuel cells, electrochemical synthesis, and corrosion) to ensure successful career opportunities and growth within electrochemical power generation industries, government agencies, and academia.

Message from the Dean, College of Sciences and Engineering (CSE) at Southern University A&M College (SUBR)

Southern University | Largest HBCU System in the Country

Largest HBCU (Historically Black College and Universities) System in the country

Five Institutions, located on three campuses:

- Baton Rouge Campus
- New Orleans Campus
- Shreveport Campus
- Law Center
- Agricultural Research Center

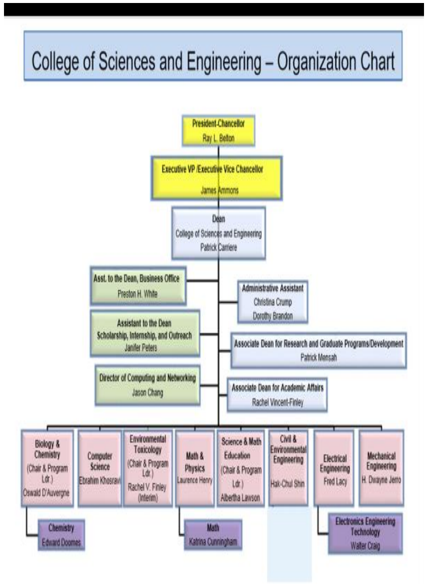
System Facts

- 1881 opened in New Orleans, La
- 1890 Agricultural and Mechanical Department established
- 1891 recognition as a Land Grant College

Southern University

Agricultural & Mechanical College

Southern University and A&M College-Baton Rouge, Louisiana



College of Sciences and Engineering – Organization Chart

Patrick Carriere Ph.D.,
Professor of Civil Engineering Dean. College of Sciences and Engineering (CSE)

The College of Sciences and Engineering (CSE) explores the opportunity to develop mutually beneficial research exchange and hopefully joint degree programs between the partnering Institutes. Our vision is to provide an effective, experienced-based instruction led by a team committed to excellence in preparing students for success in STEM professions, through research, community services, and collaborations necessary to meet the demands of a global society.

Patrick F Mensha Ph.D.,
Formosa Endowed Professor of Mechanical Engineering Associate Dean for Research (SUBR)

The vision for research of the CSE at SUBR is to build and sustain an infrastructure that promotes greater participation by faculty in sponsored and elective multidisciplinary related research activities in STEM disciplines including exchange opportunities nationally and internationally for our students to participate in scholarly activities and research with their professors and research mentors.

Advanced Nanoscale Electrodes and Electrolytes for Renewable and Sustainable Energy Technologies at SUBR [PI: Rambabu Bobba]

- Development of nanostructured thin film device architectures as drivers of next-generation electrochemical energy storage and conversion (hybrid power and energy) devices
- Optimizing the size of nano scale electrode (cathodes, anodes) in the form of bulk and thin films using advanced synthesis and characterization techniques,
- Investigating the physicochemical, structural, microstructural, and surface properties of nanomaterials is vital for achieving the required efficiency, cycle life, and sustainability in various technological applications.
- Identifying the compatible safe electrolytes with respect to device performance to produce systems having optimized power and energy density,

Nanomaterials for Energy Storage and Conversion: Batteries, Supercapacitors & hybrids, Fuel cells (HT-PEMFCs & IT-SOFCs), Hydrogen storage, Photovoltaics, Solar Cells

Nanomaterials for Sustainable Fuel Production: Hydrogen production, Biofuel, renewable fuel generation, Catalysis, CO_2 storage & conversion

Nanomaterials for Energy Harvesting and Saving: Thermoelectrics, Novel Illumination Sources, LEDs

Advanced Characterization and Modelling: Spectro-electrochemical Techniques
Nanoscience and nanotechnology: They are interdisciplinary fields that bring together physicists, chemists, materials scientists, and engineers to meet the potential future challenges that humankind will face, including the search for renewable energies for sustainable development and new technologies for carbon capture and environmental protection.

Energy Storage Systems and Batteries and Capacitors

Lithium Battery

Advantages:

- high energy density
- Flat operating voltage profile (~ 3 or 4 V)
- good discharge efficiency (>90%)
- No self-discharge

Disadvantages:

- Low power density
- slow charging

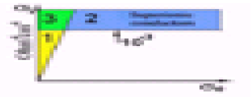
Supercapacitors

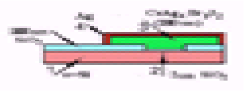
Advantages:

- high power density (> 1 kW/kg)
- high charge-discharge cycle life (>10^4 cycle)
- high discharge efficiency (>90%)
- Fast Charging (< 1 min)

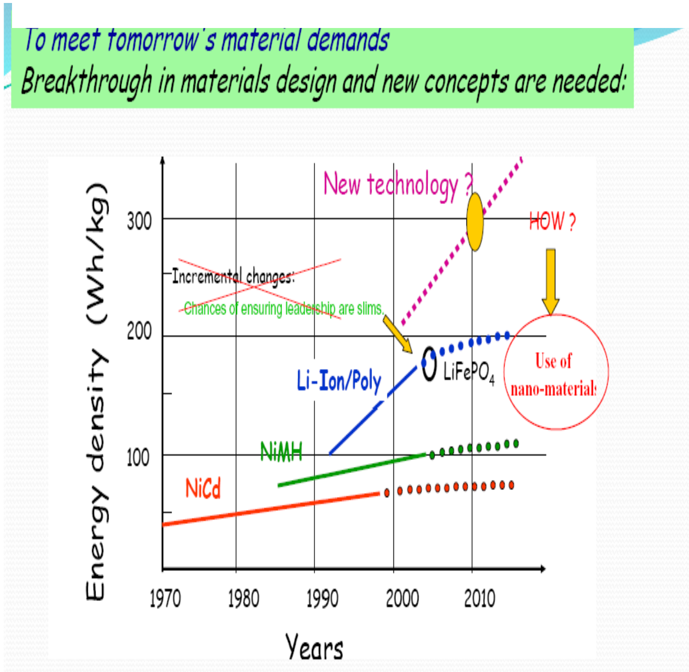
Disadvantages:

- Low energy density
- faster self-discharge



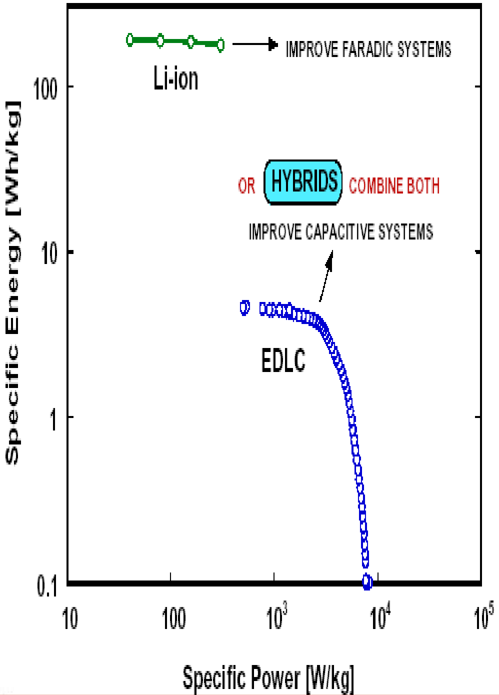


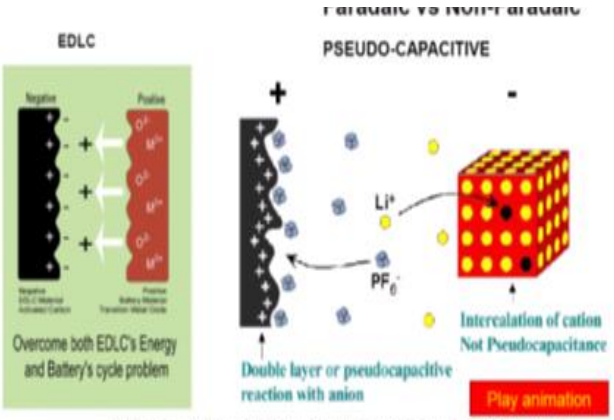
Advanced Electrochemical Energy Storage Devices



To meet tomorrow's material demands

Breakthrough in materials design and new concepts are needed:





When the energy storage mechanism involves both faradaic and non-faradaic, the EC will be addressed as HYBRID ELECTROCHEMICAL CAPACITOR (Hybrid ECs)

Why Nanoparticles and Nanocomposites as Electrodes

- **Large surface area (cm^2/g) /--**
  - higher electrode/electrolyte contact area
  - higher charge/discharge current rates
  - improved capacity utilization for cathode and anode.
- **Short migration path lengths** for electronic and ionic transport
  - leads to higher charge/discharge current rates i.e. increased power delivery
- **Better accommodation of lattice strain of Li insertion/removal**
  - improved cycle-life, enhanced electron and ion storage in neighboring phases
- **Such new types of reactions which are not possible with bulk electrodes**
  - **nano-Fe_2O_3 + 0.5Li ↔$Li_{0.5}Fe_2O_3$** (bulk Fe_2O_3 gives Fe-metal and Li_2O).
  - **nano-CoO + 2Li ↔Li_2O+Co** (Conversion) (reverse reaction does not occur with bulk Co).

Disadvantages of Nanomaterials as Electrodes

- Need **complex synthesis procedures,** especially for preparing mixed-oxides.
- **Difficult to make large quantities with uniform Nano- size.** One pot synthesis methods need to be developed for manufacturing industry.
- **An increase in the undesirable electrode/electrolyte side reactions** especially in the charged-state -- solvent dry-up; self-discharge; poor cycle- and calendar-life.
- **Inferior packing of particles-** smaller volumetric density; lower capacity utilization.

Research needed on Lithium Ion Battery (LIB)

- To reduce the cost, in comparison to Ni- MH batteries.
- To improve safety-in-operation, long life, high power and high energy,
- To extend the temp.-range of operation: from (-5°C to +50°C) to (-30°C to +80°C).
- **Research on the Electrode and Electrolyte Materials is the Key.**
- **Demand:~ 300 Million cells per year, ~ US$2 Billion, ~ Annual growth rate 40%.**

Principle of operation of Lithium Ion Battery (LIB)

The Cell (battery) uses layered compounds as electrodes (intercalation/de-intercalation of Li ions)

Cathode(positive electrode: $LiCoO_{2(}$oxide with a layer structure; layers of [O-Li-O-Co-].

Anode(negative electrode): Graphite (layer structure; layers of hexagonally packed C atoms).

Electrolyte: Li-salt solution in a solvent (Ex.: $LiPF_6$–dissolved in organic solvents, EC+DEC) or Li-salt immobilized in a gel or solid inorganic Li-ion conductor (Ex.: amorphous Li-P-O-N).

Misc. others: battery case, current collectors, etc.

Lithium ions shuttle between electrodes during operation, hence the name, Li-ion Batt

Cell is assembled in the discharged-state and has to be 'charged'

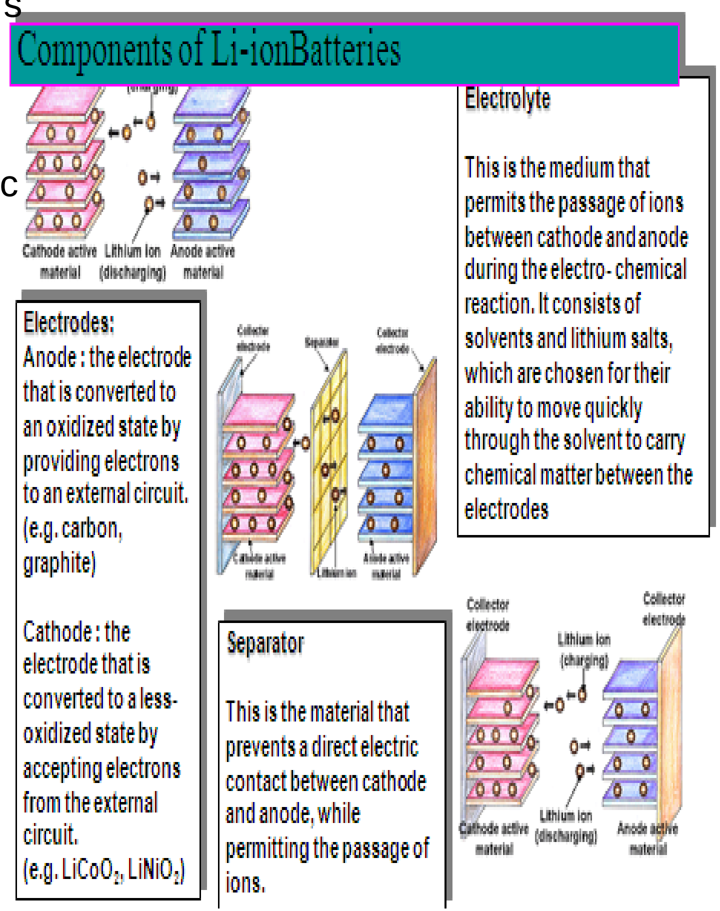
Charging reaction :

Cathode: $LiCoO_2 \rightarrow Li_{1-x}CoO_2 + xLi^+ + xe^-$
Anode: $xLi^+ + xe^- + C \rightarrow Li_xC$ Graphite; x=0.5
Electrolyte: $LiPF_6$ in non-aq. Solvent.
Due to high Voltage, water cannot be used as solvent

Overall reaction:

$LiCoO_2 + C \rightarrow Li_{1-x}CoO_2 + Li_xC$ (charge)
$Li_{1-x}CoO_2 + Li_xC \rightarrow LiCoO_2 + C$ (discharge)

Cell voltage: 3.6V; Cell capacity (product of current and time of discharge) depends on x and weight of cathode and anode



Components of Li-ionBatteries

Electrolyte

This is the medium that permits the passage of ions between cathode and anode during the electro- chemical reaction. It consists of solvents and lithium salts, which are chosen for their ability to move quickly through the solvent to carry chemical matter between the electrodes

Electrodes:
Anode : the electrode that is converted to an oxidized state by providing electrons to an external circuit. (e.g. carbon, graphite)

Cathode : the electrode that is converted to a less-oxidized state by accepting electrons from the external circuit.
(e.g. $LiCoO_2$, $LiNiO_2$)

Separator

This is the material that prevents a direct electric contact between cathode and anode, while permitting the passage of ions.

Disadvantages of $LiCoO_2$ cathode

- High cost & toxicity due to cobalt.
- Only 50% of the theoretical capacity (274 mA.h/g) is utilized.
- Large irreversibility when charged to >4.2V.
- Thermal stability is low in the charged-state (decomposes at T > 230°C).
- Charged-electrode can oxidize (decompose) the electrolyte - battery capacity degradation.

Future Generation Cathodes for Lithium Ion Batteries

Alternatives to $LiCoO_2$ developed at Southern University and A&M College [2000-2012]

Mixed oxides with Ni, Mn replacing Co partly or fully:

- $Li(Ni_x Mn_x Co_{1-2x})O_2$, $x \leq 1/2$
- $Li(Ni_{1-x}Co_x)O_2$, $x \leq 1/2$
- $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ (x=1/3)
- $Li(Ni_{1/2}Mn_{1/2})O_2$ (x=1/2)
- $Li_x(Ni_{1/3}Mn_{2/3)}O_2$
- $LiTi_4O_{12}$, $LiVPO_4F$, $LiFePO_4F$, $LiNiTiO_4$

Improved $LiMn_2O_4$ (spinel network-structure, 4.0V). Capacity fading is not completely suppressed even by doping or surface coating or morphological changes.

$LiFePO_4$---layer-structure (3.6V, without cobalt or nickel) Irreversible capacity loss, two-phase reaction, low electronic conductivity.

Nanoscale Anodes for Lithium Ion Batteries studied at Southern University and A&M College

Alternatives to Graphite have come-up

- **Modified Graphite:** Sn-coated C; C-nano-tubes,..
- **Tin (Sn):** pure and mixed oxides
- **(SnO; SnO_2 , SnP_2O_7 , $CaSnO_3$) --- CoO, NiO….1, and other mixed 3d, 4d-metal oxides ---- II, $Li_4Ti_5O_{12}$ (spinel structure; V=1.5V vs. Li).**

Mechanism of operation differs in I and II

- I: $SnO \rightarrow$ Sn-metal $\leftrightarrow Li_{4.4}Sn$(alloy) (V=0.5V vs Li)
- II: nano-CoO+2Li $\leftrightarrow Li_2O$+Co(nano)(V~2V vs. Li (Conversion

Nano-size Tin and 3d-metal Oxide Anodes for LIB

- Beneficial Effects are more clearly seen with nano-particles.
- I: SnO or $SnO_2 \rightarrow$ Sn-metal $\leftrightarrow$ Li4.4Sn(alloy) (V=0.5V vs. Li)
- II: CoO+2Li $\leftrightarrow Li_2O$+Co (V~2V vs. Li), TiO_2

Co_3O_4, NiO, FeO, CuO are also studied;

- best results are with CoO for Li-cyclability.
- Capacity of 600-700 mA.h/gstable till 100 cycles.

LIB (Cells) with CoO anode was fabricated & tested (Cathode: $LiCoO_2$; $LiMn_2O_4$).

Table 1. Comparison of lithium and sodium regarding selected physicochemical properties and cost

	Lithium	**Sodium**
Cation radius [Å]	0.76	1.02
Relative atomic mass	6.94	22.98
E°(vs SHE) [V]	−3.04	−2.71
Cost, carbonates	\$5000 ton^{-1}	\$150 ton^{-1}
Theoretical capacity of metal electrodes [mAh g^{-1}]	3829	1165
Coordination preference	Octahedral and tetrahedral	Octahedral and prismatic
Desolvation energy in PC [kJ mol^{-1}]	218.0	157.3

Enhancement of Safety, Performance, and Longevity of Energy Storage Devices Using Ionic Liquid Electrolytes

- to identify suitable hydrophobic ionic liquids, tailored as electrolyte components for metal air power sources compatible with industrial-scale manufacturing

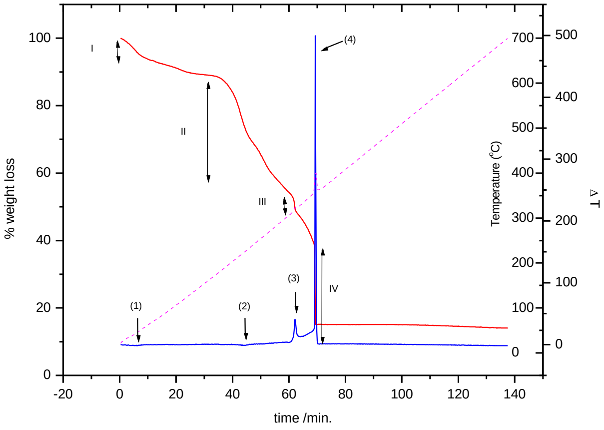
    - PVDF-co-HFP + LiTFSI+2TEGDME
    - PVDF-co-HFP + LiTFSI+ P_{13}TFSI
    - PVDF-co-HFP + LiTFSI+ P_{13}TFSI + (EC/PC/DMC/EMC)
    - PVDF-co-HFP + LiTFSI + PYR_{14}TFSI

- electrolytes to study physical and electrochemical properties. The synthetic methods of the electrolytes will be developed and optimized with a focus on environmental friendliness, process efficiency, and material costs.

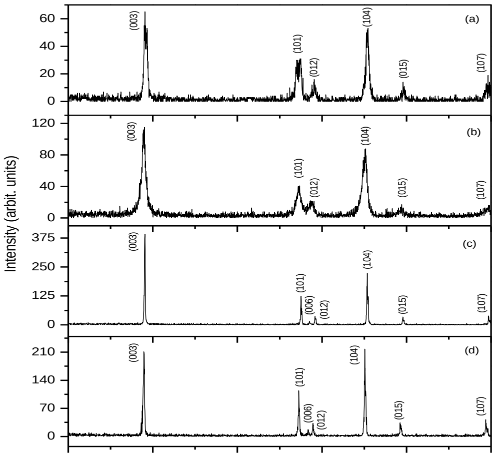
Nanorods and Nanocrystalline Highly Oriented $LiCoO_2$ and $LiCo_XNi_{1-x}O_2$ Thin Films for the Fabrication of Li-Ion Rechargeable Microbattery

K.I.Gnanasekar, and B. Rambabu, Solid State Ionics 148 (2002) 299-309

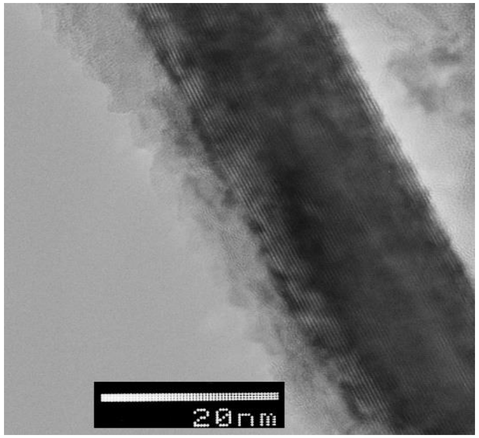
Yuri Malozowski et al and B. Rambabu, Journal of Modern Physics B, Volume 17, Issue 18n2, pp. 3648-3654



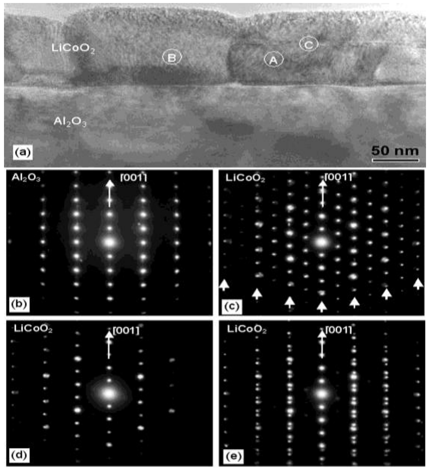
DTA/TG of $LiCo_{0.7}Ni_{0.3}O_2$ gel using glycine route.



XRD of $LiCo_{1-x}Ni_xO_2$ ($0 \leq x \leq 0.3$) heated at various temperatures: (a) $LiCoO_2$ at 400°C (b) $LiCo_{0.7}Ni_{0.3}O_2$ at 400°C (c) $LiCo_{0.7}Ni_{0.3}O_2$ at 750°C (d) $LiCoO_2$ 850°C (e) $LiCo_{0.7}Ni_{0.3}O_2$ 850°C.



$LiCoO_2$ Nanorod cathode,



Highly Oriented Thin Films of LiCoO2/Al2O3 substate by PLD

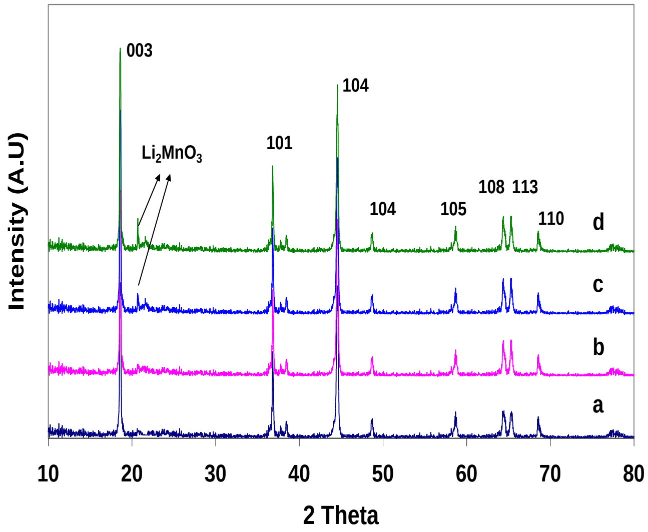
- HRTEM investigations reveal that the particle size of the samples heated at 400 ^{0}C is 10-15 nm.
- EIS and charge/discharge studies show these cycled well withy a coulombic efficiency close to one.
- A promising cathode material in the bulk, thin films and nanorods for rechargeable lithium batteries has been prepared and characterized
- Nanoionic hybrid power pack with the following layer pattern is in progress: Si/SixNy/Ti/Pt/$LiCoO_2$ nanorod/solid electrolyte/Li metal film/ nanocarbon coating/ and productive

$Li_{(1+X)}Ni_{(1-Y-Z)}Co_YMn_ZO_2$ Cathode For High Power and Capacity Lithium-Ion Cells

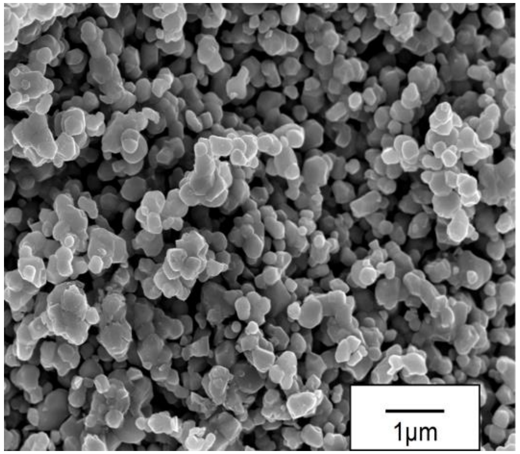
R. Santhanam, Phillip Jones, Adusumilli Sumana, B. Rambabu, J. Power Sources, V 195, P 7391-7399, 2010,

Objective: To investigate the effect of excess Li on the crystal structure and electrochemical performance such as rate capability and high rate cycleability of $Li_{1+x}Ni_{0.3}Co_{0.3}Mn_{0.4}O_2$ (x=0, 0.05, 0.10, 0.15)

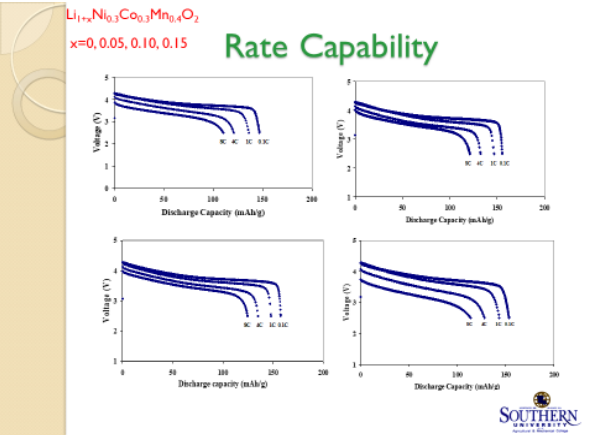
- Layered $Li_{1+x}Ni_{0.30}Co_{0.30}Mn_{0.40}O_2$ (x=0, 0.05, 0.10, 0.15) materials were synthesized using citric acid assisted sol gel process and the effect of the excess lithium on the crystal structure, and electrochemical properties of the materials was investigated.
- The materials with higher Li content showed larger cation ordering peaks at 20–25°$2\theta_{CuK\alpha}$. Li_2MnO_3 or Li_2MnO_3-like phases are present in the materials with excess lithium.
- $Li_{1.10}Ni_{0.30}Co_{0.30}Mn_{0.40}O_2$ cathode demonstrated the highest discharge capacity and capacity retention at different C-rates.
- The improved high rate cycleability of $Li_{1.10}Ni_{0.30}Co_{0.30}Mn_{0.40}O_2$ cathode is ascribed to the improved structural stability due to the formation of appropriate amount of Li_2MnO_3 like domains in the transition metal layer and decreased cation (Li/Ni) disorder.
- $Li_{1.10}Ni_{0.30}Co_{0.30}Mn_{0.40}O_2$ material can be used as a possible cathode material for high power applications in response to an expanding need for advanced rechargeable lithium ion batteries.



XRD of $Li_{1+x}Ni_{0.3}Co_{0.3}Mn_{0.4}O_2$
x=0, 0.05, 0.10, 0.15



SEM of $Li_{1+x}Ni_{0.3}Co_{0.3}Mn_{0.4}O_2$



$Li_{1+x}Ni_{0.3}Co_{0.3}Mn_{0.4}O_2$
x=0, 0.05, 0.10, 0.15

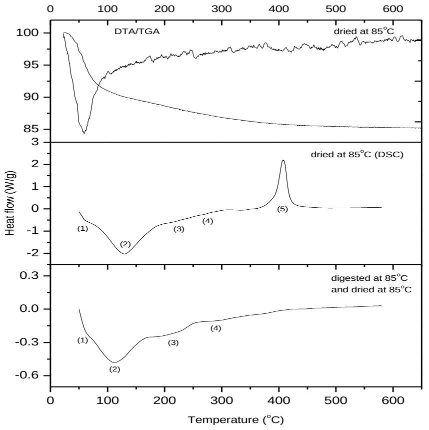
Rate Capability

Cycling performance of the $Li_{1.05}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrode at IC in the voltage range2.5 and 4.3 V

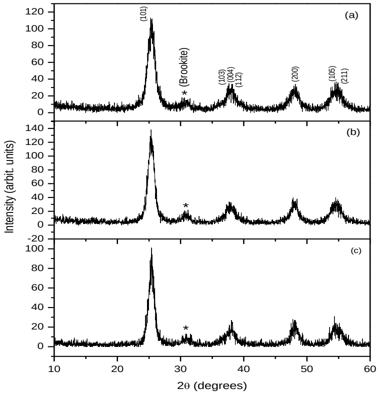
Direct conversion of TiO_2 sol to nanocrystalline anatase at 85°C

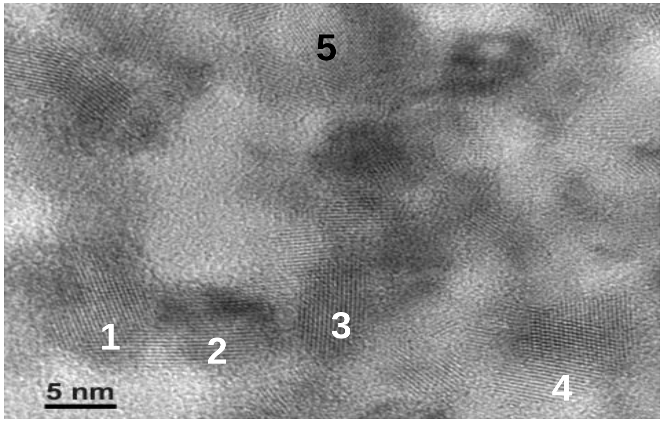
K.I. Gnanasekar, V. Subramanian, J. Robinson, J.C. Jiang (LSU), Fanney E. Posey (NREL) and B. Rambabu

Journal of Materials Research, 17 (2002) 1507-1512.
Journal of Power Sources, XX, 2005, ICMAT-2005,
Journal of New Materials for Electrochemical Systems 2005, IMRC-2005

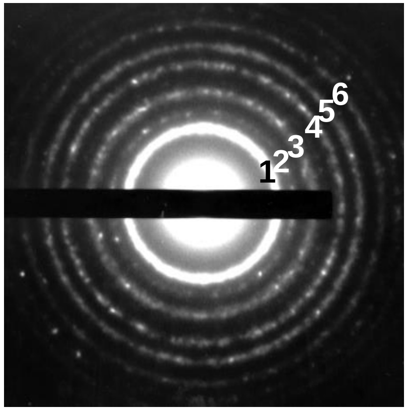


TG/DTA TiO_2 dried at 85°C at different durations

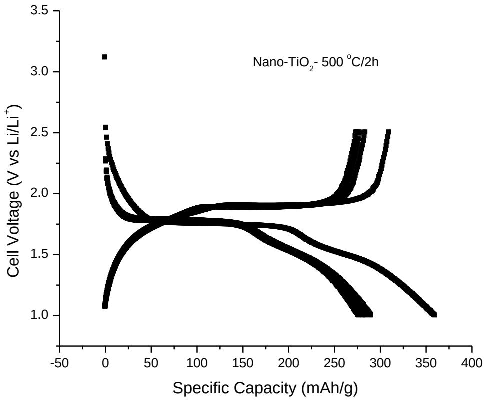


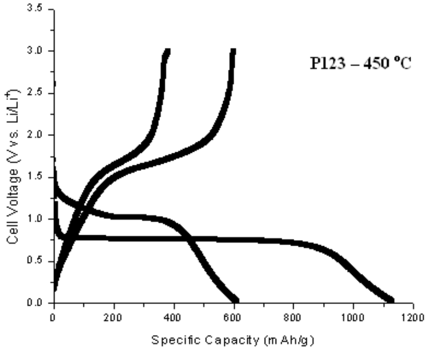


Powder x-ray diffraction patterns and HRTEM of TiO_2 prepared by hydrolysis of titanium isoproxide followed by heating at (a) 85°C for 12 hours (b) 410oC for 6 hrs (c) 510oC for 6 hours



SAED pattern of TiO_2 prepared at 85 °C

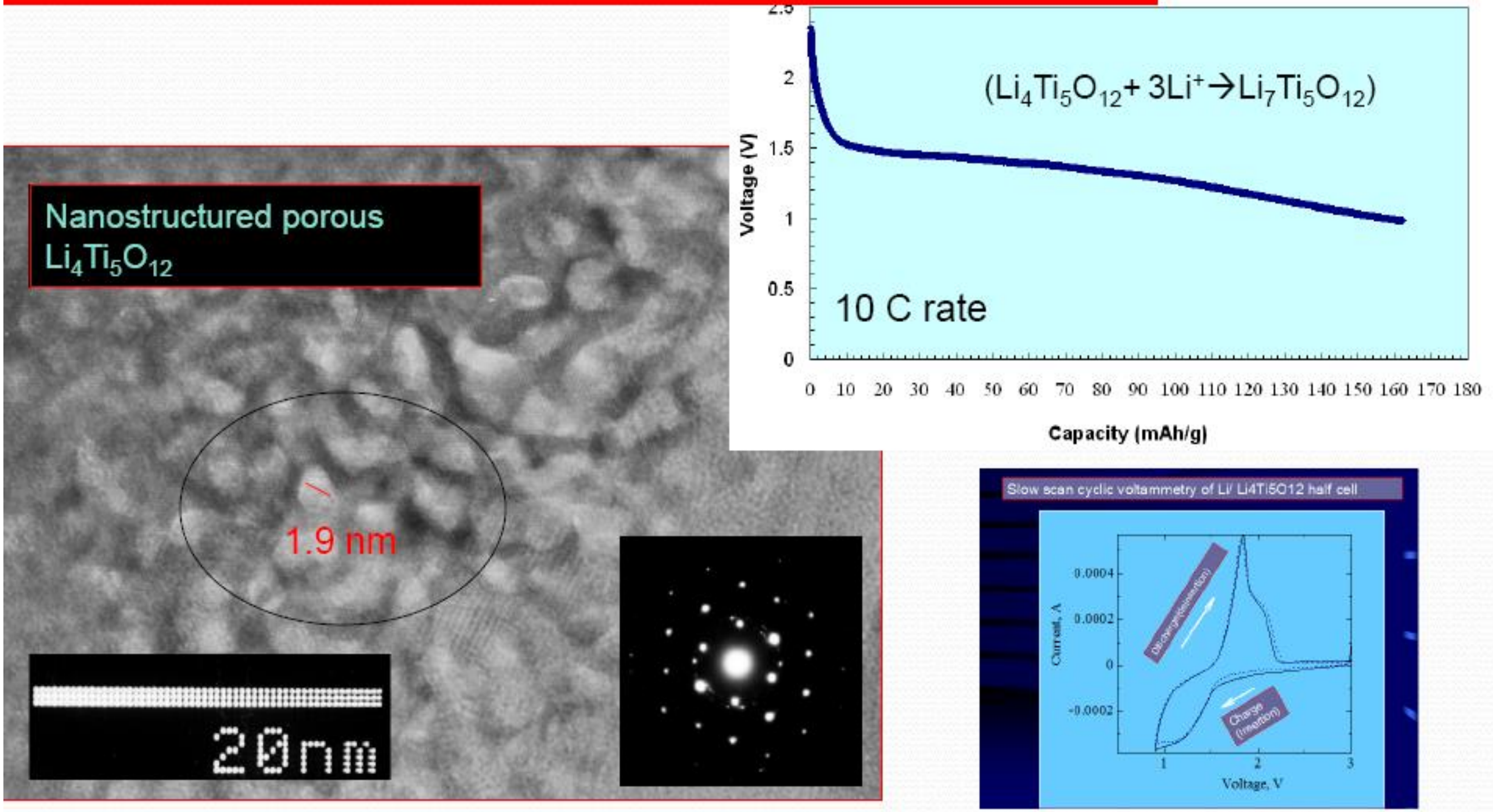




Charge/discharge characteristics were compared with mesoporous Fe_2O_3

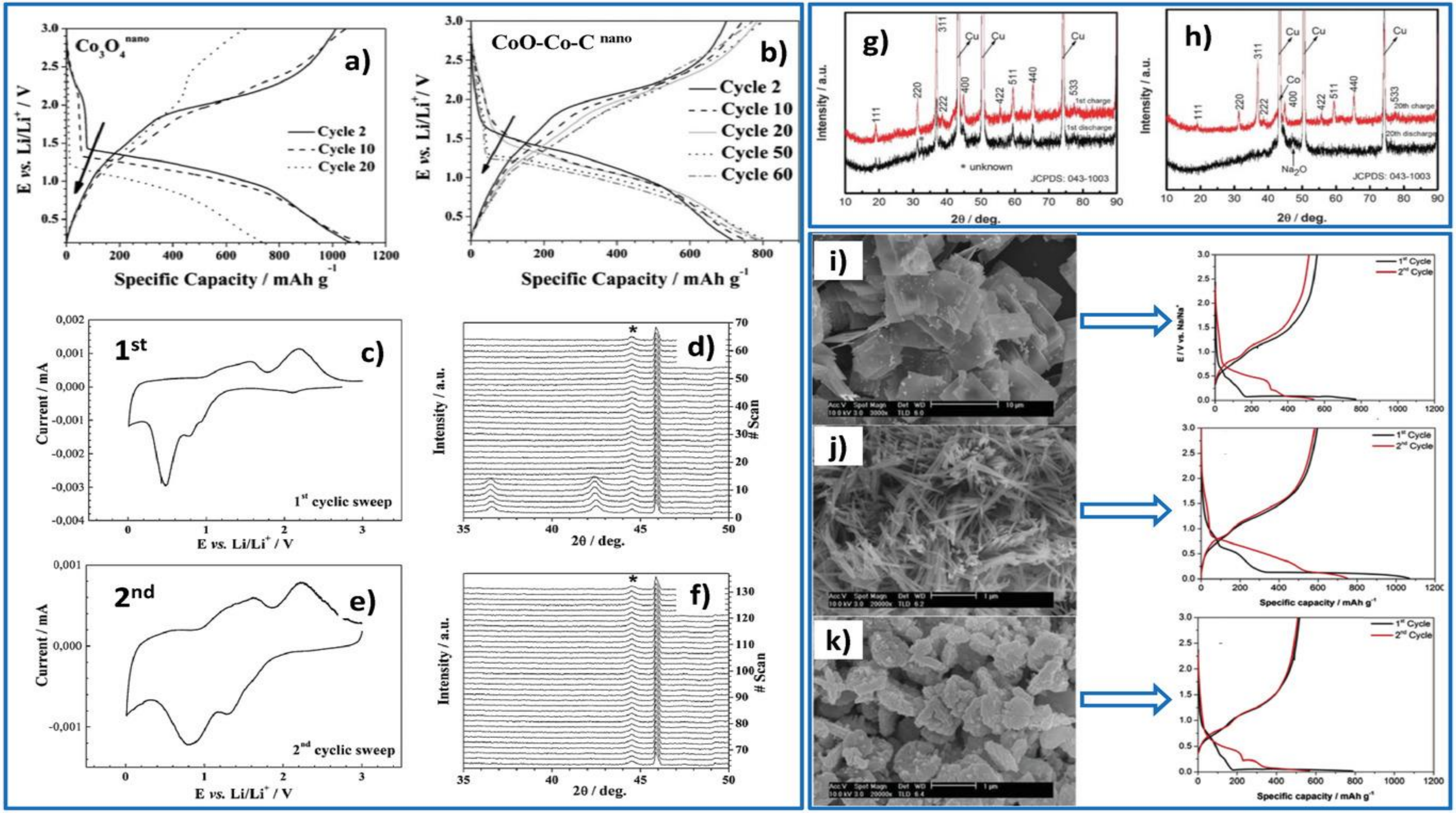
$Li_4Ti_5O_{12}$ An attractive zero strain electrode material

Combined Ultrasonication/modified solvothermal methods



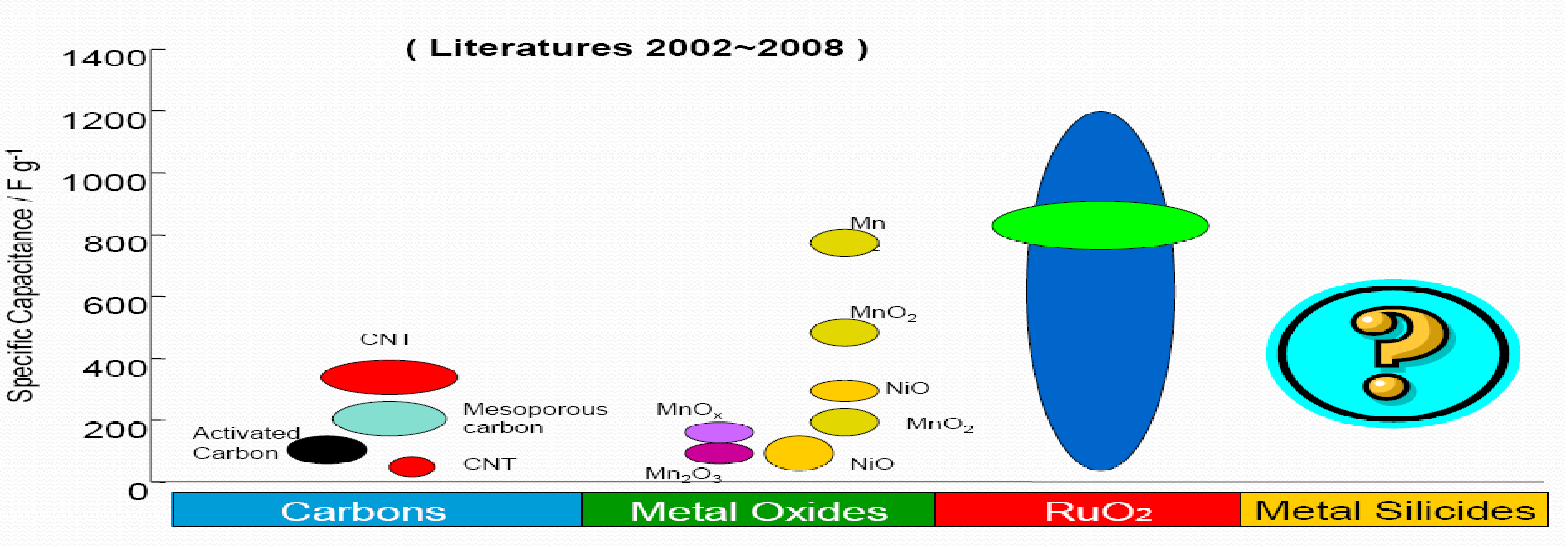
High Performance Lithium Insertion Negative Electrode Materials for Electrochemical Devices. V S Reddy Channu, B. Rambabu, *Applied Surface Science, 387*, 839-845. 2. Solid State Ionics 181 (17-18), 839-843

Co_3O_4 Anode with Enhanced Rate Capability for Lithium-Ion Batteries

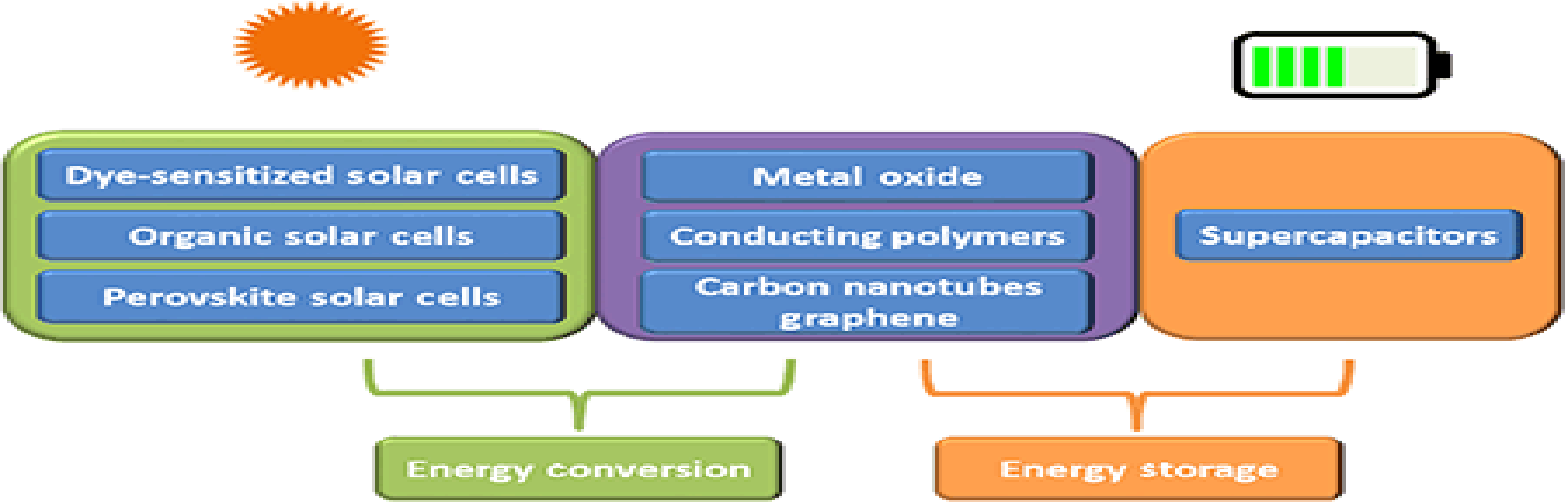


a,b) Selected dis/charge profiles for nanoparticulate Co_3O_4 and CoO-Co-C, revealing a better cycling stability for the latter, and c–f) an in situ XRD analysis of such CoO-Co-C nanocomposite: The corresponding first and second cyclic voltammogram and the simultaneous evolution of the XRD pattern.,h) Ex situ XRD patterns of Co_3O_4 in the fully discharged state for 1-20 cycles. V. S Reddy Channu, B. Rambabu, Power Sources, 2006, P 214-219 M. V. Reddy. B. V. R. Chowdari, https://doi.org/10.1021/am4047552, *Adv. Funct. Mater.* 2007, **17**, 2792.

Choice of Materials for Electrochemical Capacitors (Super-Capacitors)



Hybrid Power and Energy Storage and Conversion Devices



Dye-sensitized solar cells

Organic solar cells

Perovskite solar cells

Metal oxide

Conducting polymers

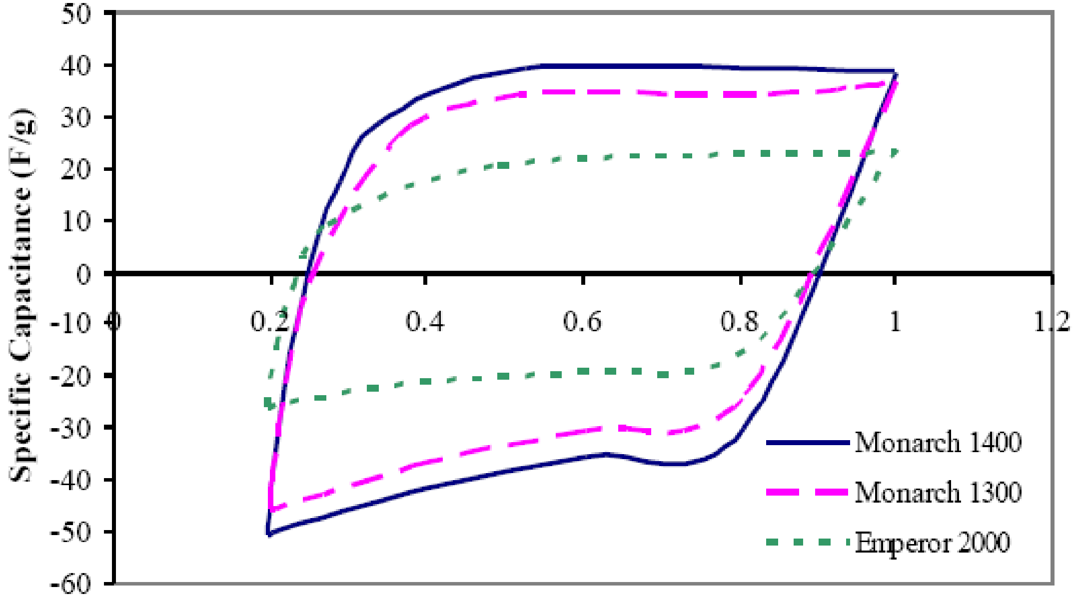
Carbon nanotubes graphene

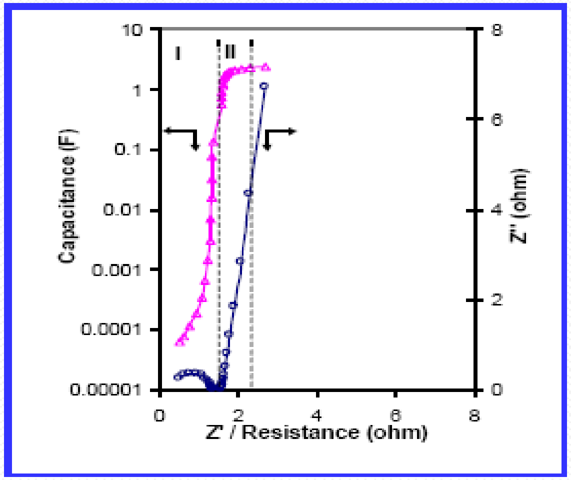
Supercapacitors

Energy conversion

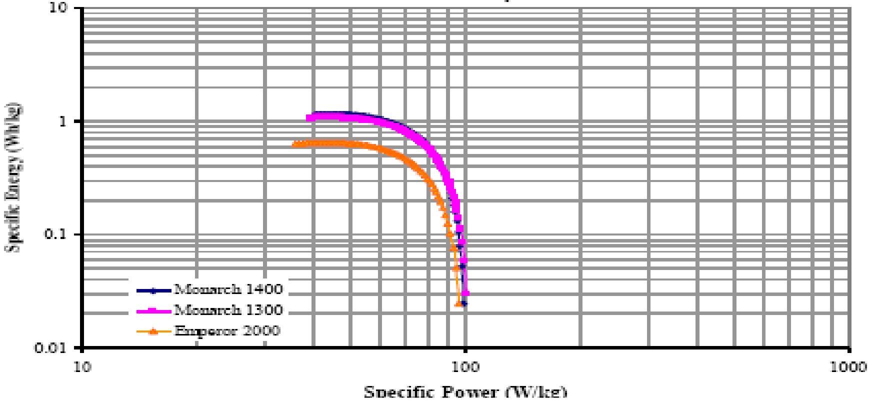
Energy storage

Nanocarbon Host: Mesoporous Carbons for Double Layer Capacitors (Super-Capacitors)



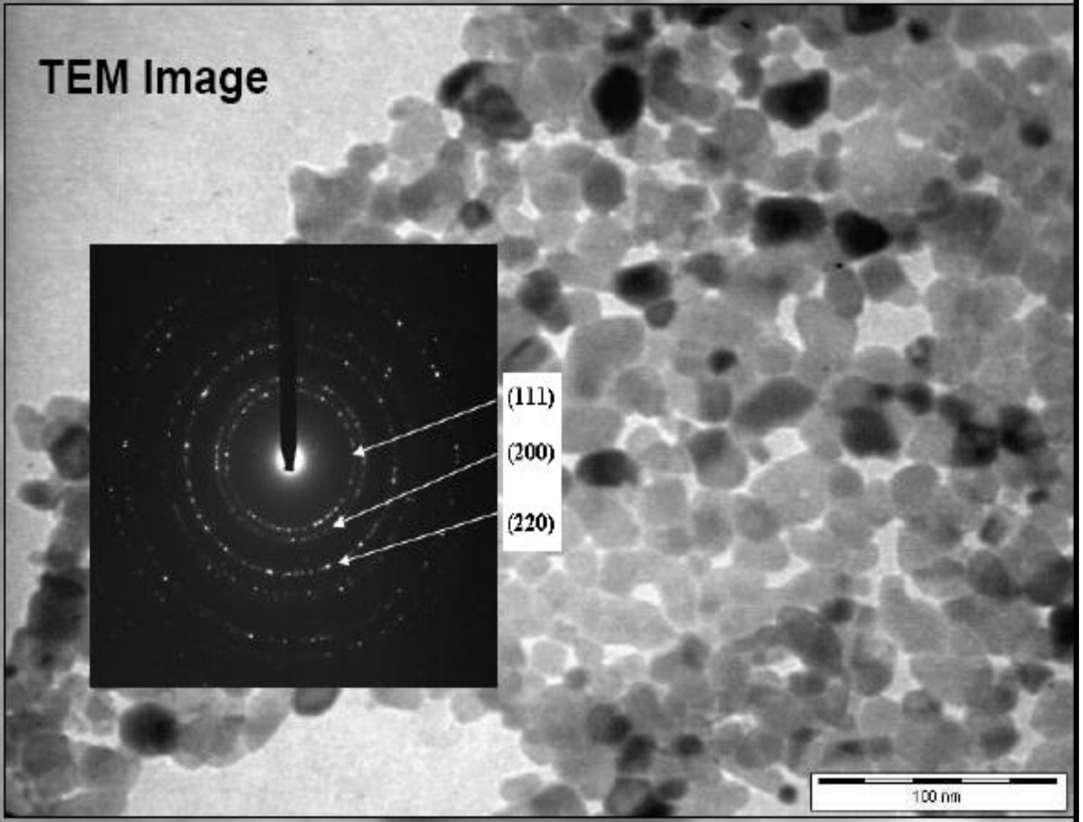


Ragone plot for Nanoporous carbons



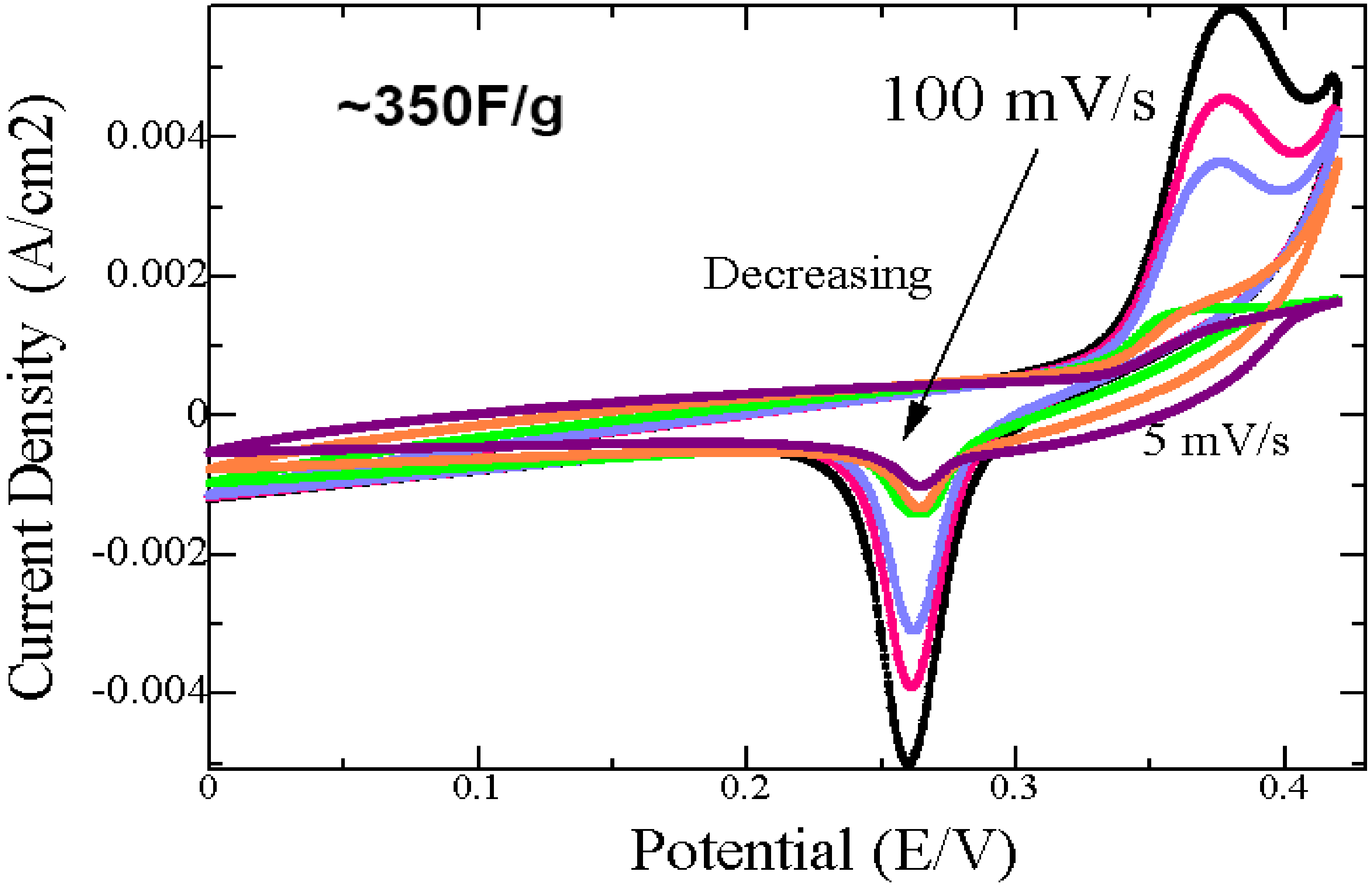
S.R.S. Prabaharan et al, J Power Sources (2006)

Nickel Oxide - annealed at 400 ° C

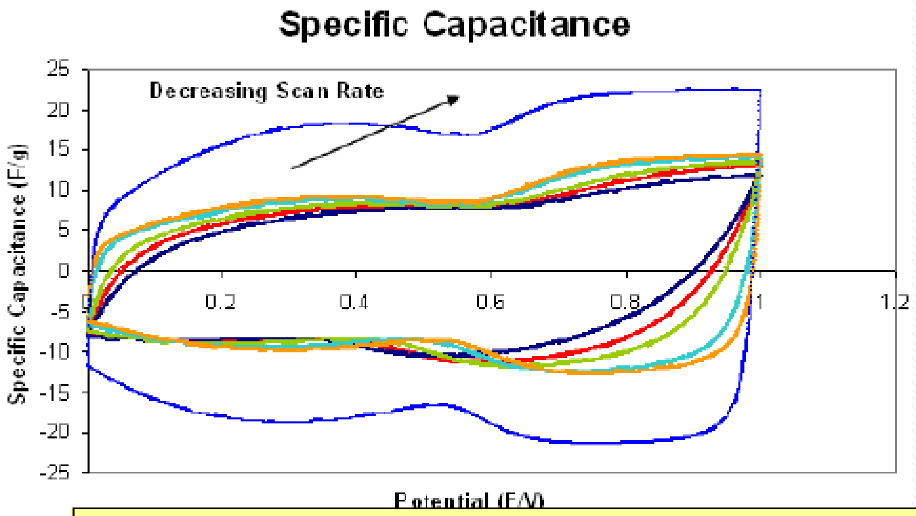


Synthesis and characterization of NiO nanoparticles for electrochemical applications, V.S. ReddyChannu, Rudolf Holze, B.Rambabu, Colloids and Surfaces A Physical and Engineering Aspects, V 414, 204-210, 2012,

Properties of Nanoscale NiO



Hybrid Capacitor, NiO (+) / Mesoporous Carbon (-)



On the positive electrode:

$$\text{NiO} \xrightleftharpoons[\text{Discharge}]{\text{Charge}} \text{NiOOH} + e^-$$

On the negative electrode:

$$C_s + K^+ + e- \xrightleftharpoons[\text{Discharge}]{\text{Charge}} \text{Cs-// K+}$$

An overall cell reaction thus for the hybrid cell is :

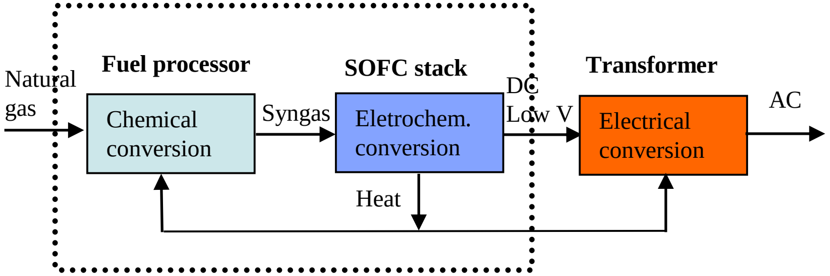
$$\text{NiO} + C_s + K^+ + e- \xrightleftharpoons[\text{Discharge}]{\text{Charge}} C_s^-\text{// } K^+ + \text{NiOOH} + e-$$

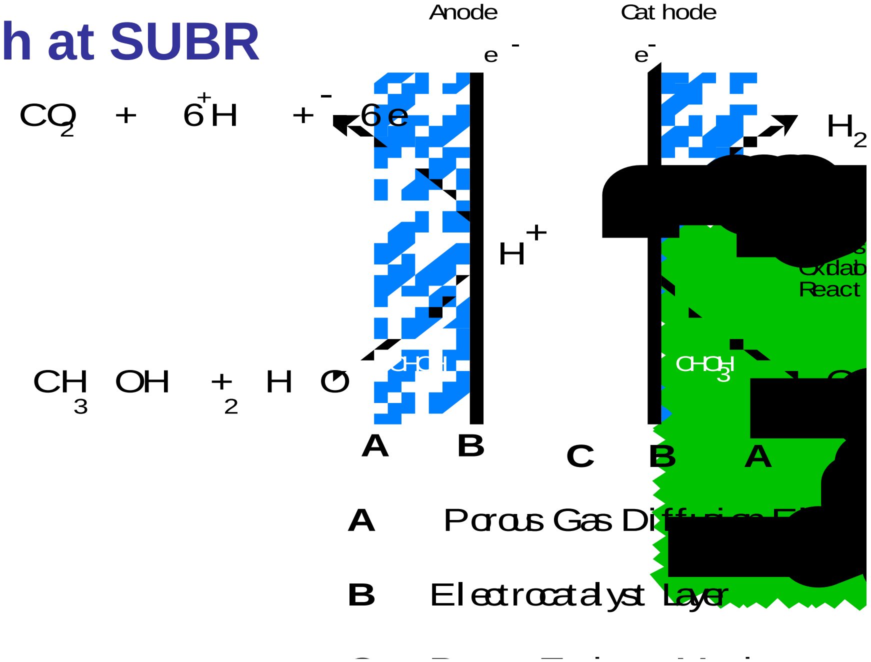
Energy Conversion [LT-PEMCs, HT-PEMCs, IT-SOFCs]

Research at SUBR

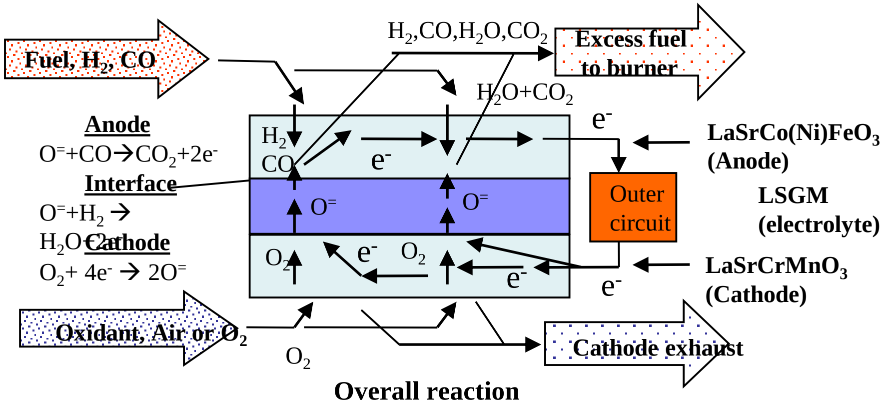
- A Fuel Cell is device that converts chemical energy directly into electrical energy.
- Fuel cells by their very nature have a potential to offer more efficient, and environmentally friendly energy production from renewable resources.
- The fuel cell is made up of four basic parts: a cathode, an anode, some form of electrolyte and a catalyst.
- There are different types of fuel cells that can be classified by their physical , chemical characteristics and specific applications.

Natural Gas Fueled SOFC





All Perovskite SOFC ~ 700^0C



Overall reaction

1/2 O_2+ H_2→ H_2O

1/2 O_2 + CO→ CO_2

Various types of Fuel Cells and their operating attributes

	AFC Alkaline	PEMFC Polymer Electrolyte	DMFC Direct Methanol	PAFC Phosphoric Acid	MCFC Molten Carbonate	SOFC Solid Oxide
Operating temp .(°C)	<100	60-120	60-120	160-220	600-800	800-1000 Low temperature (500-600) possible
Electrolyte	KOH	Perfluoro sulfonic acid (Nafion membrane)	Perfluoro sulfonic acid (Nafion membrane)	H_3PO_4 immobilized in SiC matrix	Li_2CO_3-K_2CO_3 eutectic mixture immobilized in □-$LiAlO_2$	YSZ (yttria stabilized zirconia)
Charge carrier in the electrolyte	OH^-	H^+	H^+	H^+	CO_3^{2-}	O^{2-}
Anode reaction	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$H_2 \rightarrow 2H^+ + 2e^-$	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$	$H_2 \rightarrow 2H^+ + 2e^-$	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$	$H^2 + O^{2-} \rightarrow H_2O + 2e^-$
Cathode reaction	$\tfrac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$	$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$3/2\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$	$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$\tfrac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$	$\tfrac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$
Electrode materials	Anode: Ni Cathode : Ag	Anode: Pt, PtRu Cathode: Pt	Anode: Pt, PtRu Cathode: Pt	Anode: Pt, PtRu Cathode: Pt	Anode: Ni-5Cr Cathode: NiO(Li)	Anode: Ni-YSZ Cathode: lanthanum strontium manganite (LSM)
Applications	Transportation Space, Military Energy storage systems			Combined heat and power for decentralized stationary power systems	Combined heat and power for stationary decentralized systems and for transportation(trains, boats, …)	
Realised Power	Small plants 5-150 kW modular	Small plants 5-250 kW modular	Small plants <5 kW	Small-medium sized plants 50 kW-11 MW	Small power plants 100 kW-2 MW	Small power plants 100-250 kW
Main producers	AFC Energy (UK) UTC Power (USA) Acta Power (Italy)	Ballard (Can-da) Heliocentris (Germany)	SFC Energy (Germany)	UTC Power (USA) Fuji Electric (Japan)	Fuel Cell Energy (USA)	Ceramic Fuel Cells Limited (Australia) Hexis & Vaillant (Germany) SOFC Power (Italy) Bloom Energy (USA)
*Lifetime**	Not available	2,000-3,000 h	1,000 h	>50,000 h	7,000-8,000 h	1,000 h

Development of Membranes for Polymer Electrolyte Fuel Cells

Objectives

- Develop / identify electrolytes and membranes/matrices (for low and high temperature proton exchange, alkaline membrane, molten carbonate) with improved conductivity over the entire temperature and humidity range of a fuel cell and increased mechanical, chemical, and thermal stability, with reduced/eliminated fuel cross-over •.

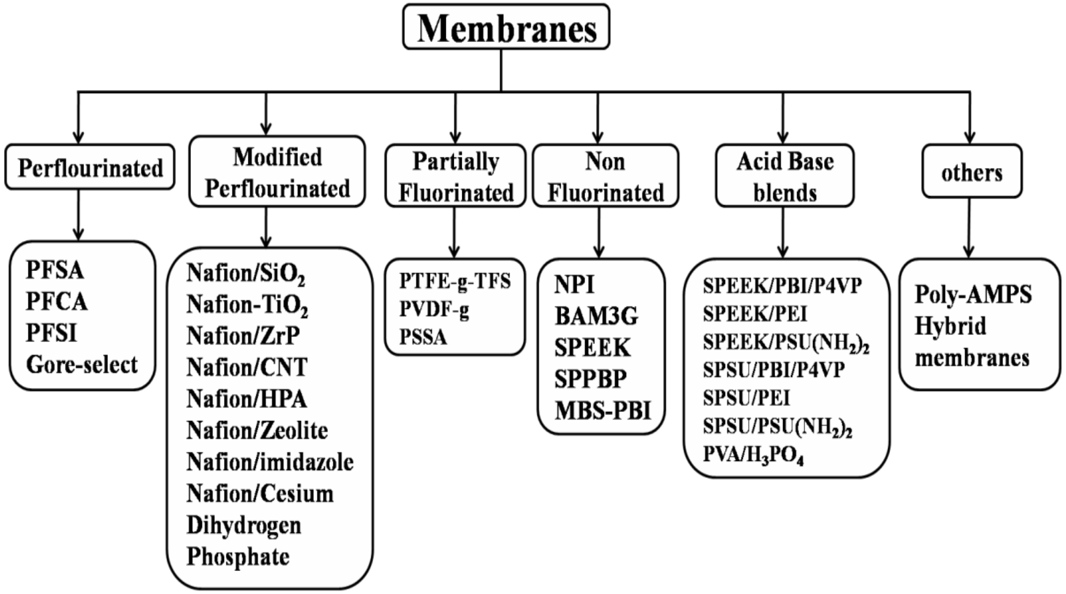
- Fabricate membranes from ionomers with scalable fabrication processes, increased mechanical, chemical, and thermal stability, and reduced cost.

- Membrane testing, characterization to improve durability

Need for new membranes alternative to Nafion® PFSA, Aquivion, 3M-ionomer, Fumapem…]

- A membrane with high proton conductivity and low methanol crossover - A membrane that operates without water at elevated Temperature.
- A membrane with high proton conductivity and low methanol crossover
- Reduce the cost.
- Temperature resistance (Nafion dehydrates at T>80 ° C and RH < 100 %)

Proton Conducting Membranes for Low Temperature PEMFCs



Membranes

Perflourinated
- PFSA
- PFCA
- PFSI
- Gore-select

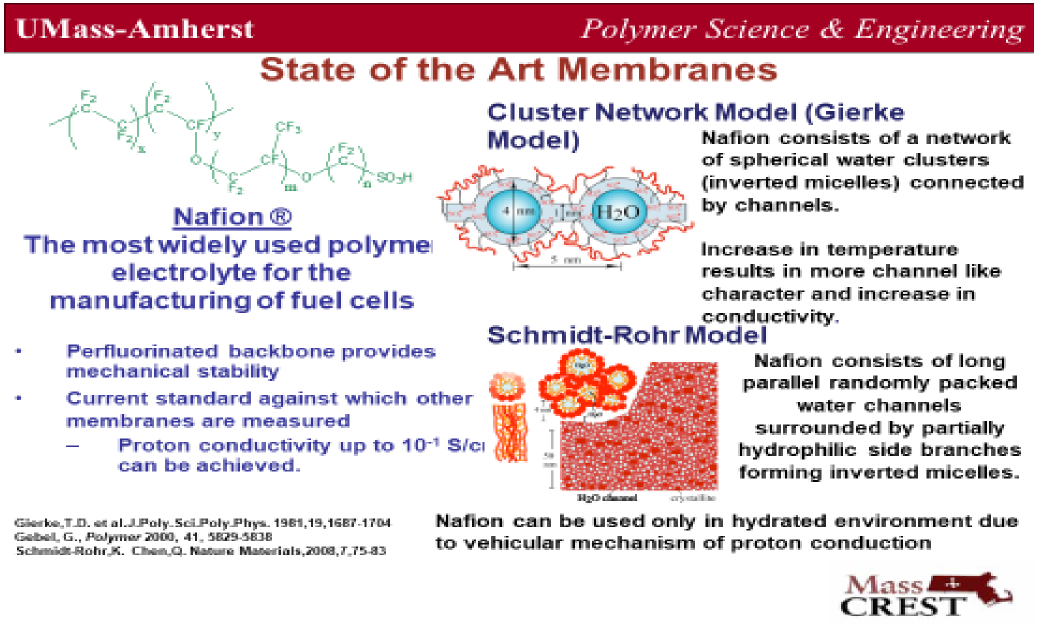
Modified Perflourinated
- Nafion/SiO_2
- Nafion-TiO_2
- Nafion/ZrP
- Nafion/CNT
- Nafion/HPA
- Nafion/Zeolite
- Nafion/imidazole
- Nafion/Cesium Dihydrogen Phosphate

Partially Fluorinated
- PTFE-g-TFS
- PVDF-g
- PSSA

Non Fluorinated
- NPI
- BAM3G
- SPEEK
- SPPBP
- MBS-PBI

Acid Base blends
- SPEEK/PBI/P4VP
- SPEEK/PEI
- SPEEK/PSU$(NH_2)_2$
- SPSU/PBI/P4VP
- SPSU/PEI
- SPSU/PSU$(NH_2)_2$
- PVA/H_3PO_4

others
- Poly-AMPS
- Hybrid membranes



UMass-Amherst *Polymer Science & Engineering*

State of the Art Membranes

Nafion ®
The most widely used polyme
electrolyte for the
manufacturing of fuel cells

- Perfluorinated backbone provides mechanical stability
- Current standard against which other membranes are measured
  - Proton conductivity up to 10^{-1} S/c
can be achieved.

Cluster Network Model (Gierke Model)

Nafion consists of a network of spherical water clusters (inverted micelles) connected by channels.

Increase in temperature results in more channel like character and increase in conductivity.

Schmidt-Rohr Model

Nafion consists of long parallel randomly packed water channels surrounded by partially hydrophilic side branches forming inverted micelles.

Gierke,T.D. et al.J.Poly.Sci.Poly.Phys. 1981,19,1687-1704
Gebel, G., *Polymer* 2000, 41, 5829-5838
Schmidt-Rohr,K. Chen,Q. Nature Materials,2008,7,75-83

Nafion can be used only in hydrated environment due to vehicular mechanism of proton conduction

Polybenzimidazoles (Poly (2,2´-m-(phenylene)-5,5´´-bibenzimidazole(PBI) based High Temperature Membranes

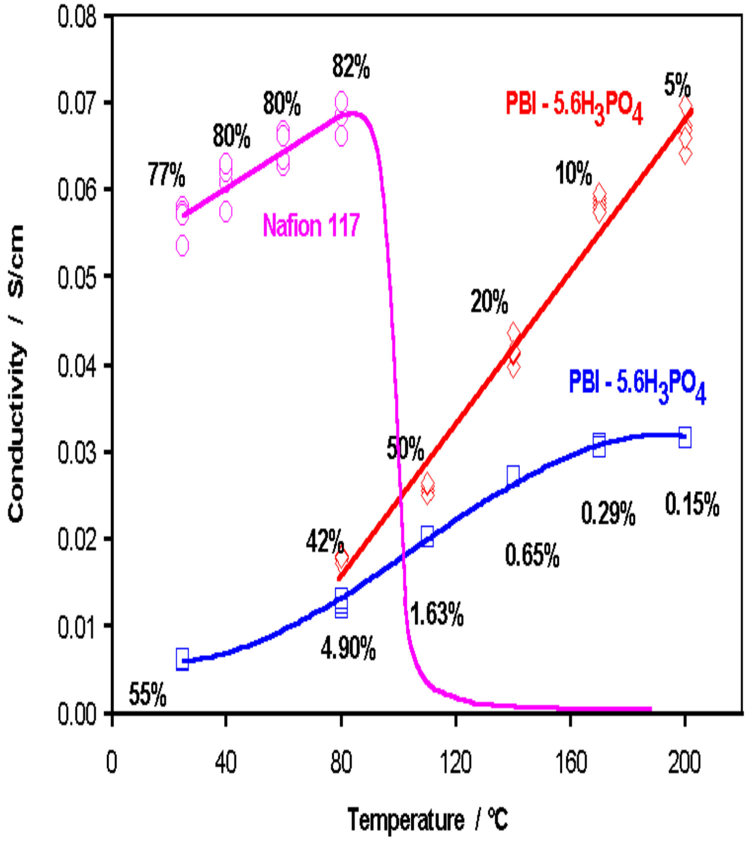
Advantages

- Kinetics of both electrode reactions will be enhanced (especially) for DMFC
- Water is in single vapor phase (management easy)
- Cooling system will be simpler (larger temp. gradient between coolant & stack)
- Heat can be recovered as steam (can be used for reforming MeOH)
- CO tolerance can be enhanced (10-20 ppm at 80^0C; 1000 ppm at 130^0C; 100000 ppm at 200^0C
- Pure H_2 is not required.
- H_2 from reformer can be used at 200^0C.
- Reduce the fuel cell cost and operating cost
- Complex network of hydrogen bonds provides proton transfer pathways

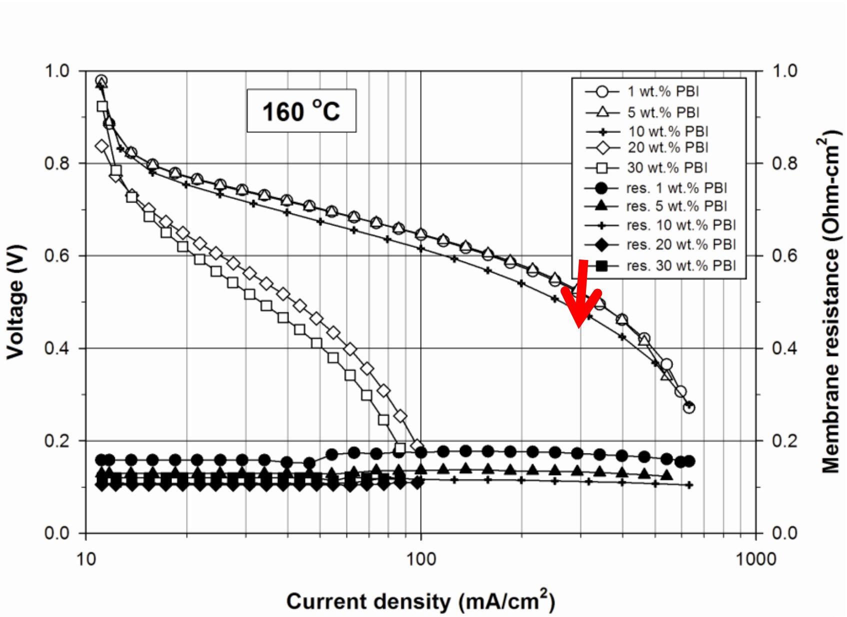
Disadvantages:

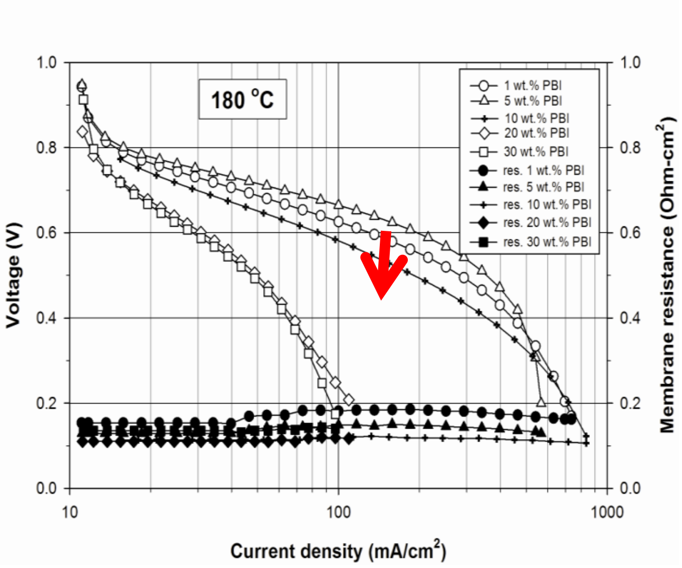
- 10 times less conductivity than Nafion
- efficiency may be affected by leaching of H_3PO_4

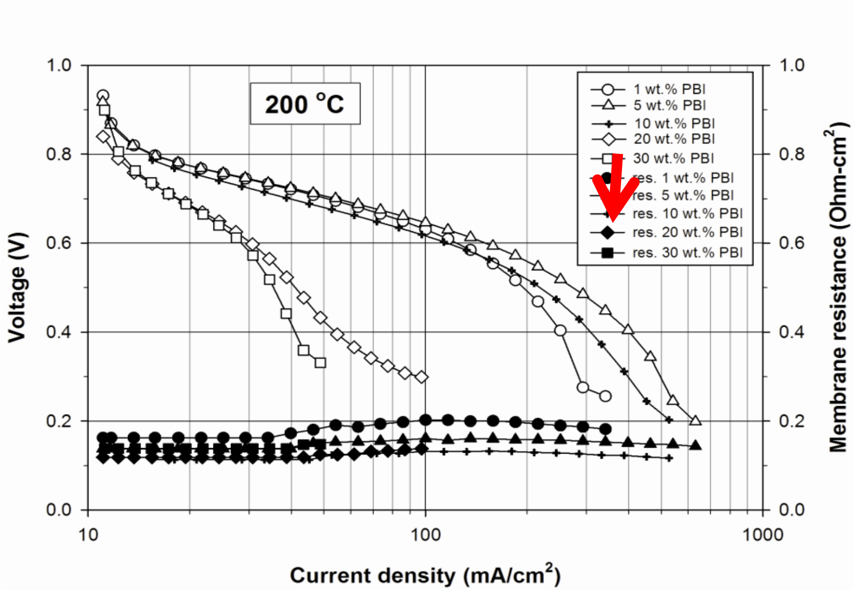
Conductivity of PBI/H3PO4 Membrane

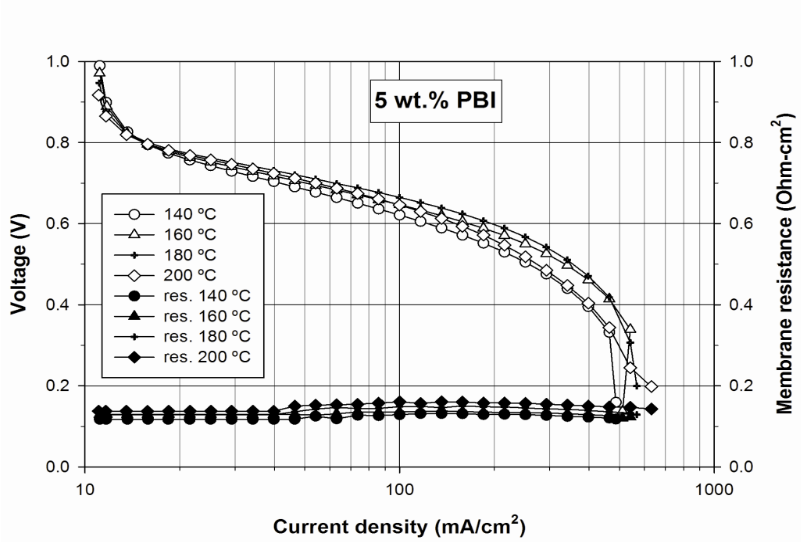


Polarization Curves of PBI/H_3PO_4 Membranes of Varied Content Measured at Different Temperatures









Perovskites for LT-SOFCs and Hydrogen Separation Membranes

Samrat Ghosh, Hrudananda Jena and Rambabu Bobba

- 1) development of low cost dense electrolyte, and porous electrode materials for reducing SOFC operation temperature to 700^0C or lower,
- 2) development of high temperature polymer electrolyte membranes for PEMFCs for avoiding stringent demands for purity levels of hydrogen fuels and withstand at $\sim200^0$C.

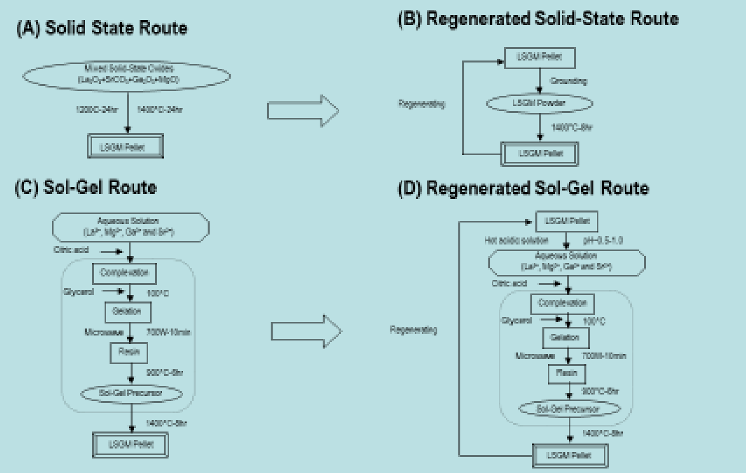
- Clearly, the convergence of these technologies might lead to a new breed of proton conducting fuel cells (PCFCs) and may be achievable through the development of thin ion (proton) conducting ceramic oxides, solid oxide/polymer nanocompsites, apatite/polymer prepared at moderate temperatures $\sim400^0$C - 600°C.

- Innovative dense electrolytes such as LSGM, $SrCeO_3$ and its doped compositions were developed. Exploring the role of proton conducting (PC) perovskites and apatites such as Calcium Hydroxy Apatite (CA-HAp) and their nanocomposites (Ca-HAp – ZrO_2, or TiO_2) as an electrolyte for developing all PCFCs.
- Mixed (ionic/electronic), protonic /electronic), conducting perovskites Porous $LaNi_{1-x}Fe_xO_3$ (LNF), $LaSrMnO_3$ (LSM) cathodes & anode (electrodes), and $LaCr_{1-x}Mg_xO_3$ interconnect materials were synthesized to fabricate SOFCs, and to be used gas(H_2 and O_2) separation membranes
- Reducing the operating temperature to 600 ^{0}C or below will be referred as LT-SOFCs Operation at less than 700°C means that low cost metallic materials and offers the potential for more rapid start up and shut down procedures.
  reduces corrosion rates
- The most developed intermediate temperature 'package'(850^0C) is:
  Anode: Ceria/Nickel cermet
  Electrolyte: Gadolinia doped Ceria (CGO)
  Cathode: LSCF (a four component oxide based on La, Sr, Co, and Fe oxides)
- Among the known geometric designs, electrolyte supported SOFCs are becoming popular and require intense investigations for commercialization. We are developing oxide-based proton conductors with high proton conductivity, and mixed (protonic/electronic, ionic/electronic) conductivities for the development of energy conversion device (fuel cells), and gas (hydrogen and oxygen) separation membrane **technologies**

Innovative processing of dense LSGM electrodes and doped Ceria electrolytes for IT-SOFC's

B. Rambabu, Samrat Ghosh, H. Jena, Journal of Power Sources 159(1):21-28, 2006, Journal of materials science 41 (22), 7530-7536, Journal of Fuel cells 2007,, Materials chemistry and physics 207, 101 (1), 20-29

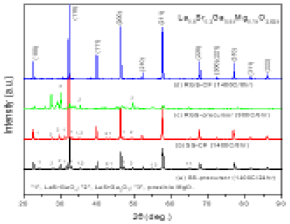
Synthesis (regenerative sol-gel) of oxide ion conducting perovskite (LSGM)



Synthetic (sonochemical/hydrothermal and mechanochemical) routes for preparing proton and mixed conducting perovskites

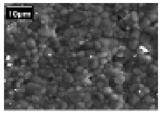
- **Sonochemical assisted reactions**
  Hydroxides of reactants were taken in stoichiometry concentrations and mixed and sonicated using ultra sound (750W). After sonicating for 30 minutes the reactant mixture was transferred to a teflon bowl and subsequently loaded into a hydrothermal cell. The stainless steel cell (auto clave was heated at 150°C/4h.
- $Sr(OH)_2.8H_2O + Ce^{4+}(NH_4)_2(NO_3)_6 + NH_4OH \longrightarrow SrCeO_3$
- **Ball milling:**
  Stoichiometric concentrations of $Sr(OH)_2$ $8H_2O$ and $Ce^{4+}(NH_4)_2(NO_3)_6$ were taken and ball milled for 1 hour in a SPEX CertiPrep 8000-series MIXER/MILL. The powder obtained after ball milled was palletized and heated in a furnace at 900°C and 1200°C.
- **Glycine nitrate combustion method:**
  Stoichiometric concentrations of $Sr(OH)_2$ $8H_2O$ and $Ce^{4+}(NH_4)_2(NO_3)_6$ were taken and dissolved to clear solution and adding 1:1 HNO_3 and ultrasonication using a ultrasonic processor (M/s. Sigma Aldrich), 750 watt power. To the clear solution glycine was added and the entire reactant beaker was heated on a hot plate (at ~100°C). The solution froth and yielded a fluffy mass. Substitution of Dy, Eu, Er were substituted at Ce site as 10 % and 5 % by taking corresponding concentrations and same procedure was followed to prepare the substituted compositions.
- **Co-precipitation method:**
  Stoichiometric amounts of $Sr(OH)_2$ $8H_2O$ and $Ce^{4+}(NH_4)_2(NO_3)_5$ were taken and coprecipitated by adding NH_4OH at alkaline pH. The precipitate was filtered and dried and heated at 1200°C/8h.

Dense $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{2.825}$ Electrolyte Prepared using RSG and sintered in microwave at different temperatures

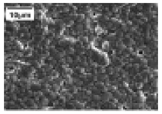


XRD spectra of $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{2.825}$ (LSGM-2015)

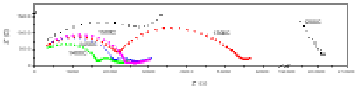
Sample	Preparation	Color	Pellet Density (g/cc)
SS-precursor	SM* was heated at 1200°C-24h, ground and heated again at 1400°C-24h in air	white	5.25
SS-CF	CP1 was ground, pelletized and conventionally heated in air at 1400°C-8h	creamish	5.65
RSG-precursor	An aqueous solution obtained by recycling of CP1 was gelled by Pechini-type sol-gel process and charred in air at 900°C-6h	white	5.1
RSG-MW1	SP1 was ground, pelletized and microwave heated in air at 1200°C-30min	creamish	5.8
RSG-MW2	SP2 was again microwave heated in air at 1200°C for another 30min	creamish	6.0
RSG-CF	SP1 was ground, pelletized and conventionally heated in air at 1400°C-8h	brown	6.5



RSG pellet of LSGM-2015

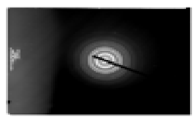


RSG pellet of $LaGaO_3$

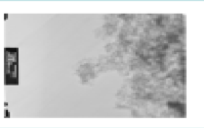


Complex plane plot of impedance spectroscopy measured in air when the samples are at 325°C.

TEM of $SrCeO_3$ precursor gel

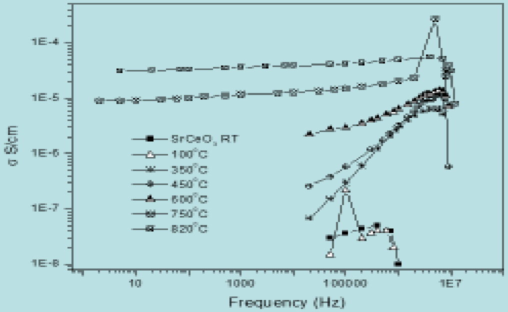


SAED of precursor gel



TEM micrograph of precursor gel

Electrical conductivity measurements on $SrCeO_3$ at various temperatures



Electrical conduction at RT corresponds to adsorbed water and hydroxyl proton in the lattice.

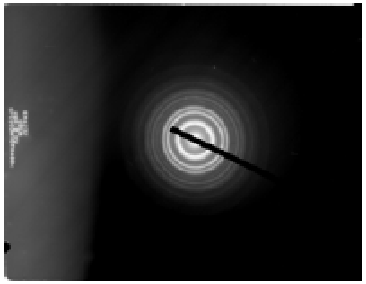
Electrical conductivity observed at 350°C is attributed to the mobility of the hydroxyl protons in the perovskite lattice.

The conductivity measured falls under regime needed for PCFC electrolyte (σ = ~ 10^{-4} S/cm at 800°C)

Conductivity increases with increasing temperature up to 1000°C for dense pellets.

Electrical conductivity is expected to increase on allovalent doping at A and B sites of ABO_3 structure.

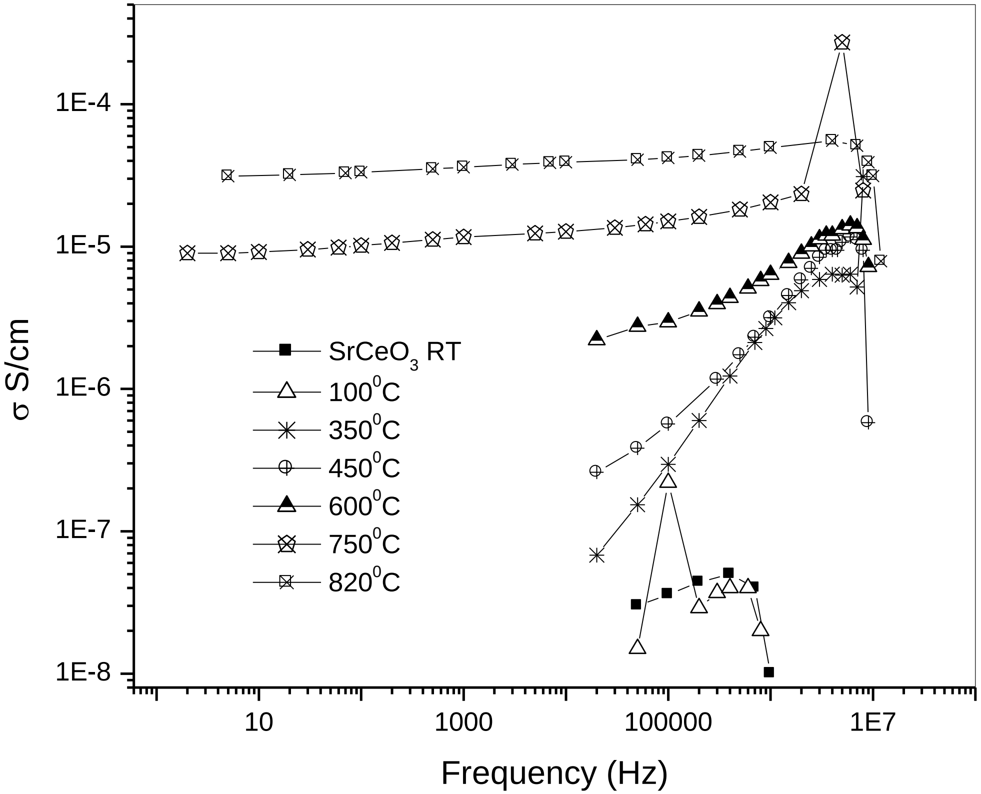
TEM of $SrCeO_3$ precursor gel



SAED of precursor gel

TEM micrograph of precursor gel

Electrical conductivity measurements on $SrCeO_3$ at various temperatures



Electrical conduction at RT corresponds to adsorbed water and hydroxyl proton in the lattice.

Electrical conductivity observed at 350^0C is attributed to the mobility of the hydroxyl protons in the perovskite lattice.

The conductivity measured falls under regime needed for PCFC electrolyte ($\sigma = \sim 10^{-4}$ S/cm at 800^0C)

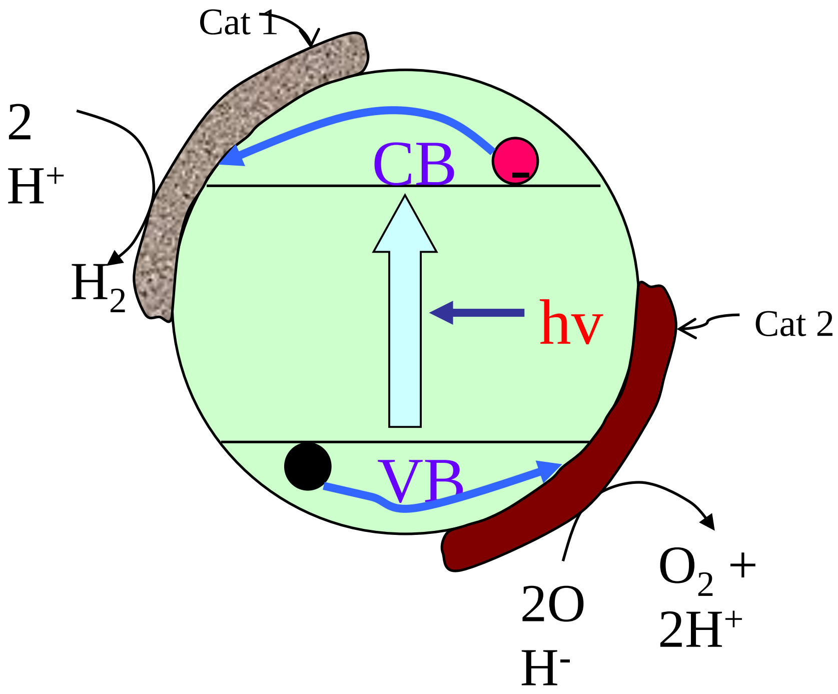
Conductivity increases with increasing temperature up to 1000^0C for dense pellets.

Electrical conductivity is expected to increase on aliovalent doping at A and B sites of ABO_3 structure.

Visible Light Nanocrystalline Photocatalysts for Photocatalytic Water Splitting

- Nature preserves this world by not activating various metal oxides with visible light that would have destroyed organic matter.” However, we are challenging what the Creator has forbidden: the visible light activation of metal oxides in a controlled manner!(Hiskia et al., Chem. Soc. Rev., 2001, 30, 62)

TiO_2, NiO, In_2O_3, NiOx/$In_{0.9}Ni_{0.1}TaO_4$), Fe_2O_3, $CaTiO_3$, Ni/$SrTiO_3$, Layered Complex Pervoskites,



Objective: Develop nano scale photocatalyst that splits water into hydrogen and oxygen in a single step using visible light, which accounts for about half of incoming solar energy.

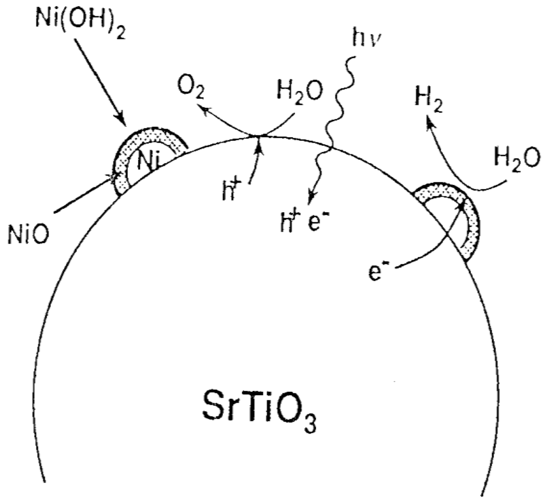
Factors that Affect the Photocatalytic Activity

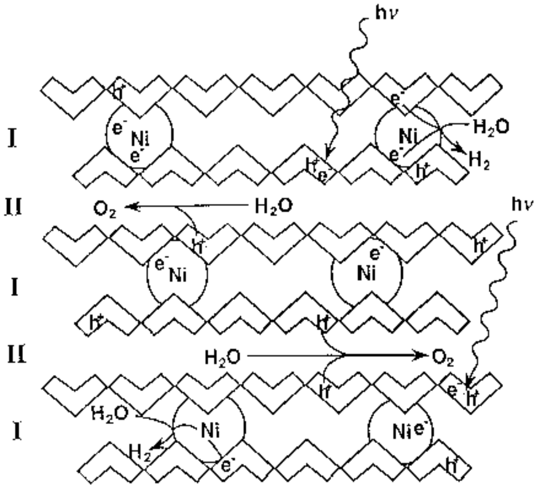
- Electronic Structure
- Bulk Structure
- Surface Defects

Factors that Affect the Photocatalytic Water Splitting

- Band Borending
- Cocatalysts; Junction Band gap and band position
- structure
- Surface area
- Defects in crystal structure and composition
- Solution pH; External additive
- Stability against photocorrosion

Photocatalytic Activity in Perovskite Type Materials





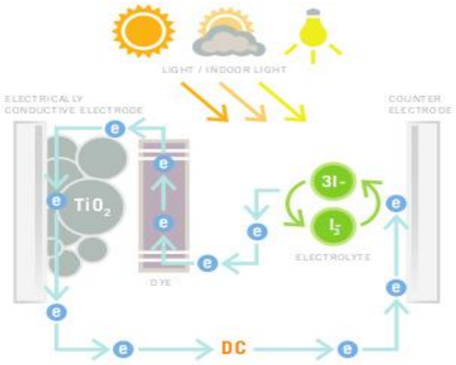
Ni/SrTiO3 << Layered Ni/K4Nb6O17

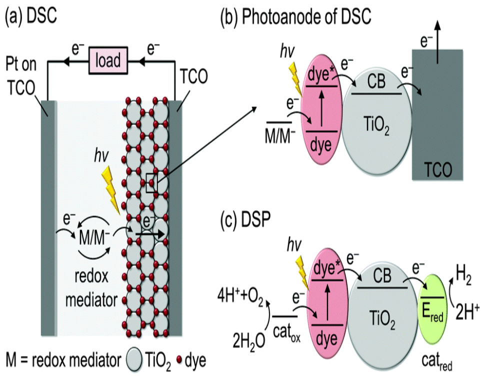
Perovskite[1]	Structure	Cation Valency	Activity[2] (μmol H_2/gcat.h)
$SrTiO_3$	bulk	+6	8
$Sr_3Ti_2O_7$	Layered	+6	11
$Sr_2Nb_2O_7$	Layered	+7	402
$Sr_2Ta_2O_7$	Layered	+7	796
$La_2Ti_2O_7$	Layered	+7	474
$LaTiO_3$	bulk	+7	137

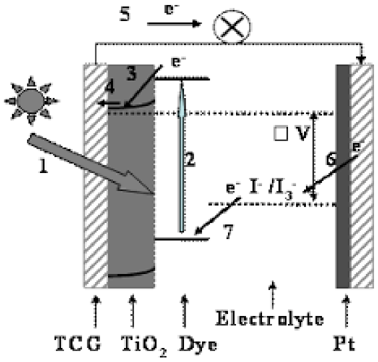
- **Dependence of photocatalytic activity on the electronic band structure as well as bulk structure of photocatalyst materials**

Both bulk structure and electronic structure was not sufficient to determine the photocatalytic activity. Therefore, other factors such as crystal defect and surface property should be considered, as shown in Ba-doped $La_2Ti_2O_7$.

Dye-Sensitized Solar Cell



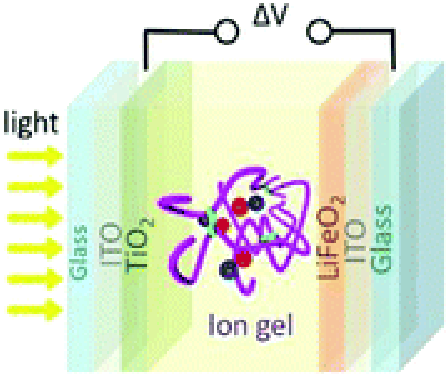


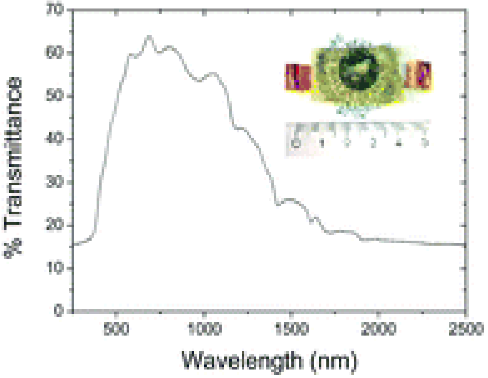


- The dye-sensitized solar cell (DSSC) consists of a dye/mesoscopic semiconductor oxide photoelectrode (PE), a dark (in the sense of not needing light for its operation) counter electrode (CE), and a charge-transport medium in the between, such as a liquid electrolyte containing a redox mediator or a solid-state hole conductor.
- The DSSC processes can be divided into two categories: that of useful processes, leading to conversion of the energy of photons to that of electrons flowing to the external circuit, and that of deleterious processes, limiting the efficiency of the solar cell.
- The charge-transport medium should not undergo any modification in its overall chemical composition during cell operation; in other terms, the DSSC should operate as a regenerative device. The most common cell configuration from the sunlight-to-electricity power conversion efficiency point of view is based on a dye-coated mesoporous n-type semiconductor oxide PE, e.g., TiO_2, ZnO, SnO_2, Nb_2O_5 Zn_2SnO_4; most commonly TiO_2.
- In particular we report the direct photo-oxidation of $LiFeO_2$ nanocrystals in the presence of a dye as a hybrid photo-cathode in a two-electrode system, with lithium metal as anode and lithium hexafluorophosphate in carbonate-based electrolyte; a configuration corresponding to lithium ion battery charging

Self Charging transparent Photobatteries and Photocapacitors

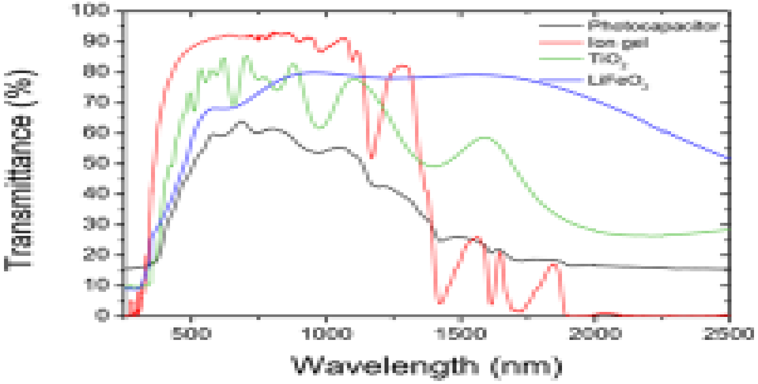
Subba Reddy Channu and Rambabu Bobba; Southern University and A&M , Baton Rouge, Louisiana-70813





- TiO2 photoanode
- LiFeO2-Ag counter electrode
- Electrolyte{PVP/LiClO4
  or PVP/[HEMIm][BF4]}

Optical Measurements



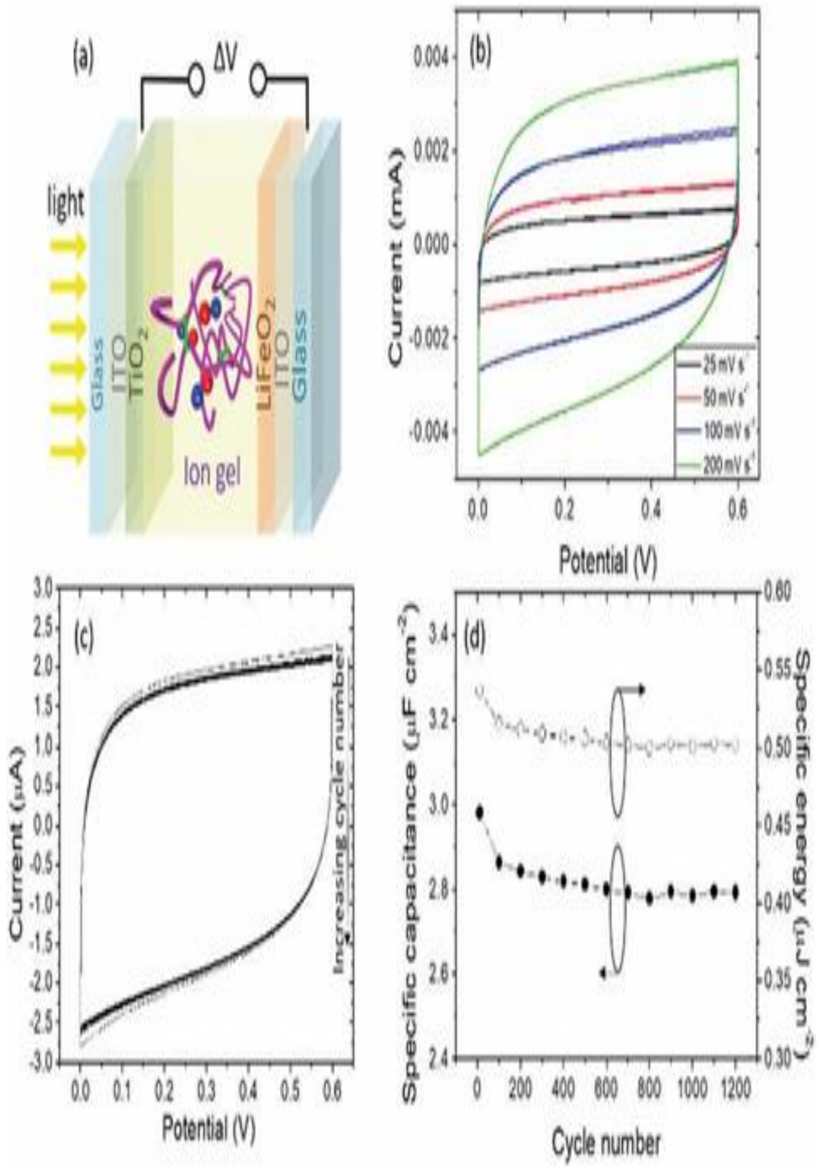
At λ= 555 nm (optical transmittance evaluated at this wavelength because the photopic eye sensitivity function has maximum sensitivity in the green spectral range at 555 nm).

The transmittance of the different components of the photocapacitor was the following:
77% for the TiO_2 electrode,
67% for the $LiFeO_2Ag$ electrode and
91% for the ion gel electrolyte,
being the transmittance at 555 nm for the whole device 57%.

Optical transmittance of each electrode, the ion gel electrolyte and the

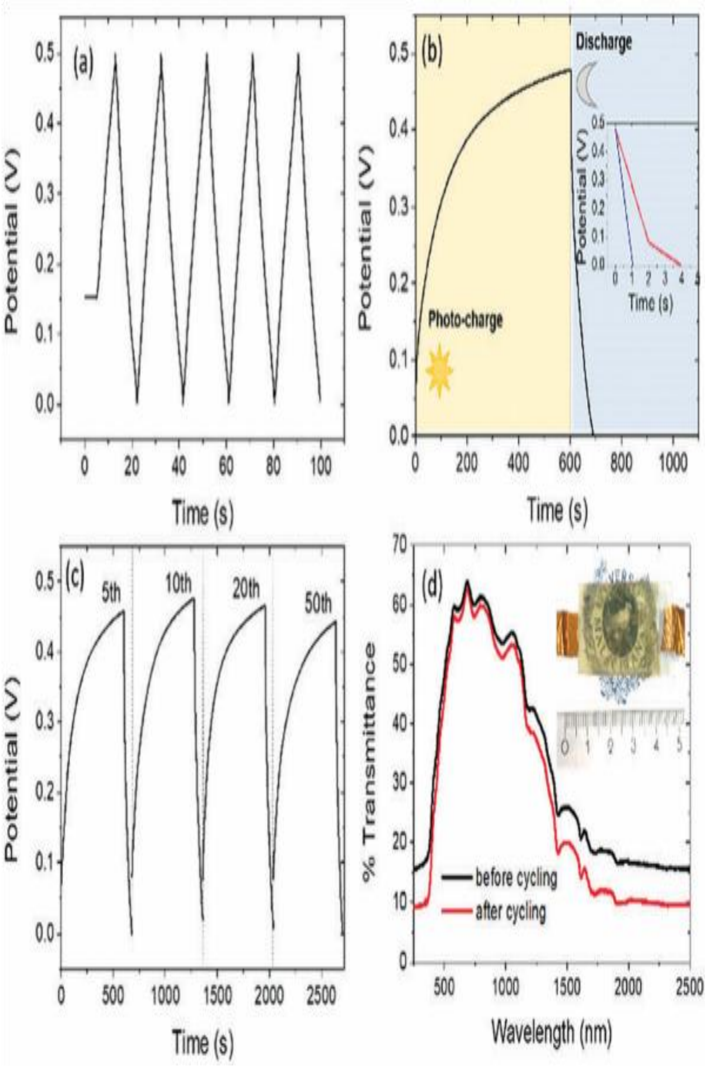
photocapacitor itself

Electrochemical Characterization of Photobattery/Capacitor



- **Scheme of the photobattery.**
- **Cyclic voltammetries at different scan rates in the dark.**
- **Cyclic voltammograms of the photobattery measured at 100 mV s^1. They were measured up to 1200 cycles (in the dark).**
- **Specific energy (J) and specific capacitance (K) obtained from the CV curves for the photobattery.** Specific capacitances from 2.78 mF cm^2 to 2.98 mF cm^2 were achieved under dark conditions depending on the voltammetry cycle number. On the other hand, specific energies from 0.50 mJ cm^2 to 0.54 mJ cm^2 were obtained. Both values decreased with the cycle number, but this decrease was not very relevant taking into account the number of cycles that were carried out (1200).

Electrochemical Cycling (Charge/discharge) of a Photobattery/capacitor



- **Galvanostatic charge and discharge of the photobattery** based on the ion gel electrolyte at a current of ±17 mA cm-2 under dark conditions.
- **Photocharge under AM 1.5 G simulated sunlight (100mWcm) illumination and galvanostatic discharge at 0.17 mA cm-2 under dark conditions** (the inset shows the galvanostatic discharge at 1.7 mA cm-2 (red line) and 17 mA cm-2 (blue line) current densities).
- **Some cycles of photocharge/ galvanostatic discharge at 0.17 mA cm-2 . Cycle numbers are indicated.**
- **Optical transmittance spectra of the photobattery with the ion gel as electrolyte before (dark color) and after (red color) cycling.** The inset shows a digital photograph of the transparent device after cycling.

Overall Efficiency (η-overall) of the Photobattery

- The $\eta_{overall}$ of the photobattery was calculated according the equation eq. S1, where E_{sp} is the specific energy, E_{light} the incident light power density (100 mW cm^{-2}) multiplied by the photocharge time and $A_{photobattery.}$ the area of the photocapacitor (6 cm^2).

$$\eta_{overall} = \frac{E_{sp}}{E_{light} \cdot A_{photocap.}} \qquad (eq.S1)$$

- a specific capacitance of 2.98 μF cm^{-2} and a specific energy of 0.54 μJ cm^{-2}

CONCLUSIONS

- In the past, **electrochemical engineering dealt more with electrochemistry and chemical engineering disciplines; taught in those departments.** However, for solving problems arising in the interface between electrode and electrolytes, cell scaling, optimization, and particularly those with three-dimensional electrodes, electrochemical processes and phenomena; closer collaborations with the other STEM disciplines has to be established and definitely a need to promote a new and dynamic academic program to meet the demand in energy and environmental Industry for sustainable development.
- **Electrochemical engineering contributes to the development of Environmental Technologies** related to materials recovery, waste minimization and recycling?. Still, There are lot of unsolved problems exits and need to be addressed. In particular, this relates to the recycling of electronic devices and scrap and the recovery of valuable materials. Bioelectrochemistry, bioelectrochemical engineering, photochemistry are undergoing very fast development. Electrochemical engineering has lot to do in and for nano-technologies?. Special interface design and new variant of interface engineering ***"from advanced materials to advanced devices* with Nanoionics"** are the key for producing nanomaterials with desirable properties. A sustainable energy future will require new thinking and new systems – essentially a transformation in the way we produce, deliver and consume energy.

- **Nanoionic batteries and supercapacitors,** should have high voltage, energy density, safety, cost effective, long life, and specific energy and capacity up to 10^{-4} F/cm^2, record value of specific power up to 10^8 W/kg at the record high frequencies, 1-10 MHz. To reach the vision of replacing the IC based vehicles with **the PEMFCs based electric vehicles,** increased research in the development of innovative materials, systems and high-volume manufacturing is needed. Carbon nanomaterials (graphene, CNTs and CNFs), non-carbonaceous supports (electrical conducting ceramics), novel Pt free or low Pt loading are currently explored as electrodes, and non-fluorinated polymer membranes as electrolytes, graphites and carbon composites as bipolar plates, high surface area carbon as GDL in MEAs are recent trends in Materials Research. The nanoscale perovskite type electrodes and rare earth doped CeO_2 electrolytea are successfully used in the development of **LT_SOFCs.** Self Charged photobatteries & Photocapacitors) and Conversion (DSCs and perovskite based solar cells) Devices are under progress in various laboratories.

- Investigation of state-of-the-art materials for energy devices is an **OPEN FIELD FOR MATERIALS RESEARCH**. There is a critical need to revise and develop the curriculums across STEM disciplines to promote interdisciplinary unique degree programs such as **"Electrochemical Engineering and Environmental Technology [E^{3}T]"** in the progressive Universities designed to promote **"21st Century Sustainable Energy and Environmental Technologies".**

Acknowledgements

- U.S-DOD-AOR Electrochemistry and Advanced Energy Conversion Division for providing graduate assistantship through the grant # W911NF-08-C-0415 and W911NF-07-1-0426

- I can be reached at: Rambabu_bobba@subr.edu, 225-505-4561.

- Mailing address: Rambabu Bobba Ph.D., Professor of Physics,
  Southern University and A&M College,
  Baton Rouge, Louisiana-70813, USA