Storage options and materials for renewable applications

Mridula Dixit and Mohd. Saquib

mdixit@cstep.in , May 10 2013

Center for Study of Science, Technology and Policy, Bangalore

Acknowledgements

Arun Kumar V
Arghya Bhowmik
Tanmay Sarkar
Vinay Kandagal
Bishal Mozumdar
Ritesh Jain
H.S. Ramakrishna
Anshu Bharadwaj
Rekha N
DRDO
BESCOM, GoK
web sources: EPRI,DOE etc

Outline

- Vision and Objectives
- National Targets across sectors
- Current energy storage scenario
- Materials for Renewables and storage
- Fundamental R&D : innovative methods
- Way Forward

Vision

To apply innovative storage solutions to challenges associated with

- large – scale deployment of renewables in India and achieve energy security, energy access and low carbon energy generation
- Large scale penetration of electric /hybrid transportation including aviation sector
- Defence applications
- Telecom sector
- portable electronics
- specialised sectors like nuclear plants

Objective

Development of optimal energy storage technologies keeping in mind the benefits, costs, risks, policy instruments, performance and reliability.

Scope

Fundamental and applied research
Economic and Policy Analyses
Pilot Projects
Outreach and Impact

National Context: Renewable energy

Aggressive renewable capacity addition

National Action Plan for Climate Change: 15% renewables by 2020
25% renewables by 2030?
wind energy: 18 GW (50 GW by 2030)
solar energy : 1.5 GW (20GW by 2022 by JNNSM)

Intensive rural electrification

Using grid connected and off grid generation (storage to be planned accordingly)

Grid Management:

Peak load management (reduce peak by 10 – 15%)
Reduction in AT&C losses (30% to 12%)
Self healing grids: Avoiding black outs

National Context: Clean Transportation

Aggressive EV/PHEV capacity addition

National Electric Mobility Mission 2020: 7 million EV by 2020
➢ saves 2.5 million tons of fossil fuels and lowers emissions from automotives by 1.5%

Planned investments ~ $ 4.2 Billion to increase domestic manufacturing and incentivize sales of EV

Challenges

Battery
charging infrastructure
manufacturing know how

National Context: Defence

- ☐ **Navy**

Torpedoes, Missile systems, air/sea targets, submarines,
Deep sea diving , starter versus deep cycle battery capability

- ☐ **Air force**

Drones, Mini UAV like Entomopter etc

- ☐ **Army**

Land combat, Communications equipments, Emergency radios, Night vision goggles,
Battlefield planning devices, GPS, Missile guidance and control

- ➢ **Current High altitude location issues** (Siachen, Kargil, Dras sector)
- ➢ electrolyte freezing, low ionic mobility, poor kinetics
- ➢ lower operating voltage and poor material utilization leads to reduced power and energy density

Storage for Renewables

Top 10 countries by wind power installed capacity (December 2012)

Country	**Capacity (MW)**
China	75,564
United States	60,007
Germany	31,332
Spain	22,796
India	**18,445**
United Kingdom	8,445
Italy	8,144
France	7,196
Canada	6,200
Portugal	4,525
Rest of world	39,853
Total	**282,482**

Current scenario (Wind Power): INDIA

India		
Potential (MW)		Installed Capacity (MW)
C-WET	LBNL*	
49,130 @50 m 102,788 @80 m	676,218 (on-shore)	18,445
	214,304 (off shore)	None Off shore
Karnataka		
13,236		2,195

* 80 m hub height, below Rs. 6/kWh

Intermittency Challenge

Wind power intermittency can be addressed by:

- Stored energy at grid scale
  - capture of wind energy as it is produced and store it for delivering when required
- Alternate capacity available on demand at short notice
- Reduce demand if the wind output falls unexpectedly

Wind may be free but the equipment needed to turn it into useful energy when needed is still in development and quiet costly at present.

Main Storage Options

- ❑ Mechanical: Pumped Hydro (PHS), Compressed air and Flywheel

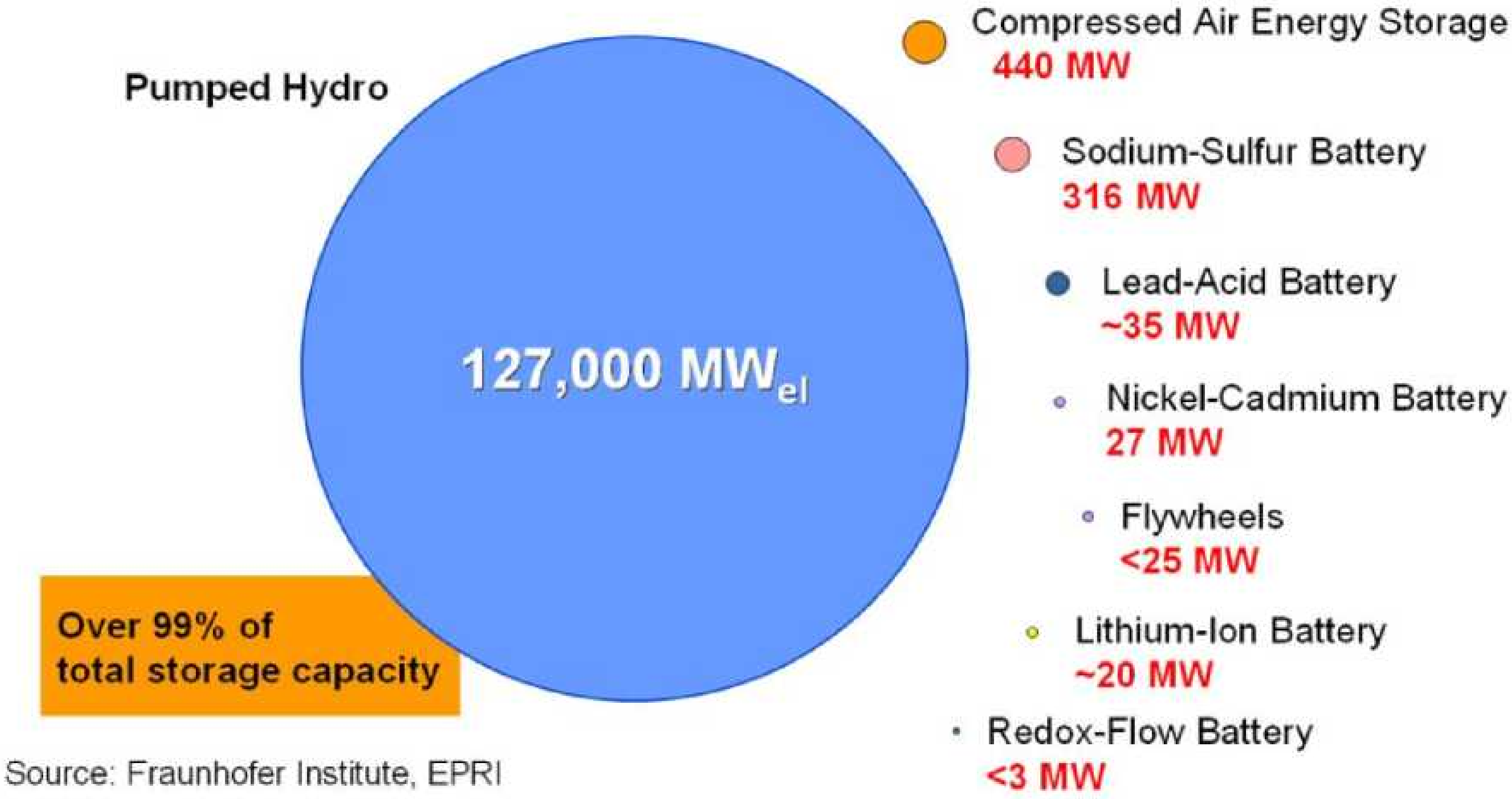
- ❑ Electro chemical: Batteries (Na-S, Pb acid, Ni Cd, Ni MH etc)

Storage status:

At present no commercial scale storage solutions in India

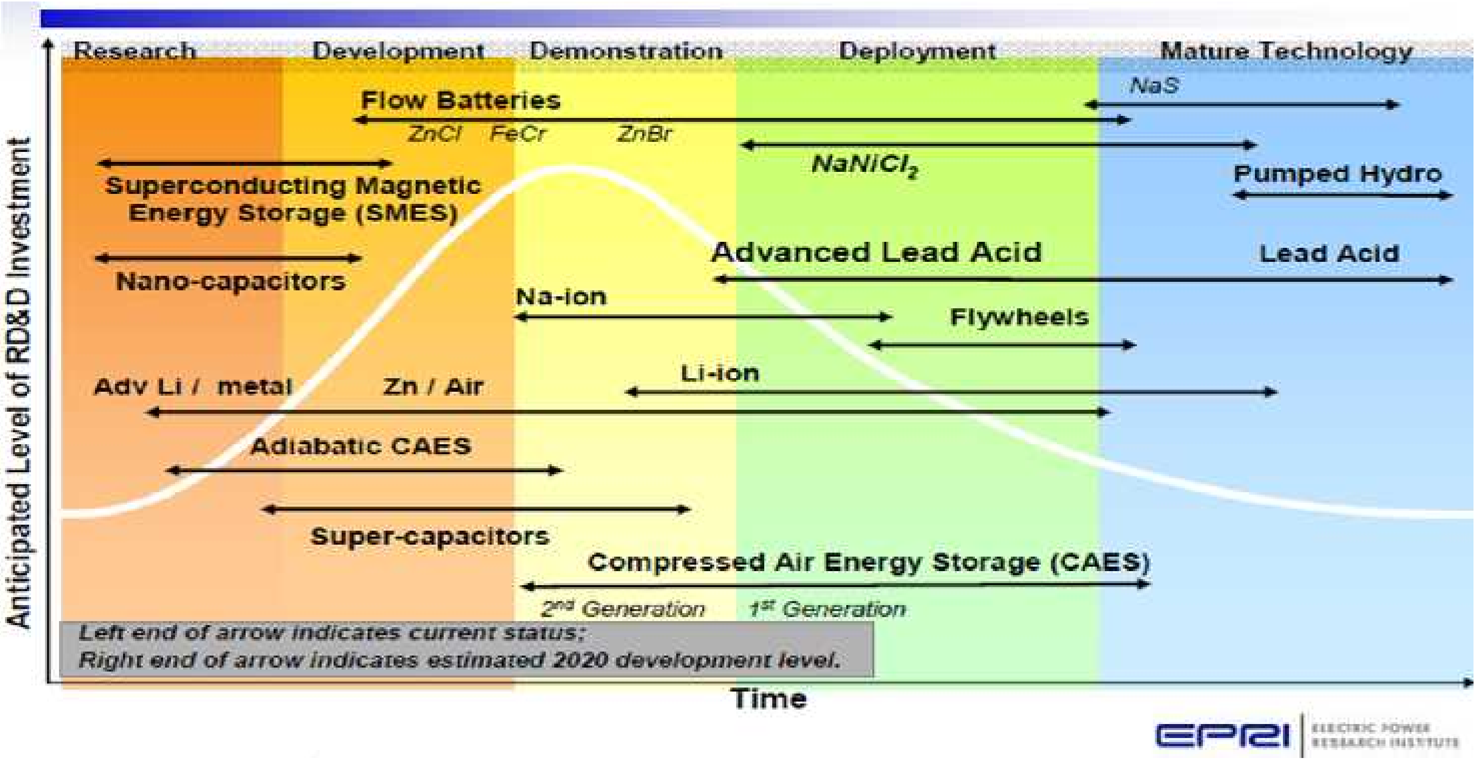
  - ❑ electricity is used as it is generated

Worldwide installed storage capacity for electrical energy



Source: Fraunhofer Institute, EPRI

Current Status of Storage options



PHES

- ➢Potential: 94000MW , 56 sites (CEA, Min of Power)
- ➢Existing : Around 6000MW
- ➢Sardar Sarovar (2006), 1200MW
- ➢Tehri Stage II (2006), 1000MW
- ➢Shravathi (planning), 900MW.

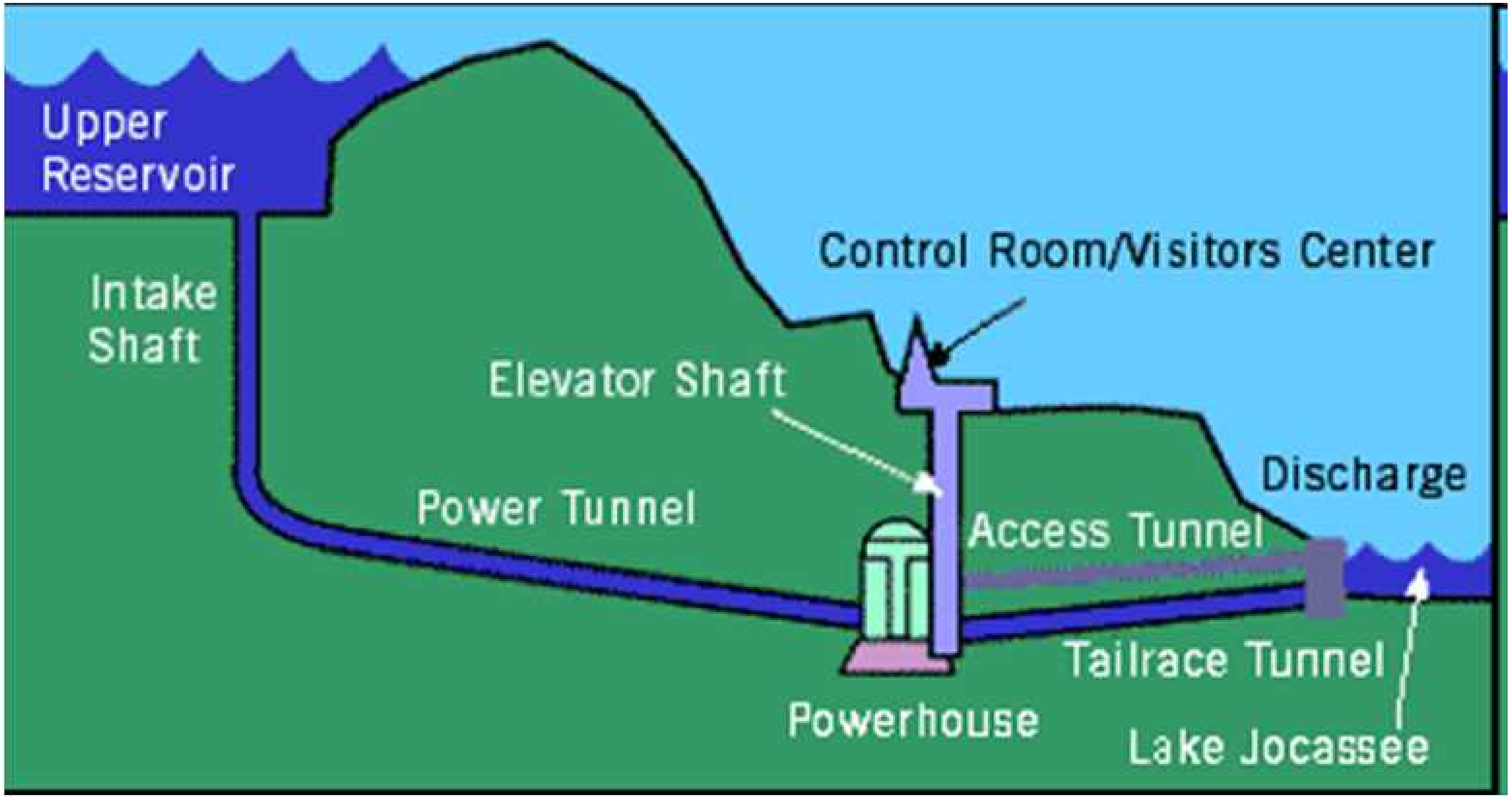
CAES

- ➢None in India
- ➢Huntorf, Ge : 290MW
- ➢McIntosh, USA :110MW
- ➢Shanghai : 300MW (Devlp stage)

Na-S

- ➢None in India
- ➢Globally, 350-400MW
- ➢Mainly in Japan. China & USA
- ➢Demonstration stage in Europe

Pumped Hydro Storage



Ref. PHS at Koko Crater, Hawaii island

Pumped Hydro

SALIENT FEATURES and CHALLENGES

☐ Stores energy in the form of water pumped to an elevation when the demand for electricity is low and utilizes stored water to generate power; long life time, > 80% Efficiency

☐ Restricted to wind regions that offer sufficient geographical elevation difference, water and land availability

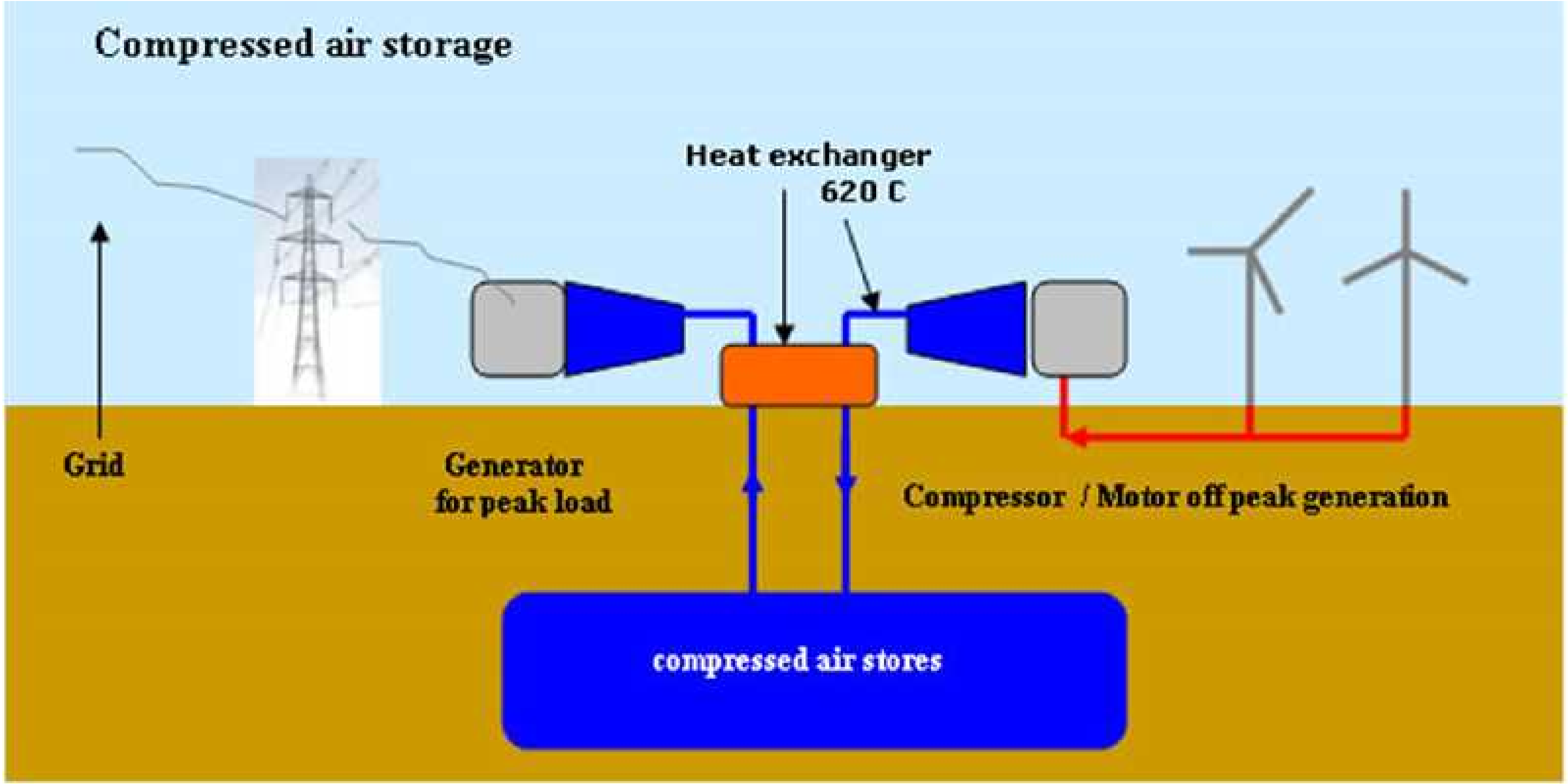
☐ Other issues: long lead time, cost is highly site specific

☐ India has a few PHS (e.g. 150 MW, Tata)

☐ US:150 plants with 22,000 MW capacity, Worldwide: 125,000 MW

Need for-
Feasibility studies of PHS option for different states in India

Compressed Air Energy Storage (CAES)



Concept image: climateandfuel.com

Compressed Air Storage

SALIENT FEATURES and CHALLENGES

- Uses wind energy to compress air and store it underground;

- When required, the compressed air is expanded through a turbine

- In addition, natural gas could be added as auxiliary fuel to achieve higher temperatures

- Typical pressures ~ 65 – 70 atm;
- Compressed air temperature ~ 600 ^{0}C,
- Store heat by ceramic bricks and reuse for generation; > 75% efficiency in practice
- Limited by proximity to abandoned mines, volume of mines and the pressure at which it is stored

Global installations:
1978:Germany 290 MW
1991: Alabama, US: 110 MW
Planned: 270, 300, 150 MW (USA); 200 MW (Germany)

Flywheel Energy Storage

- mechanical devices, store energy in a rotating mass
- energy from windmill drives electric motor that spins a fly- wheel
- stored energy released through an electrical generator
- long life time, high energy density (130 Wh/Kg),
- Efficiency ~ 90%
- Issues: tensile strength of the rotor material, energy storage time (20-50% energy loss in 2 hrs)
- Beacon Power (NY) : largest FWES plant 20 MW storage

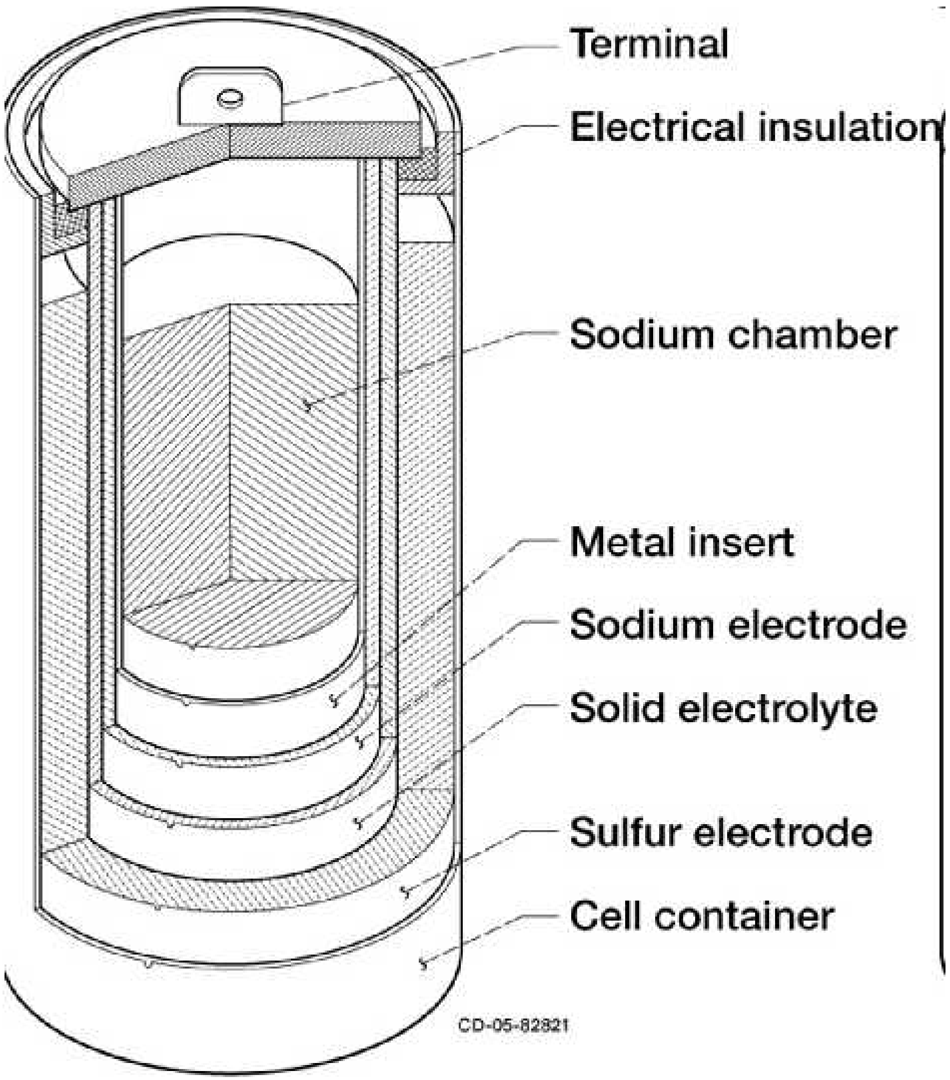
Key Battery Systems

Battery Type	**Cell Reactions/Features**	**Cell voltage**
Lead Acid (LAB)	$Pb+PbO_2+2H_2SO_4 = 2PbSO_4+2H_2O$	(2.1V)
Ni- Cd	$Cd+2NiOOH+2H_2O = 2Ni(OH)_2+Cd(OH)_2$	(1.35 V)
Ni-MH	$MH+NiOOH = M+Ni(OH)_2$	(1.35V)
Li-Ion (LIB) $LiCoO_2/LiBF_6/C$	$Li_xC_6+ Li_{1-x}CoO_2 = LiCoO_2+ C_6$	(3.8 V)
Nanobatteries ($LiCoO_2/LiBF_6/Li$ Titanate)	Modified Li-Ion system, Anode:nanocrystals of Li titanate, > 12,000 cycles); Recharge time 6-10 min!	(> 2.7 V)

Electrochemical Storage : Batteries

Battery Type	Volts	Specific Energy Wh/kg	Specific Power W/kg	Life (# of cycles)
PbO_2/H_2SO_4	2.1	35	180	400
NiOOH/KOH/Cd	1.35	60	150	500
NiOOH/KOH/MH	1.35	70	500	1500
$LiCoO_2/LiBF_6/C$	4.2	100	1000	500
Na-S & Zebra Battery	2.6	90	155	2500
Vanadium redox	1.2	30		10,000
Zn/Br Flow Battery	1.8	50		2000

Batteries: Na-S

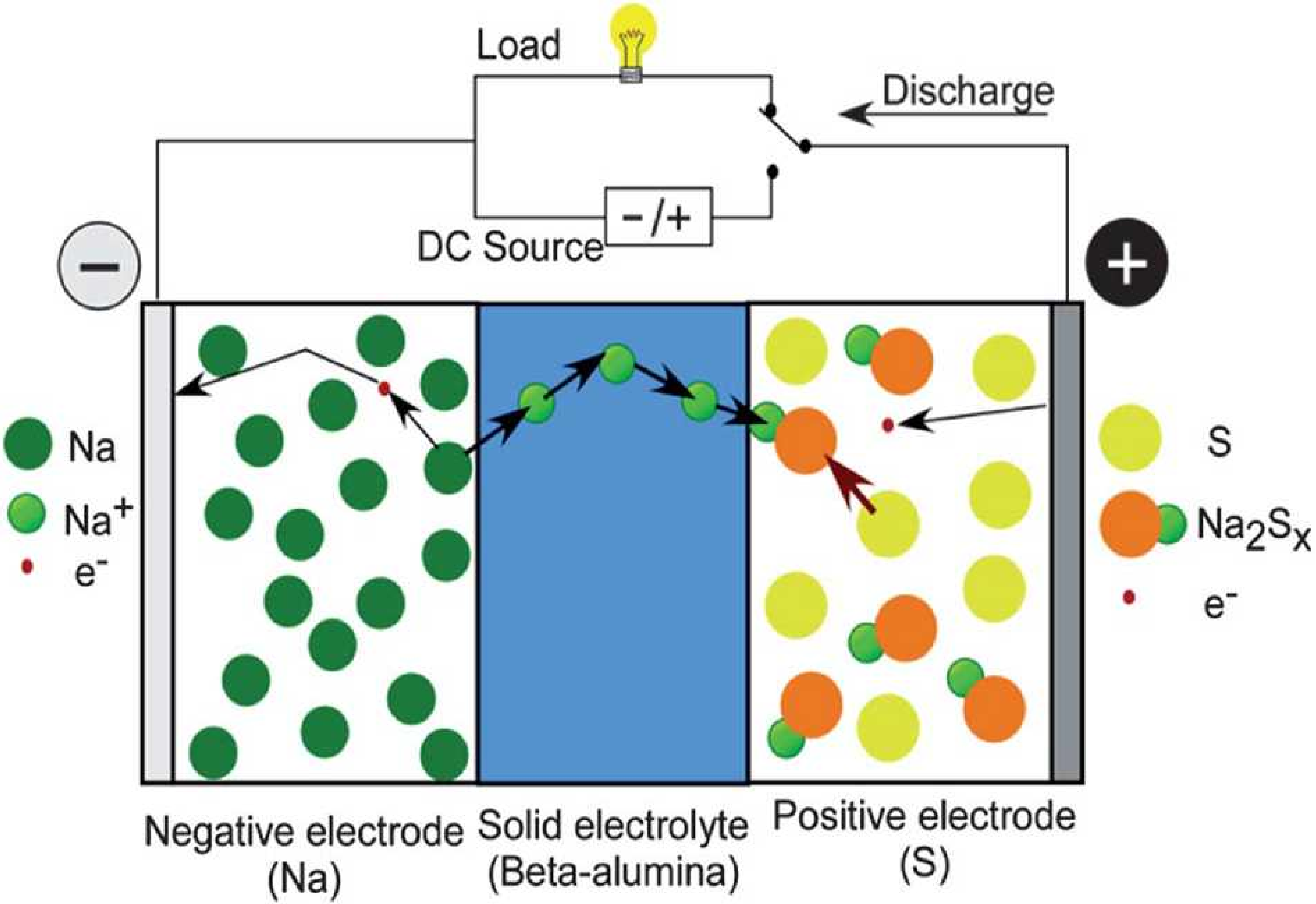


Sodium sulfur battery schematic

(Anode)
2Na <-> $2Na^+ + 2e^-$

(Cathode)
xS + $2e^-$ <-> Sx^{2-}

(Overall cell)
2Na + xS <-> Na_2S_x, *E = 2.08–1.78 V*


Load
Discharge
DC Source
−/+
−
+
Na
Na+
e-
S
Na2Sx
e-
Negative electrode (Na)
Solid electrolyte (Beta-alumina)
Positive electrode (S)

Batteries: Na-S

SALIENT FEATURES and CHALLENGES

- Molten metal battery, operating temperatures of 300-350 C
- High energy density, low maintenance, coulombic efficiency > 90 %
- Lifetime of 2500 cycles at 100% DOD or 4500 cycles at 80% DOD
- Limited by short life of insulator, high rate of self discharge

- In India, sodium manufacturing is an issue

- Tested extensively in Japan for use in utility based load leveling and peak shaving
- NGK/TEPCO providing 90 MW/ year storage capacity
- Japan Wind Dev: 51 MW wind farm has 34 MW Na S battery pack (2008)
- Presidio, Texas Na-S battery installation largest

Li Ion Battery for Energy Storage: Status on Lithium

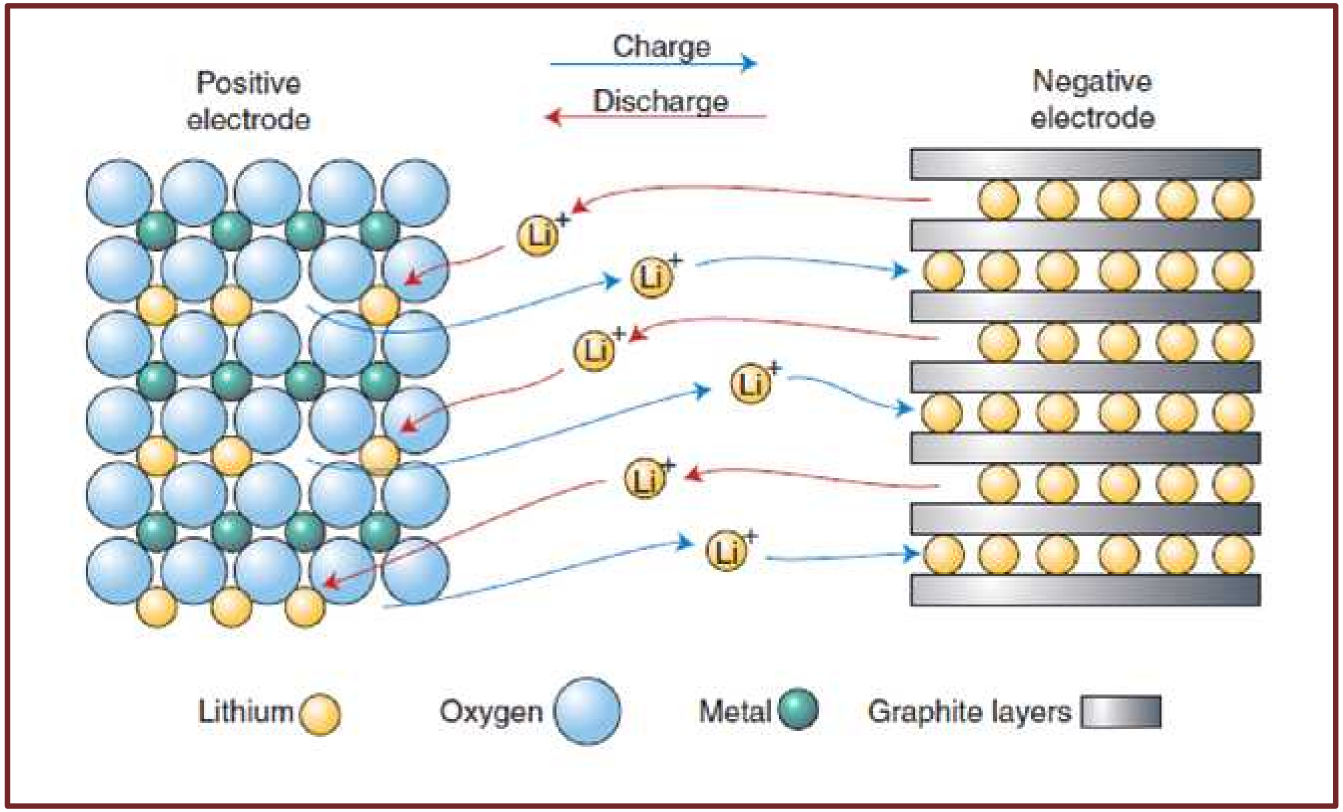
- Total Li reserves 28.5 million tonnes world wide
- China to make 0.5 million Li battery based cars per annum
- Rising volumes of Laptops, portable electronics, Defense equipment's
- Current cost: $ 1000 per kWh of Battery power
- 24 kWh Nissan (EV) and 16 kWh Chevy Volt (PHEV)
- Li metal= $ 660/kg; Li weight= 0.3 kg/kWh

Amount of Li metal per 100,000 cars : 480,000 Kg (Rs. 1500 Crores)

- *China ranks third after Chile and Australia in mining* Li_2CO_3
- *South America has nearly 80% of global Li reserve base*
- ***Can Indian Rare Earth / other reserves help in development of next generation batteries?***

- *LIB : slow penetration into renewable energy applications*

Li-Ion Battery



Better electrolytes can lead to higher power density and safer batteries

SCIENCE, Vol 296, p-1224, 2012

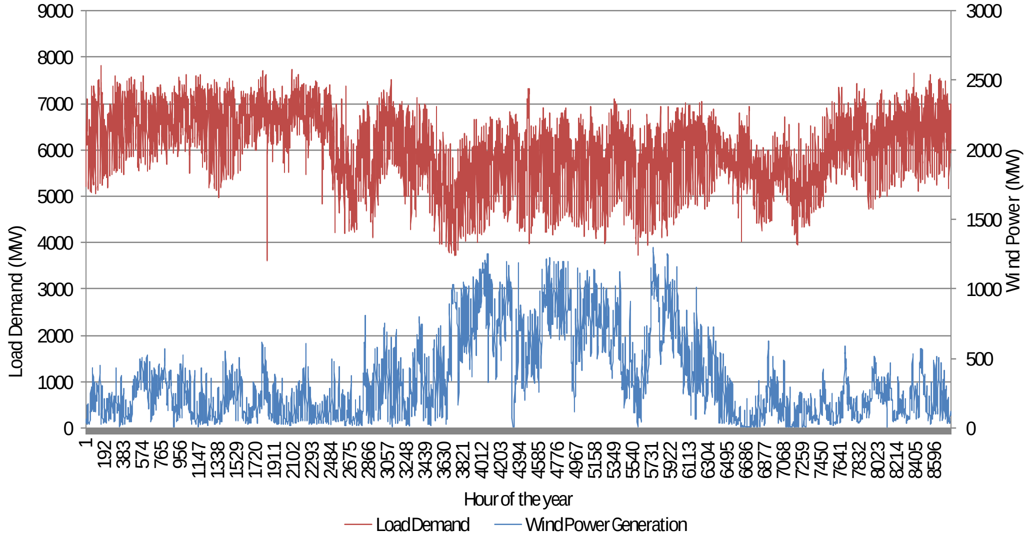
LiB: Electrolytes

- *Organic liquids*
  - **Pros** High diffusivity (~10^{-2} $mScm^{-1}$),
  - **Cons** Low voltage (< 5V), unsafe,
- *Ionic liquids*
  - **Pros** Good Li-conductivity (~10^{-3} $mScm^{-1}$), high voltage (> 5 V), safety, high temp. compatible.
  - **Cons** unstable at low voltage, unstable solid electrode interface (SEI)
- *Polymer (solid and gel)*
  - **Pros** High energy density, safe, inexpensive
  - **Cons** Low diffusivity, low voltage window (4.5 -4.8 V)

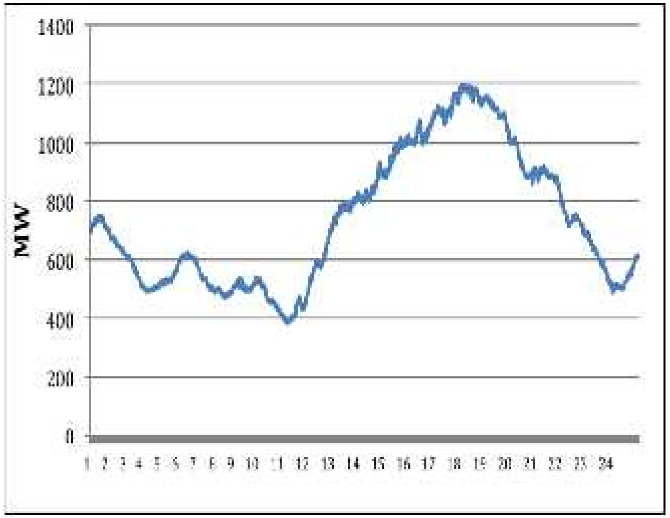
Comparison of performance parameters

Energy Storage Systems	Mechanical			Chemical		Electrical
Technical Description	PHS	CAES	Fly-wheels	NaS battery (300-350°C)	Na/$NiCl_2$ or Zebra battery (270-350°C)	Super Capacitor
Storage capacity/ Specific Energy	1680-14000 MWh	1080-2700 MWh, up to 3600 MWh for CT-CAES	5 MWh	150-240 Wh/kg	95-120 Wh/kg	2.5-15 Wh/kg
Power capacity/ Specific Power	280-1400 MW	135-180 MW	20 MW	150-230 W/kg	150-200 W/kg	500-5,000 W/kg
Duration	6-10 hours (>10 hours)	8-20 hours	~0.25 hours	<6 hours	~ 2-6 hours	1-30 seconds
Roundtrip Efficiency	80-82%	60-80%	90%	80%	70-80%	90-98%
Lifetime (Cycles, Years)	>13,000, ~ 40-60 yrs	>13,000 ~ 30 yrs	>20,000, ~ 15 yrs	2,500(100% DOD); 4,500(80% DOD), ~ 15 yrs	> 2500 ~3500 at 80% DOD lifetime~ 10-15 yrs.	~ 20 yrs
Response time	60-90s from shutdown; 5-15s from on-line to full load.	5-12 min with ramp rate of 30% of maximum load per min	4 ms	1 ms	1 ms	4 ms

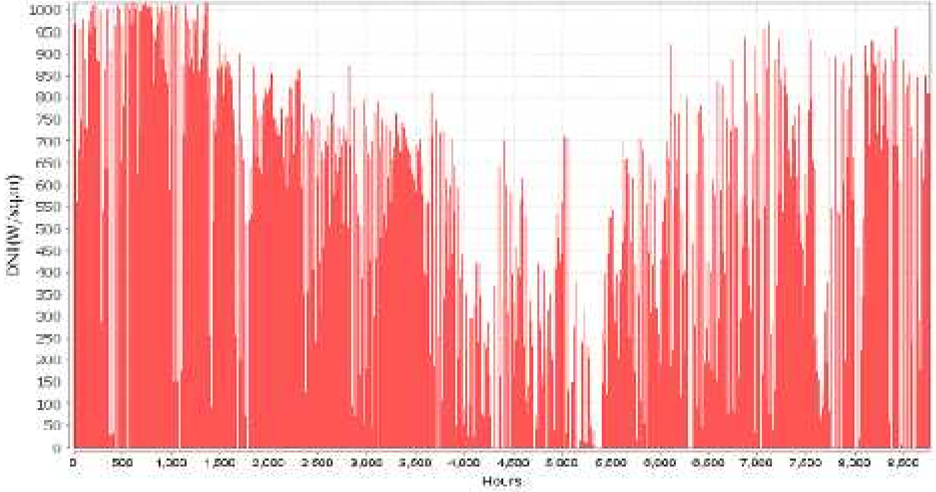
Fluctuations in renewable energy output make batteries necessary



Hourly average load demand and wind power generation in Karnataka (2011)

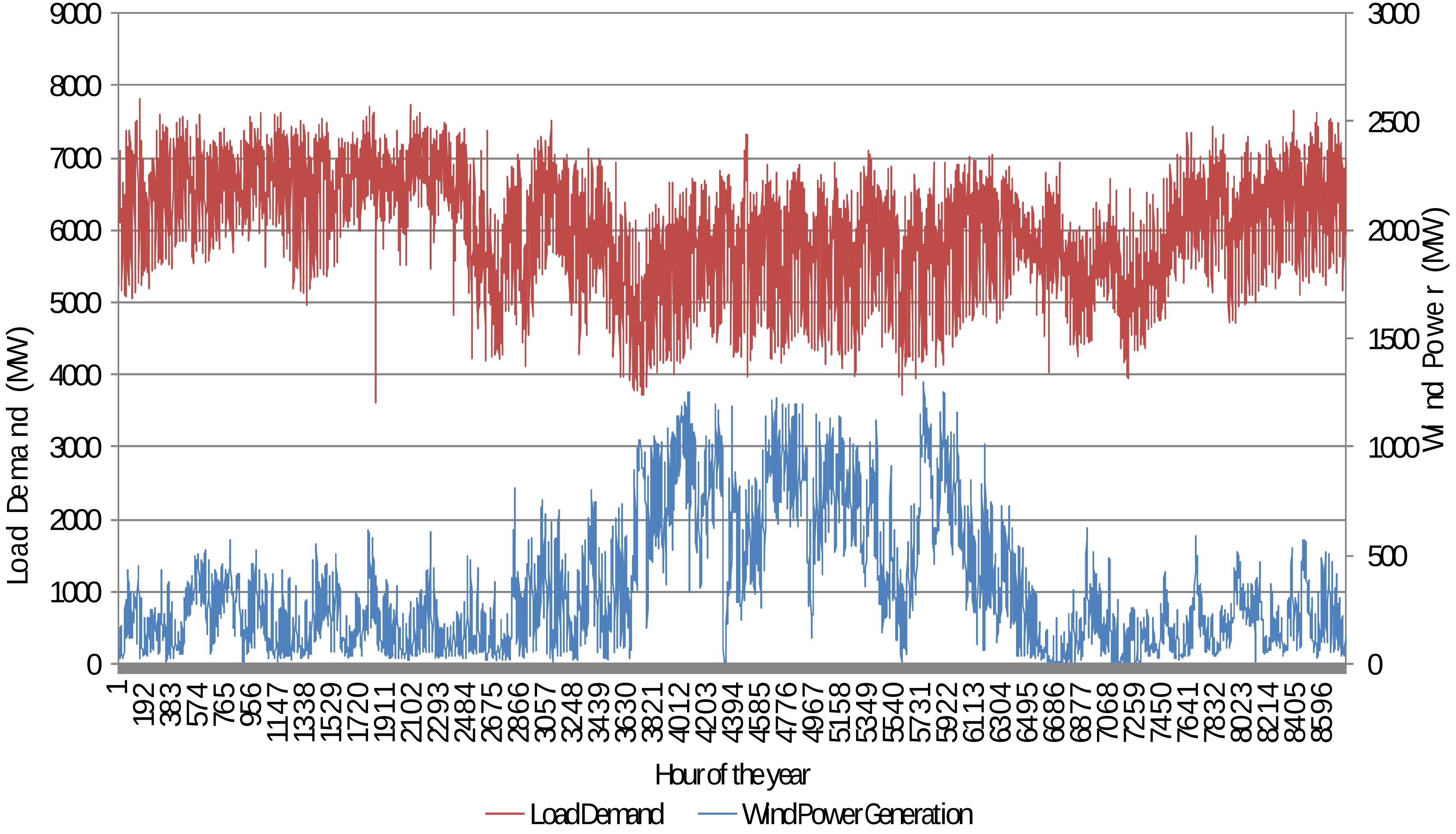


Wind power generation on July 27th, 2011 in Karnataka. The generation fluctuated by 800 MW within a few hours poses a challenge to the system operator to maintain stability.

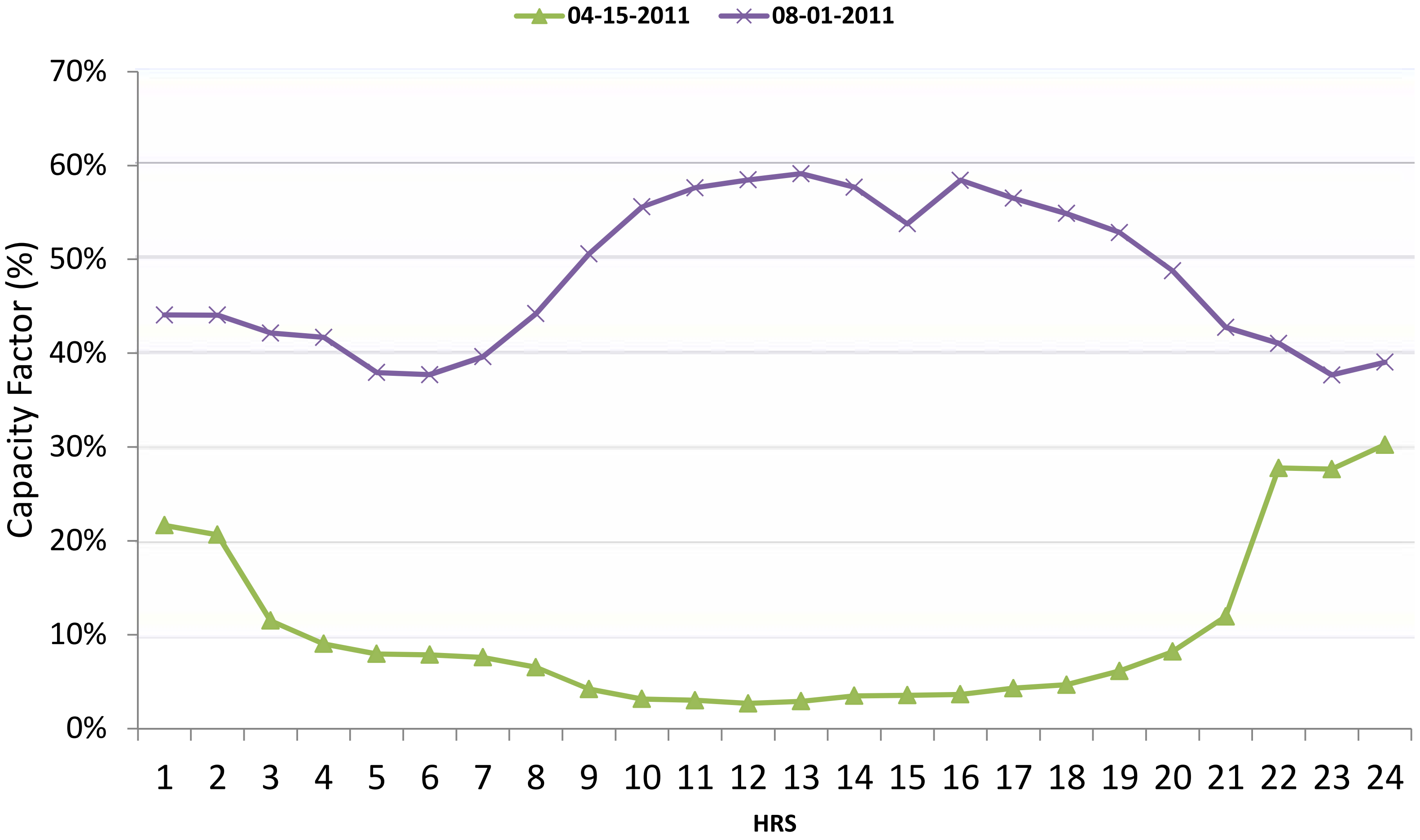


Hourly average Direct Normal Irradiance per sq.m. in Bangalore for a year

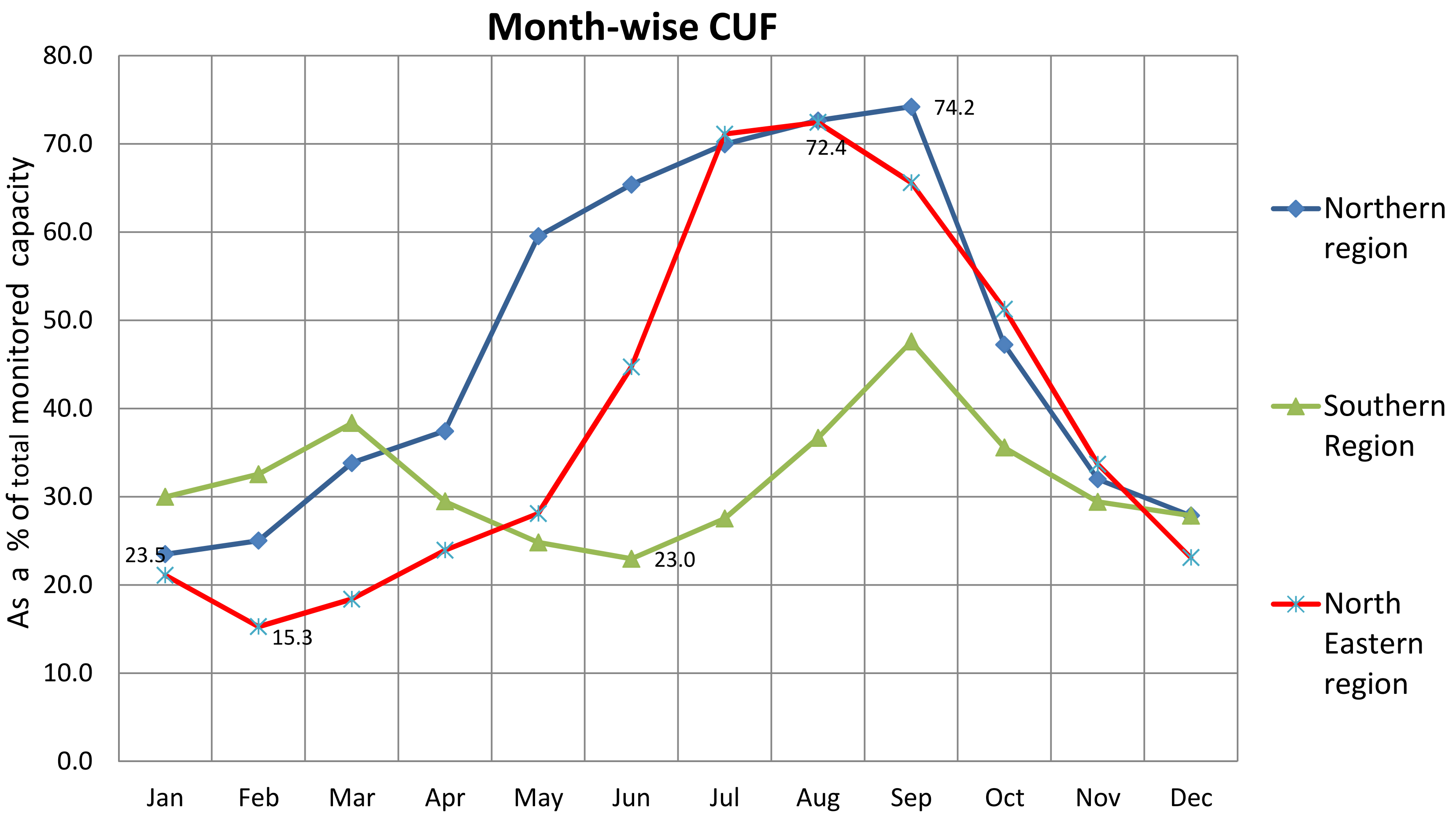
Intermittency of Wind Power : Karnataka



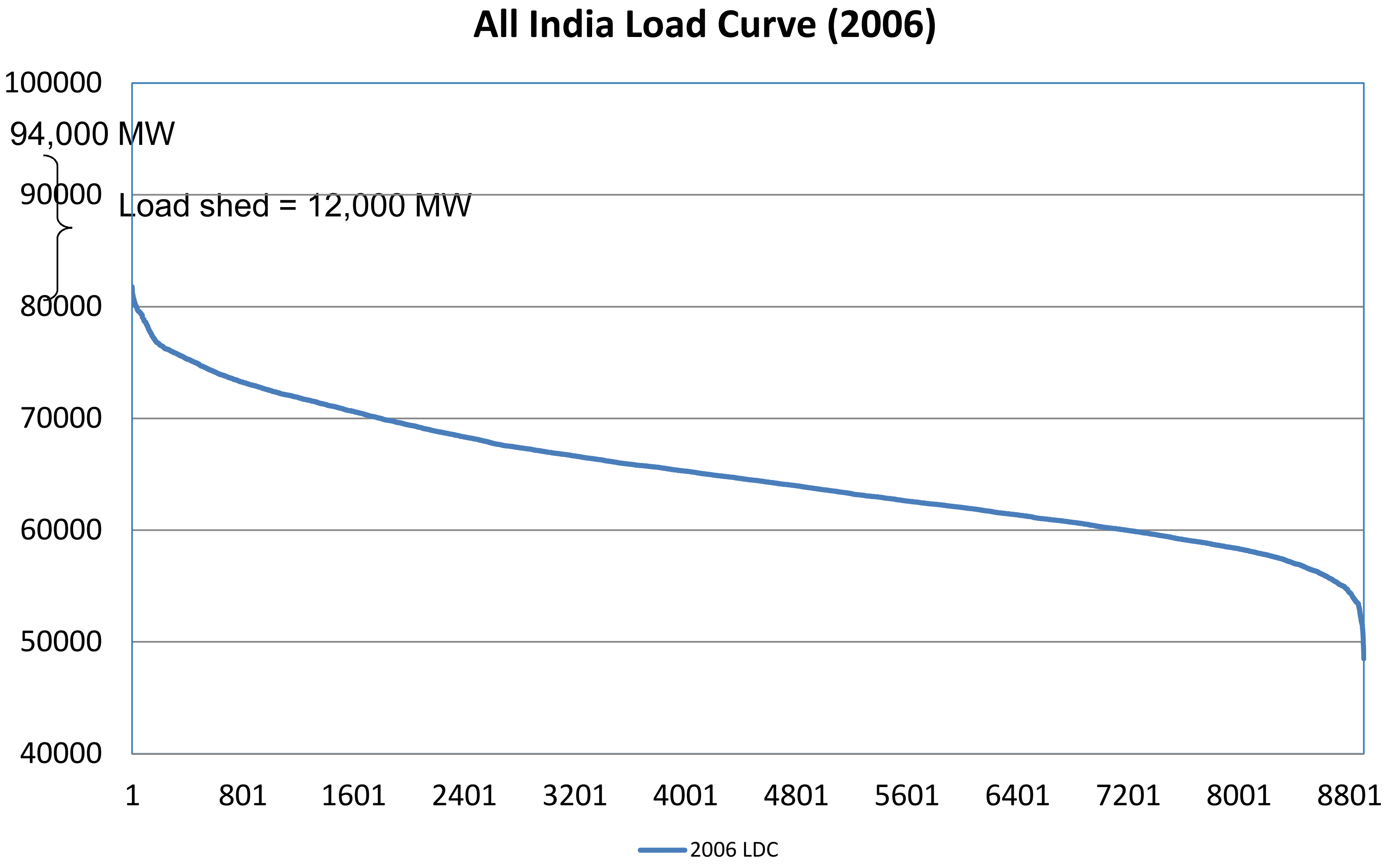
Wind in Karnataka: Seasonal and Diurnal Variations



Seasonality of Hydro Power



Peak Load Management



Future Shape of Grid

- Smart Controls and Communications
  - Peak management, loss reduction, self healing
  - Renewable integration
- Storage:
  - Grid level and off grid

Techno Economic analyses: NaS illustration*

Following parameters were considered as the basis for cost estimation and analysis-

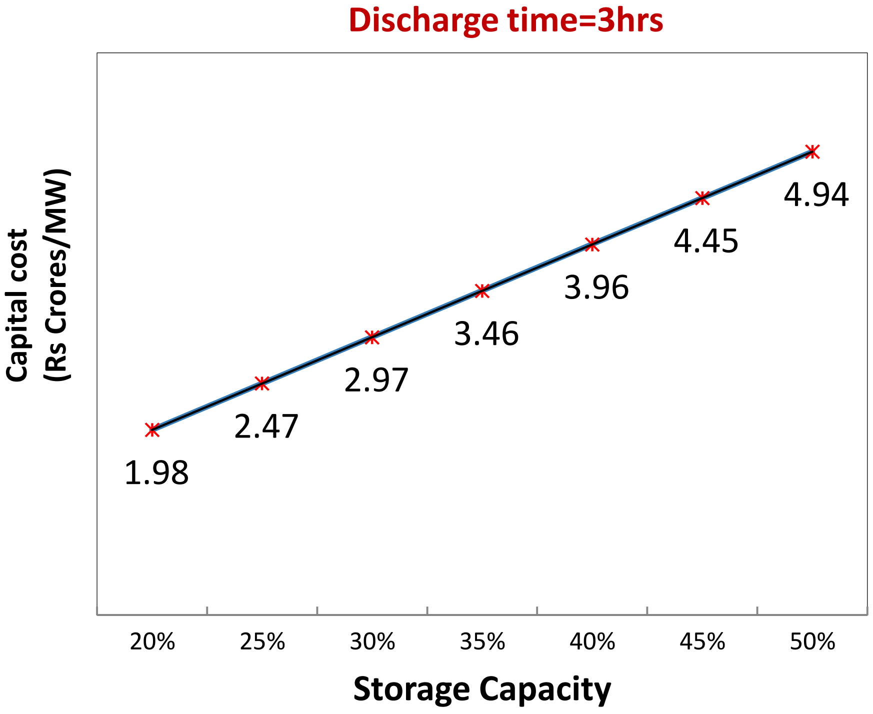
Wind plant capacity : 1 MW
Wind Turbine life: 25 yrs
Capacity Factor: 22%
Plant Life: 25 years
Storage System : Na-S battery with net efficiency of 80%
Storage capacity : 20% of installed capacity (200 kW)
Backup duration : 3 hrs
Cost of Battery : USD 550 per kWh ($ 1= Rs. 50)
Discount rate : 13.8%
Escalation rate: 5.72%
O&M cost : 2.5% of aggregate capital cost
Charging cost: Rs 3.5 per kWh.
Battery Life : 12.5 years

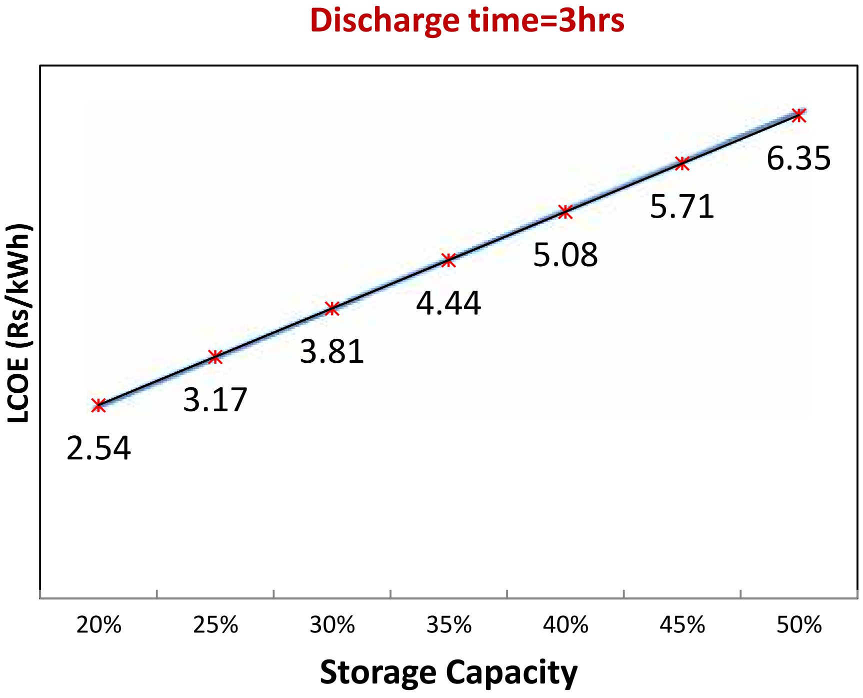
* CSTEP-Shakti Foundation report :http://www.cstep.in/node/377

Techno Economic analyses: NaS illustration*

Wind Turbine Capacity:	1 MW
Capital Cost	Rs 6 Crore
LCOE	Rs 5.10 per kWh

Incremental Capital Cost and LCOE





•CSTEP-Shakti Foundation report :http://www.cstep.in/node/377

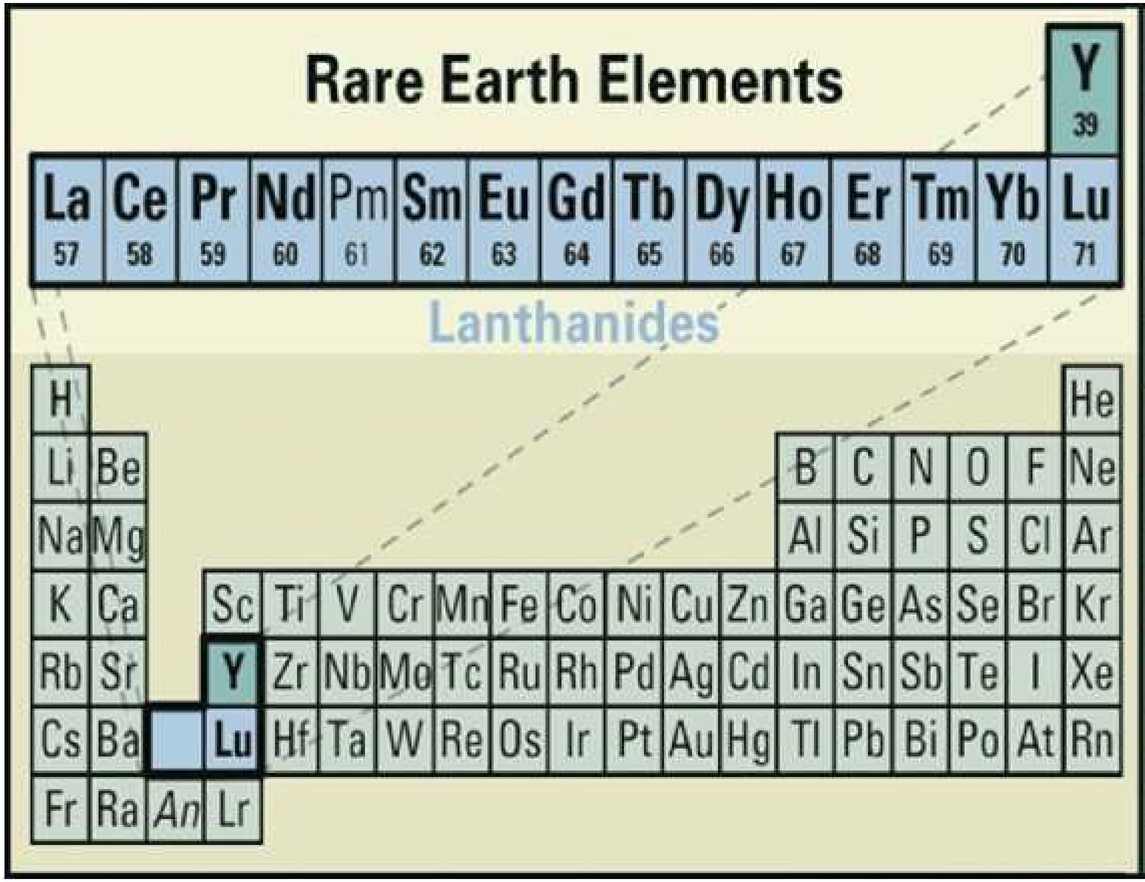
Distributed and Grid Level Storage				
Techno-economic and policy analysis of energy storage options for utility scale and off grid in India	Multi-disciplinary design & optimization of low-temp. Na-S/Na-MX and other systems like Pb acid, LIB	Design & optimization of energy storage with renewables	Novel process technologies & prototype device fabrication Battery stability & reliability assessment	Economic assessment of chosen storage systems

Batteries: Issues and Roadmaps

Batteries	Issue	Roadmap
Ni-MH	Cell weighing 28.9g contains 19.5 g mixed electrode material (~70% of weight). 7.0% of NiMH batteries contains Res	Waste recovery (e.g. from blast furnace slag, and recycling from e-waste, spent component from Ni-MH battery, bacterial leaching) Countries like Afghanistan, Mozambique and Ukraine hold potential for rare earths and ECE . India should use the Joint Working Group (JWG) route to acquire assests in these countries. Govt needs to take an aggressive role for negotiating on the acquisition of assets
Li-ion battery	Availability of Li, Safety , Expensive ,Stability of electrolyte at higher voltage	Bolivia holds large potential for lithium. Similar roadmap as for RE and ECE should be designed for Li Investment in Li-ion R&D and collaboration with foreign research institutes Integrated Computational Materials Science
NaS	Corrosion of steel container for molten S	Integrated Computational Materials Science, new coatings etc
Lead acid	Toxicity, low energy density	
NiCd	Phasing out due to Cd	
Zn-Air	Zn corrosion can produce hydrogen. Mercury amalgam used for prevention of Zn corrosion which is toxic in nature.	Mercury free technology to prevent Zn corrosion.
Li-Air	Design: Atmospheric oxygen need at the cathode side but cathode’s property can be degraded by humidity . Significant charge overpotential causes side reactions.	Need to be concentrate on battery design and fundamental research.

Materials for renewables and storage: Rare Earth (RE) and Energy Critical Elements(ECE)

Rare Earth Elements

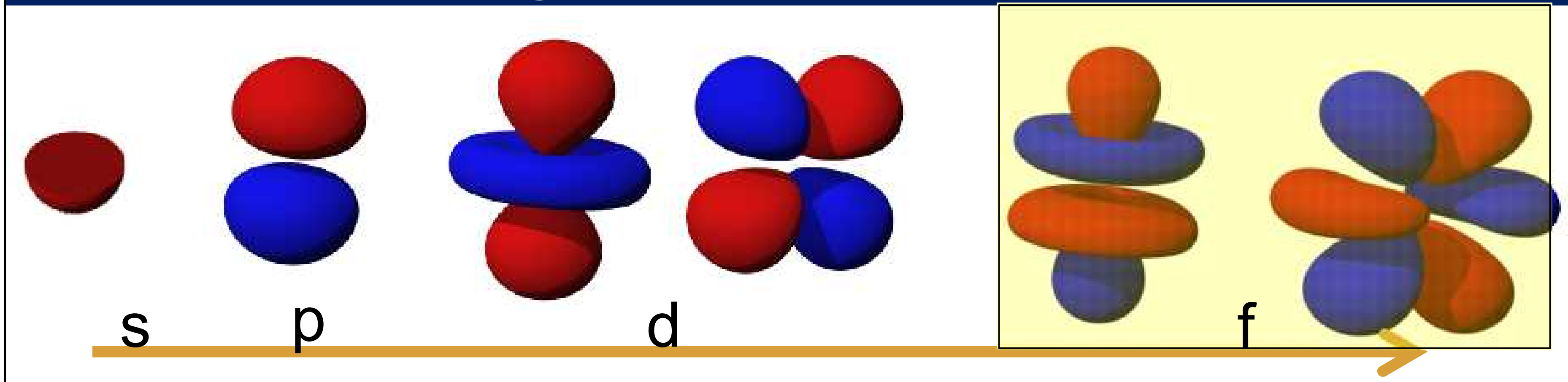


Lanthanum (La)
Cerium (Ce)
Praseodymium (Pr)
Neodymium (Nd)
Samarium (Sm)
Europium (Eu)
Gadolinium (Gd)
Terbium (Tb)
Dysprosium (Dy)
Holmium (Ho)
Erbium (Er)
Thulium (Th)
Ytterbium (Yb)
Lutetium (Lu)
Yttrium (Y)

Rare Earth elements

- Set of 17 elements in the periodic table 15 lanthanides + Y, Sc
- ‘Rare’ as they are very dispersed and not available in *economically* exploitable concentrations
- Thulium and Lutetium are two least abundant but have 200 times greater crustal abundance than gold
- Ce, Y, La, Nd: most abundant ; average crustal abundance similar to Cr, Ni, Zn, Mo etc

Unique Chemistry of REE

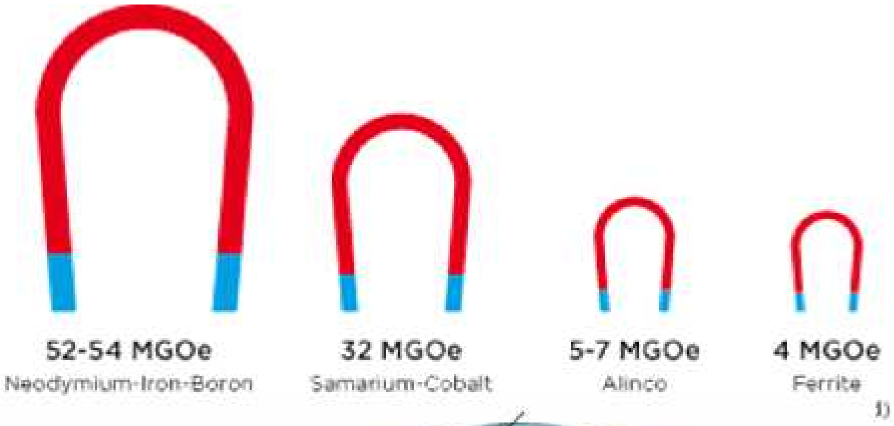


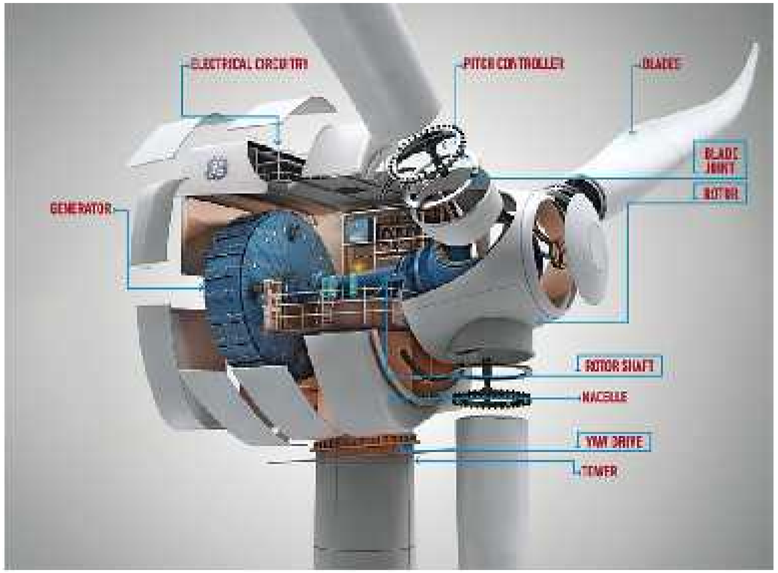
Salient features of lanthanide elements

❑ f-orbitals are "buried" inside the atom and shielded from the atom's outside environment by the outer (4d and 5p) electrons

❑ Large number of unpaired electrons impart high magnetic moment and interesting magnetic and electric properties

Applications of REE





3 MW wind power station = 1 MT Nd
“Critical Thinking”, Chemistry World (RSC), Jan 2011, 50-54

1 toyota prius hybride = 15 kg La (Ni-MH battery) 1 kg Nd, Dy, Tb, Ce (electric motor)

Rare Earth and Energy Critical Elements: A Roadmap and Strategy for India

A joint report by CSTEP and Ministry of Mines, GOI
(submitted July 2012)

RE-ECE National Steering Committee

- Co-Chairs: Ministry of Mines and CSTEP
- Department of Science and Technology
- Geological Survey of India
- Defence Research and Development Organization
- Bhabha Atomic Research Centre
- Institute of Minerals and Materials Technology (CSIR)
- National Metallurgical lab (CSIR)
- Department of Atomic Energy
- Indian Rare Earth Ltd

Steering Committee

Motivation

Need for alternative/ indigenous REE supply sources due to increased Global demand and Chinese export restrictions

Objective

Prepare a strategy paper for the govt to-

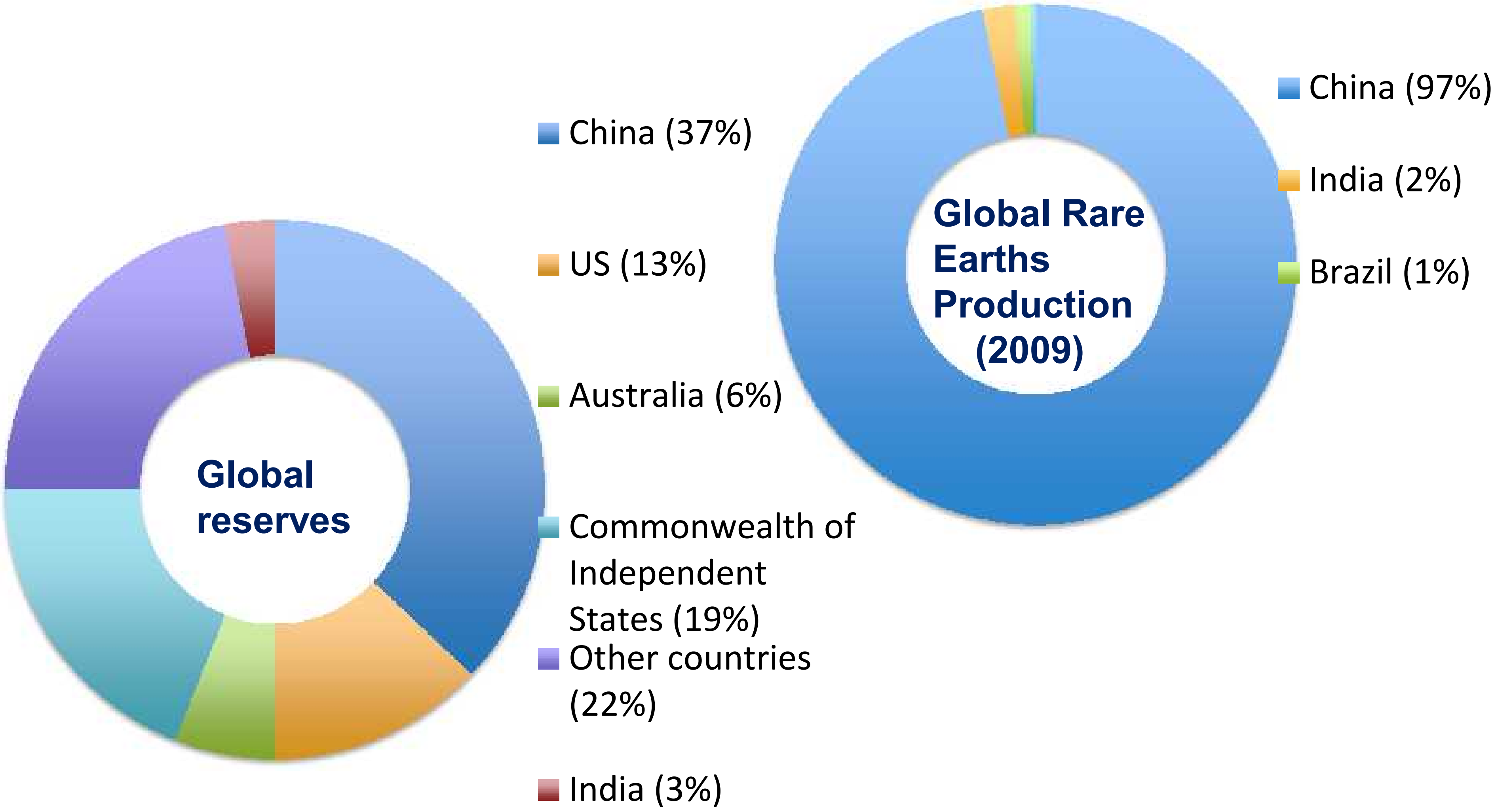
(1) review the status of availability and indigenous production capability of REE and ECE

(2) recommend short, medium and long term options along with policy and legislative interventions

Report: Scope and contents

- RE and ECE introduction
- Identify high value RE and ECE for strategic and civilian applications
- Primary and secondary Sources of supply,
- Demand and supply (economics etc)
- Recommendation
  - Extraction
  - Recycling
  - Substitution
  - Radical Approach
  - Policy Initiatives

Global Reserves and Production



Important Rare Earth Minerals

❑ Monazite (secondary mineral): India, Brazil, SA Australia, Bolivia

Monazite in Indian placer sands
Chavra: 1%
Chatrapur: 0.27%

❑ Bastnaesite (Primary mineral): USA, China-inner Mongolia. richer in lighter RE

❑ Xenotime: China , Norway, US, Nigeria, Afghanistan. richer in heavier RE

China's domestic consumption of REO was 73,000 tonnes in 2009 versus 70 tonnes in India

RE Distribution in Monazite & Xenotime

REO	Monazite	Xenotime	REO	Monazite	Xenotime
La_2O_3	22.0	0.5	**Dy_2O_3**	0.18	8.7
CeO_2	46.0	5.0	**Ho_2O_3**	0.02	2.1
Pr_6O_{11}	5.5	0.7	**Er_2O_3**	0.01	5.4
Nd_2O_3	20.0	2.2	**Tm_2O_3**	Trace	0.9
Sm_2O_3	2.5	1.9	**Yb_2O_3**	Trace	6.2
Eu_2O_3	0.016	0.2	**Lu_2O_3**	Trace	0.4
Gd_2O_3	0.06	1.0			
Tb_4O_7	0.06	1.0	**Y_2O_3**	0.45	40.0

- Monazite rich in lighter RE
- Xenotime rich in heavier RE
- Bastnaesite richer in lighter RE (Ce49%, La33%, Nd12%, Pr5%)
  - *Eu content double than Monazite*
  - *Bayan Obo-Inner Mongolia major supplier*

Potential RE Markets in India

End Use	RE required	Present Status	Expected (2030)
Magnets for wind turbines	Nd , Pr, Dy, Tb (high strength magnets have 30 % RE)	12,000 MW of wind power capacity	~ 50,000 MW
EV, Hybrid vehicles (batteries, motor, catalytic converter)	La (15 kg per car) Nd (1 kg per car), Dy, Tb, Ce	Negligible EV	Perhaps up to 1 million vehicles
LED	Y, Eu, Tb	Negligible LED	Being promoted by government, could reach ~ 1 million bulbs
Al, Steel, Mg industry, grain refinement	Ce, La , mischmetal		Huge growth rate
Screens brighteners (cell phone, computers, TV screen)	Eu	mostly imported	Huge growing market
Other magnets	Pr, Sm, Gd	mostly imported	Computer hard disks, microphones

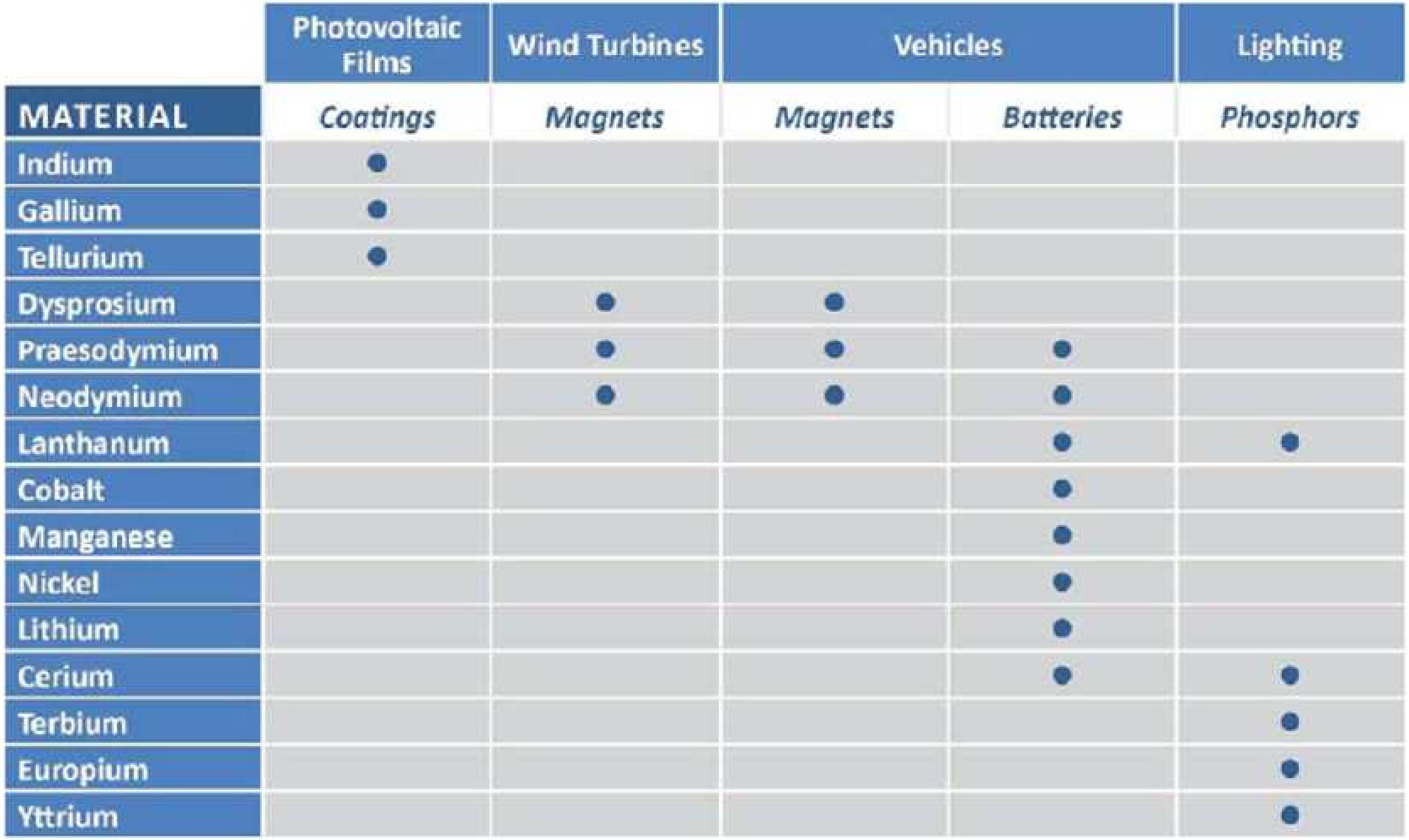
Other Energy Critical Elements

Element	Production	Application
Gallium	Al, Zn processing (China tops)	Solar cells, hydrogen generation
Germanium	Zn, Cu, Pb refining (China tops) *100 t/yr*	substrate in Ga-Arsenide Solar cells, fiber optics
Selenium	Cu refining (Japan tops)	Solar cells
Indium	Zn, Cu, Tin refining (China tops) *1500 t/yr*	LED, Solar cells, Battery
Tellurium	Cu refining (Canada tops)	Solar panels (Cd-Te), *NREL demo solar cells Thermoelectric appl*

Recommendations

- Exploration
- Extraction
- Recycling
- Substitution
- Radical changes
- Policy initiative

Materials in Clean Energy Technologies

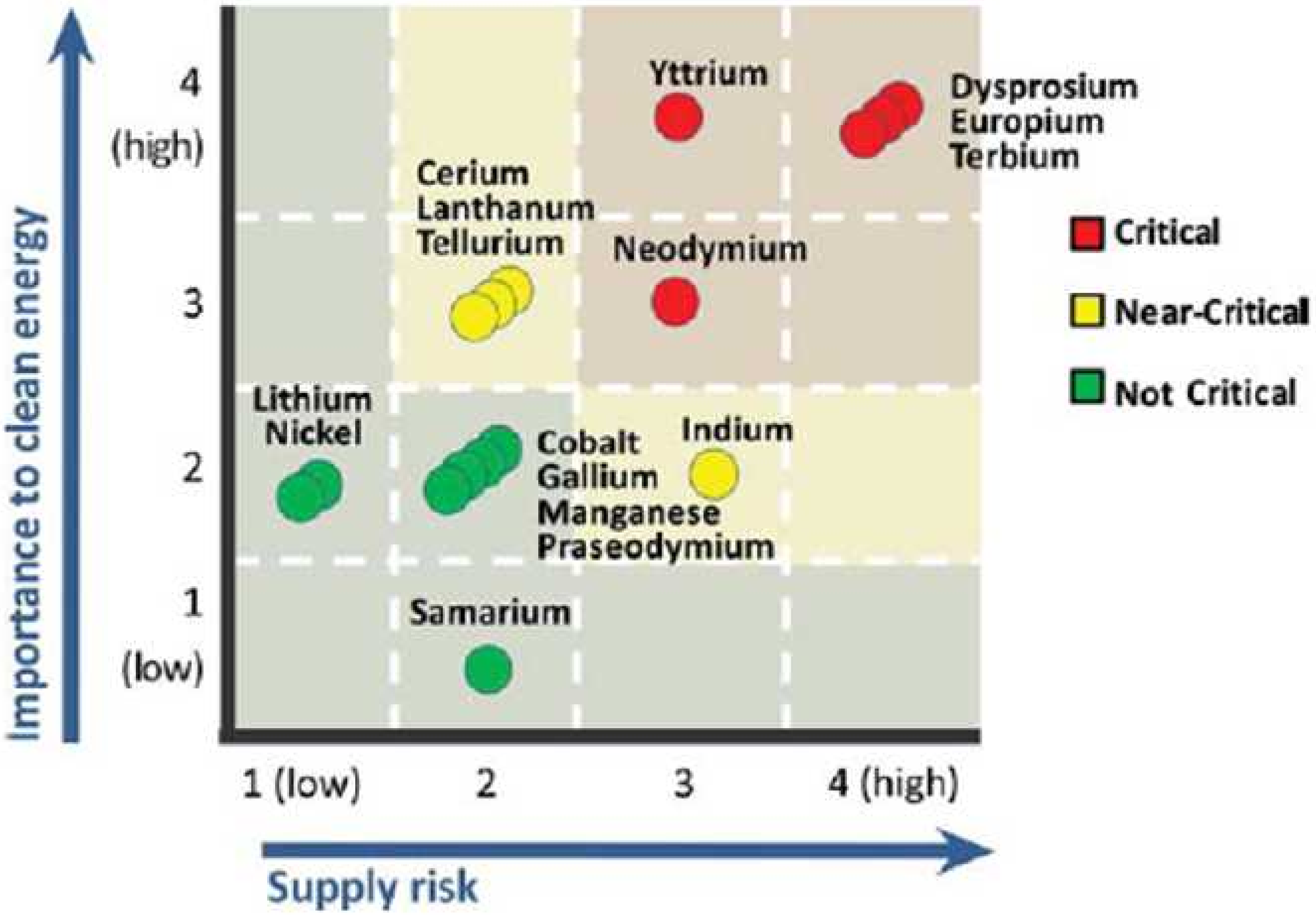


	Photovoltaic Films	Wind Turbines	Vehicles		Lighting
MATERIAL	*Coatings*	*Magnets*	*Magnets*	*Batteries*	*Phosphors*
Indium	●				
Gallium	●				
Tellurium	●				
Dysprosium		●	●		
Praesodymium		●	●	●	
Neodymium		●	●	●	
Lanthanum				●	●
Cobalt				●	
Manganese				●	
Nickel				●	
Lithium				●	
Cerium				●	●
Terbium					●
Europium					●
Yttrium					●

US DOE Critical Materials Strategy 2011

US DOE Critical Materials Strategy 2011

Need to develop Criticality Matrix-short , medium and long term for India



Develop a criticality matrix for India

Batteries: Fundamental R&D

New Approach to Design and Development of Advanced Battery Materials

CSTEP, DRDO, IIT Kgp

Motivation - Human Genome Project

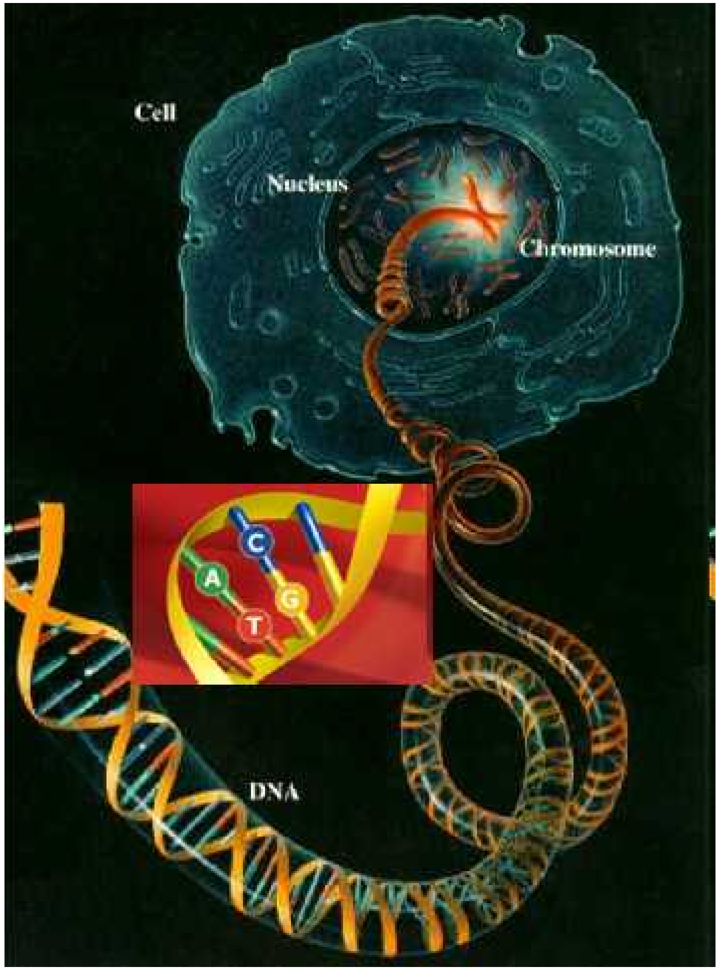
Human genome-

- **Helped understand genetic blue print of an organism**
- DNA/gene structure and function co-related with type and behavior of 'person'

Material Genome

To better design functional materials by developing correlation between structure at atomistic scale to behavior at performance scale

New Material "blue prints" to target desired properties



* Pictures from open web sources

Motivation - Human Genome Project

- New materials can be discovered using the successfully demonstrated human genome methodologies
  - Examples:
    - Rat gene modification for cancer resistance
    - Drugs for newer strains of viruses
- Analogies
  - Molecular Dynamics (MD) and atom level computations to tailor material properties similar to Genetic engineering modifications
  - Genetic Algorithm (GA) which we could use for Data Mining (DM)

Objective

Utilize theory, computations and experiments to discover new materials for next generation batteries

Theory: pre-existing knowledge of co-relations between material properties and composition/ structure / processing history etc.

Computations: data mining/machine learning/ multiscale modeling to predict material behavior at various length scales

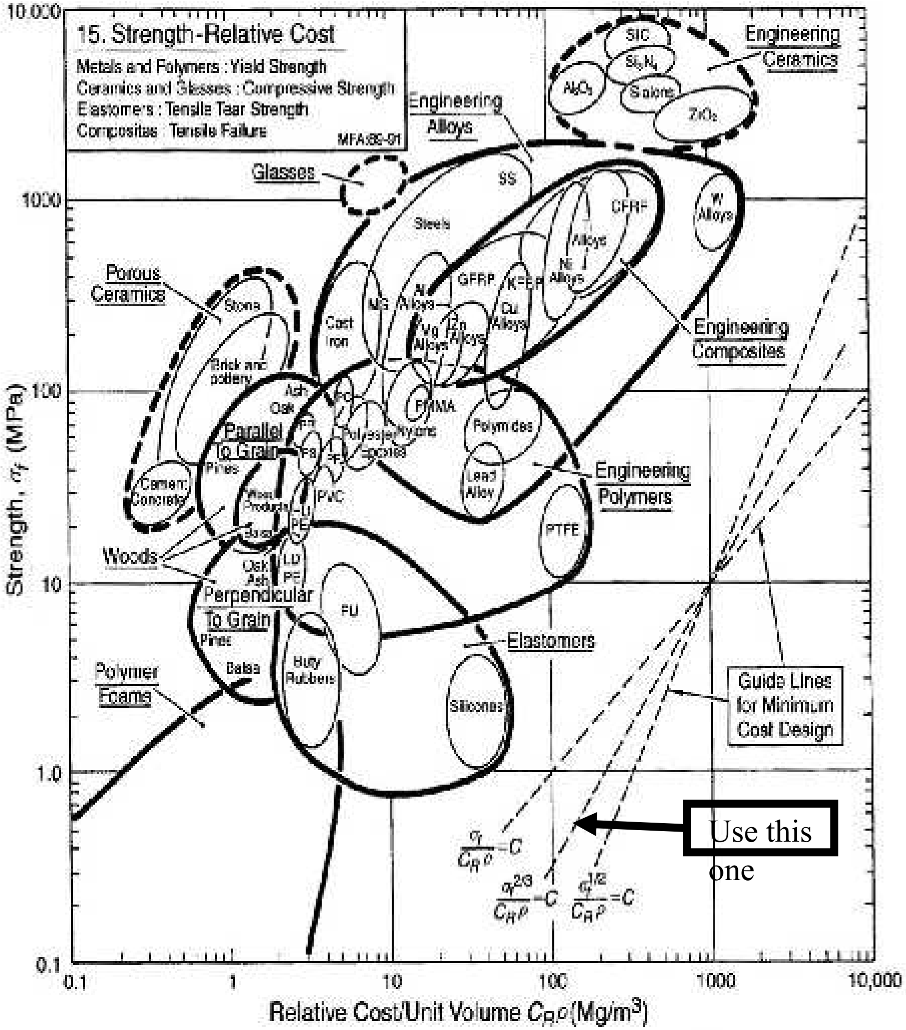
Experiments: validate computational models

New Materials Selection

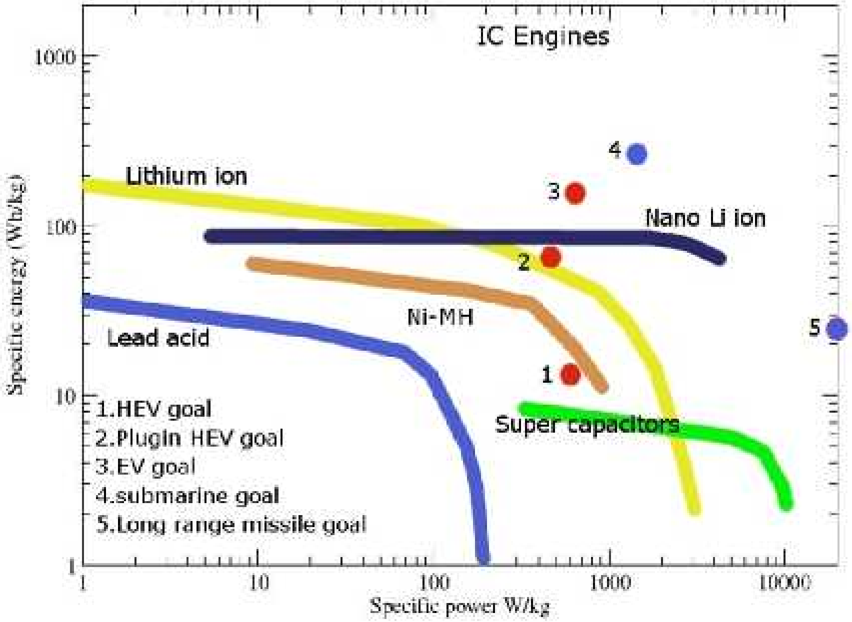
Need to select new materials for any battery systems

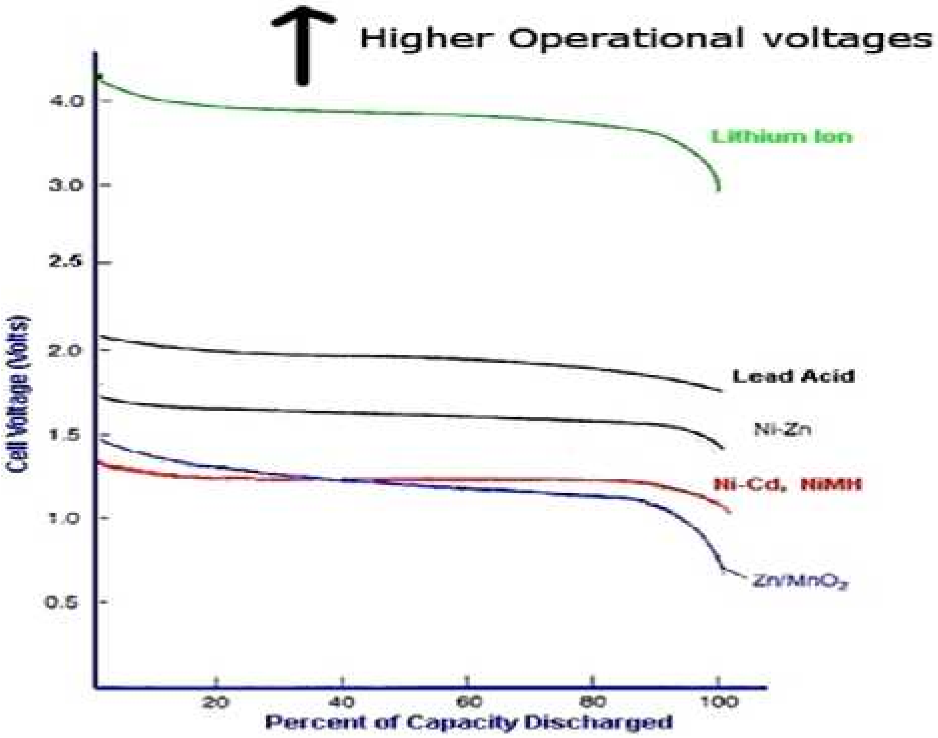
Ashby Approach:
Map <u>existing</u> materials across several properties
Chose material that achieves the desired performance

Our Approach
Combinatorial techniques
“Ashby type” charts for new materials
Experimental validation



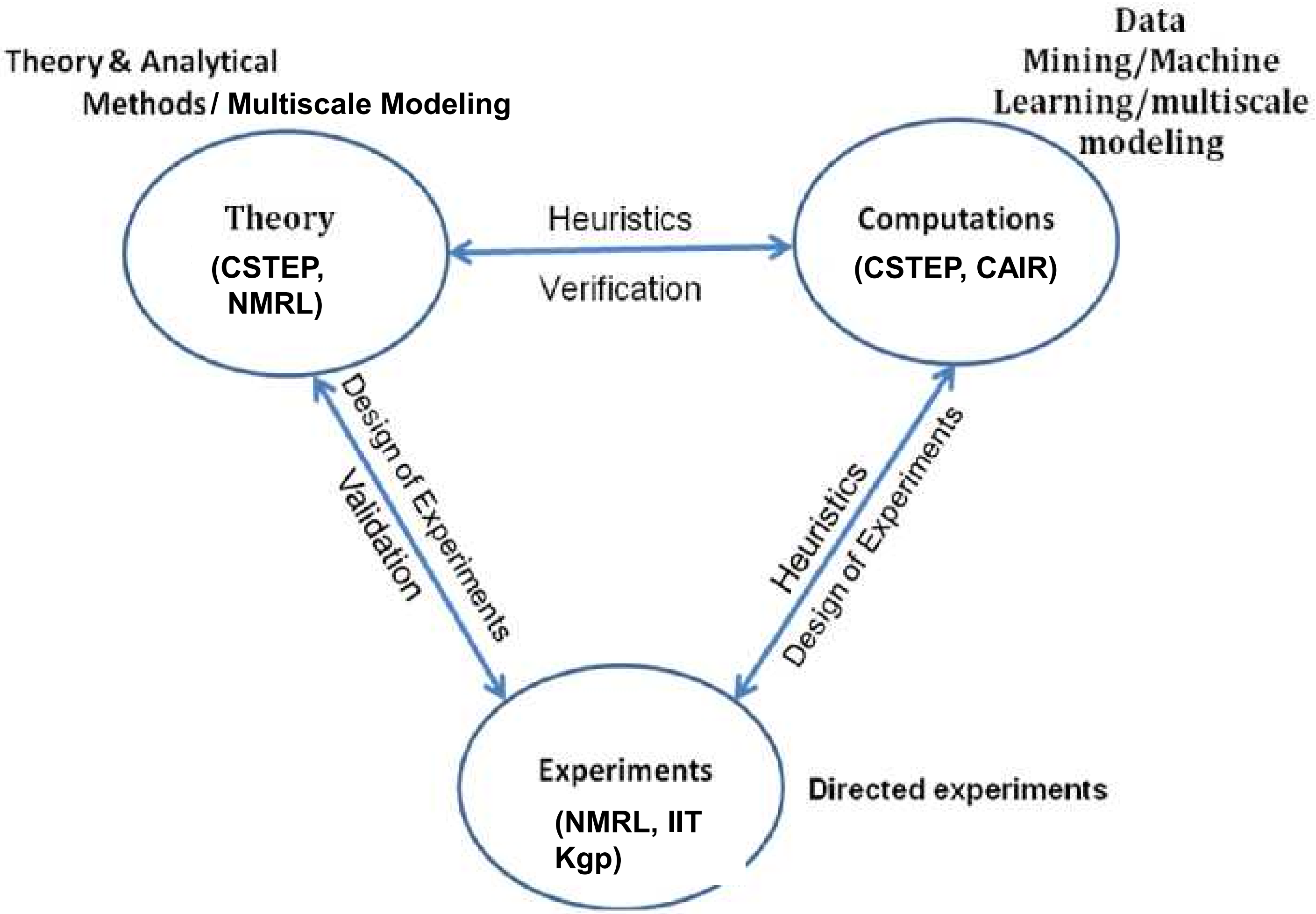
Ashby type Design Maps (inputs from Ragone Plots)



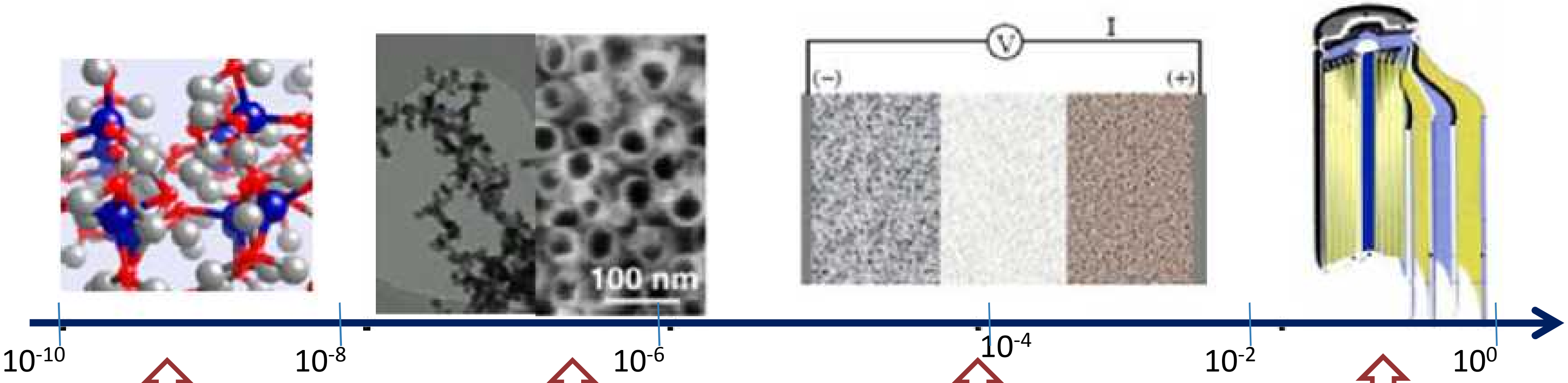


Correlate various key parameters
Identify regions of current application requirements
Example - Peak power vs. Continuous power

CSTEP: Materials Design Approach



Multi-Scale Modeling Framework



Materials Design

Data Mining Crystal Structure
- Heuristic (Hume-Rothery)
- Knowledge Representation

Ab Initio Calculations
- Band structure
- Density of States
- Formation Enthalpy
- Voltage, Capacity
- Lattice stability, Kinetic barrier
- Transport property (diffusivity)
- Elastic constants (E,G,K)

Electrode Design

Data Mining
- Ashby type correlations
- Electrode materials

Thermodynamic Calc.
- Molecular Dynamics
- Structure Stability
- Phase transformation

Kinetic Calculations
- Surface Physics (SEI)
- Intercalation Reactions
- Deformation
- Fatigue – strain relaxation
- Local diffusion

Cell Level Design

Data Mining
- Ashby type correlations
- Electrode/Electrolyte selection

Thermodynamic Calc.
- Structure Stability
- Phase stability

Kinetic Calculations
- Load conditions
- Potential, Temperature
- Electrolyte diffusion
- State Of Charge (SOC)

Battery Pack Design

Data Mining
- Battery Pack Selection

Component Simulations
- Performance
- Battery Life
- Cost
- Safety
- Heat dissipation

Motivation for Li Ion battery research

- Total Li reserves 28.5 million tonnes world wide
- China to make 0.5 million Li battery based cars per annum
- Rising volumes of Laptops, portable electronics, Defense equipments
- Current cost: $ 700-1000 per kWh of Battery power
- 24 kWh Nissan (EV) and 16 kWh Chevy Volt (PHEV)
- Li metal= $ 660/kg; Li weight= 0.3 kg/kWh

Amount of Li metal per 100,000 cars : 480,000 Kg (Rs. 1500 Crores)

- *China ranks third after Chile and Australia in mining Li_2CO_3*
- *South America has nearly 80% of global Li reserve base*

Need for an Indian program starting from first principles to find alternate new materials to reduce the cost of battery

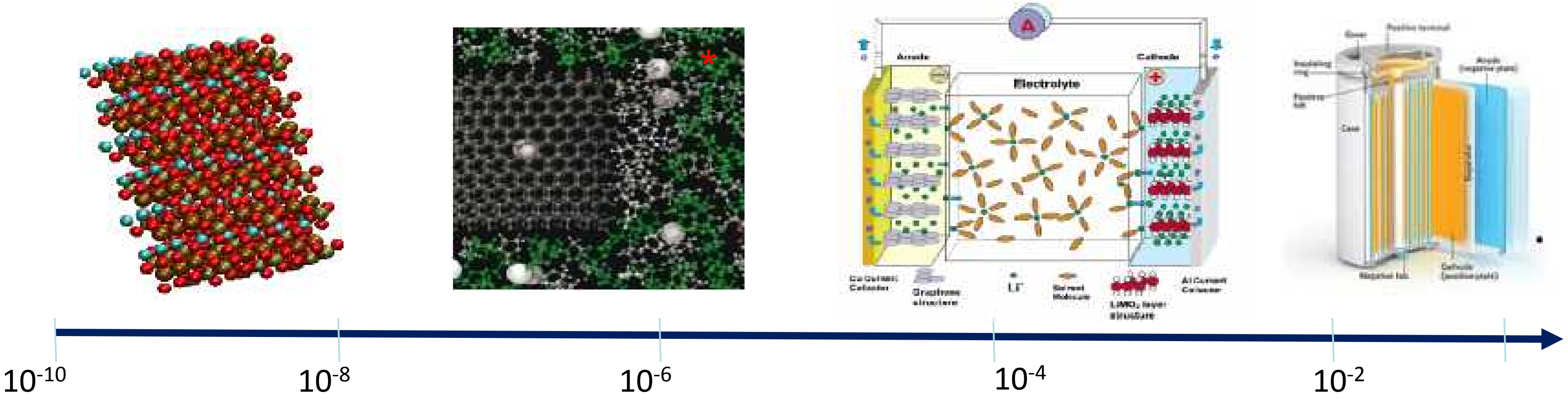
Materials Genome Project at CSTEP

Materials Informatics- Data management and Knowledge aquisition

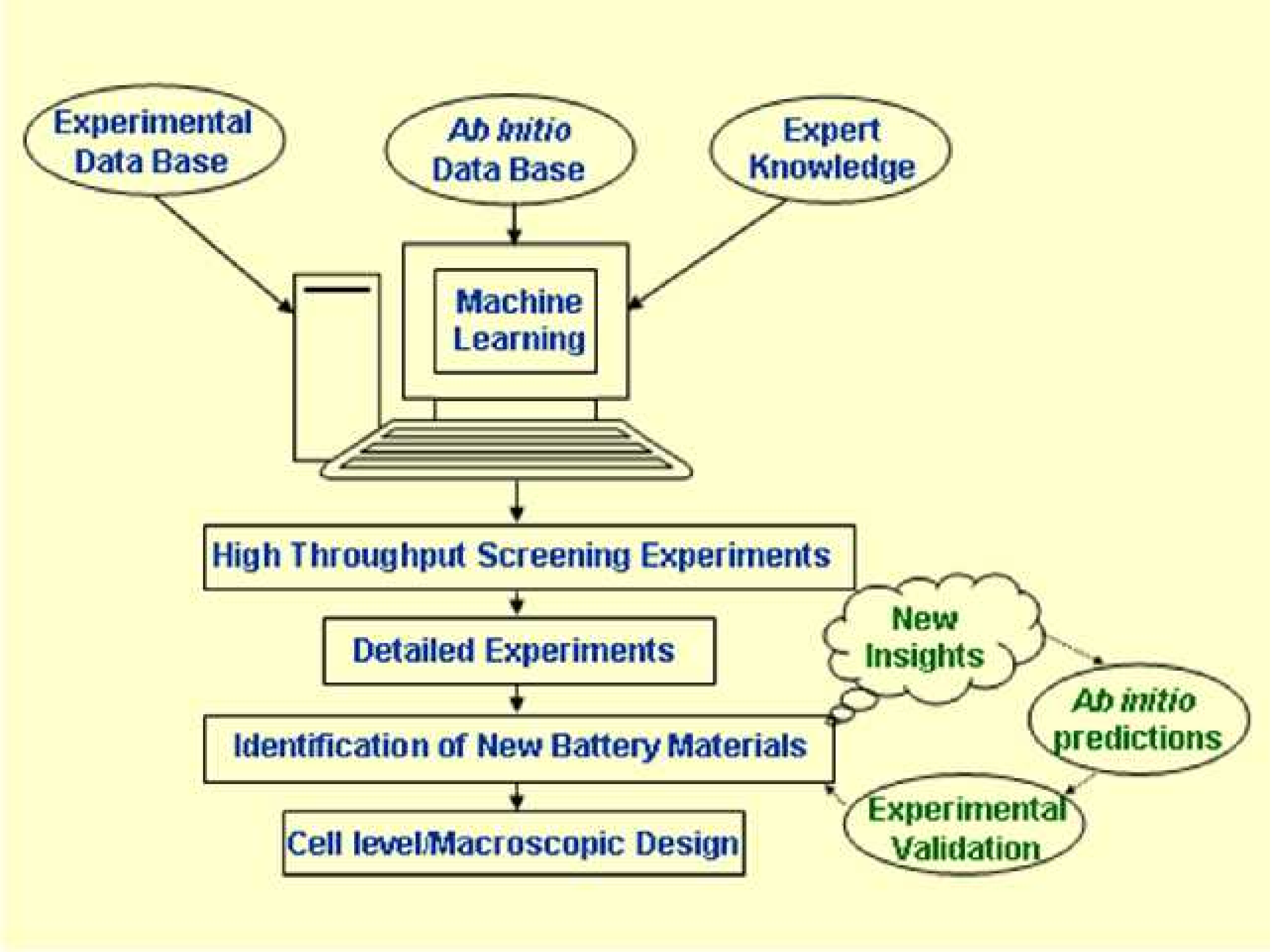
- **Material Design via Data Mining and Machine Learning**
- **Material selection capability via Combinatorial material science**

Theory: Correlations between material properties and composition/ structure / processing history etc.
Computations: data mining/machine learning/ multiscale modeling to predict material behavior at various length scales
Experiments: validate computational models

Develop Graphical User Interface: Integration of computational tools



Schematic of Our Approach



Overall Goal

Design new battery materials using multiscale modeling including Data Mining and apply them in clean technology areas

Approach

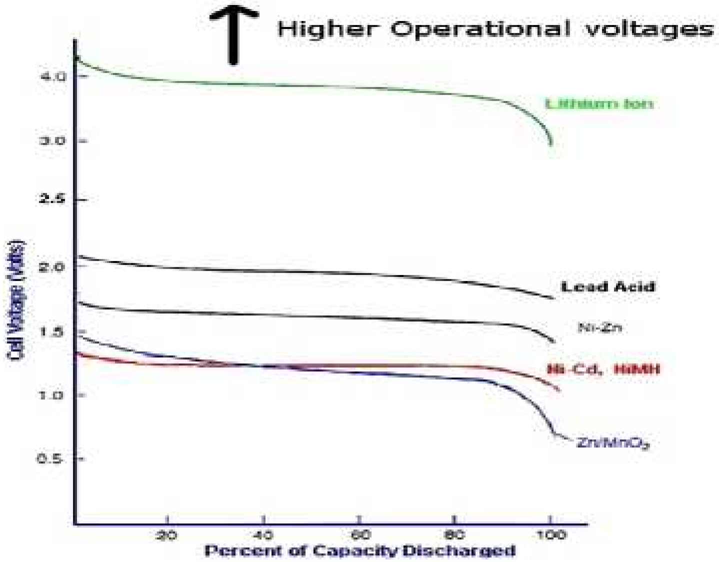
- Apply data mining techniques on material property data obtained from computational modeling, theory and experiments to extract new structure-property correlations
- Conduct validation experiments and prototype development

CSTEP Focus

Electrode challenges

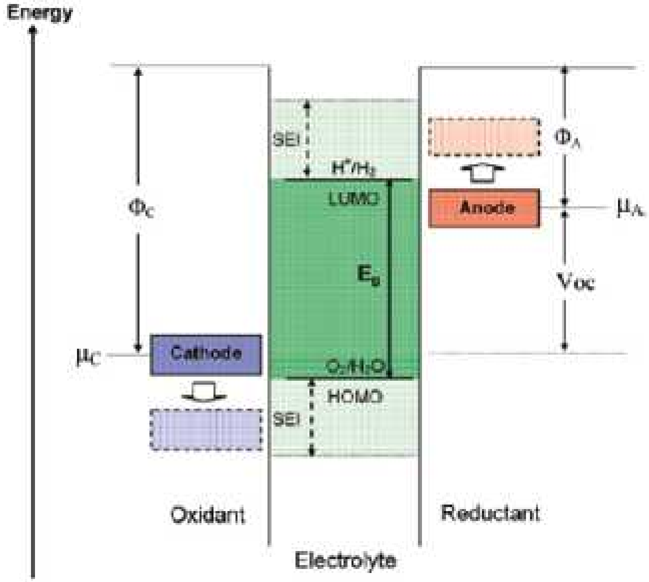
1. **Next generation battery materials (Defense,EV)**
   Batteries for High altitude (< -20 C) military and marine applications (corrosive atm)

2. **Structural instability of electrode materials in current batteries and low cycle life**



Electrolyte challenges

1. **Organic solvents are not stable above 4.5 V in Lithium Ion Batteries**
2. **Need for Novel electrolytes with large operational window (LUMO-HOMO)**
3. **Optimization of ionic and electronic conductivities, safety and cost factors**



DFT approach

First principle Density Functional Theory simulations using VASP

Why DFT?

Useful for new materials design

Computationally less expensive for the above objective compared to traditional methods of solving Schrodinger equation for multi-body system

What is DFT?

Electronic structure method to predict new materials and their properties based on electron density.

Ground state energy given by

$$E[\rho] = T_s[\rho] + \int d\mathbf{r}\ v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) + V_H[\rho] + E_{\text{xc}}[\rho],$$

LDA* vs GGA vs DFT+U

According to DFT, Total energy of a system as a functional of electron density

$$E[\rho] = T_s[\rho] + \int d\mathbf{r}\ v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) + V_H[\rho] + E_{\text{xc}}[\rho],$$

-The first term on right side is Kohn-Sham Kinetic Energy
-The second term represents nuclei-electron interaction (external potential)
-The third term represents electron-electron coulomb interaction
-The last term is exchange-correlation term which includes self-interaction and effect of non-interaction while considering the kinetic energy term among others

The different functionals mainly differ in the way the exchange-correlation term is calculated-
*LDA (Local Density Approx): Considers uniform electron gas density in evaluating E_{xc} term
GGA: Considers gradient of electron density along with local electron density in evaluating E_{xc} term
DFT+U: For systems involving d- and f- electrons (localized electrons), their electronic structure cannot be simply described with normal DFT functional
In this regard, the Hubbard U parameter accounts for the localization of d- and f- electrons

Tools & Methodology

Import the crystal structure from ICSD

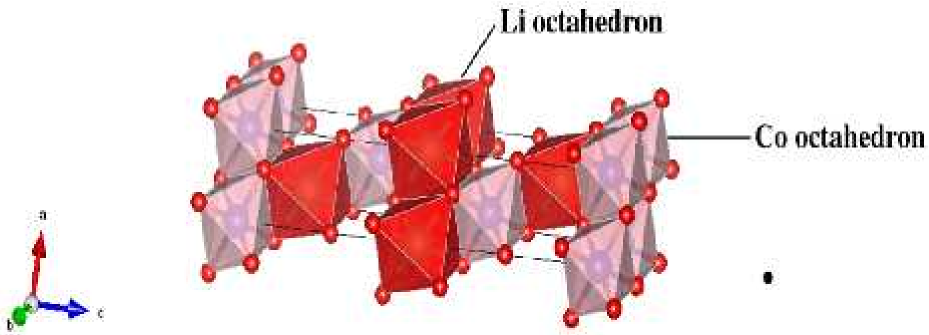
VASP DFT Simulations

Determine DFT Optimized Ground State Energy of the Structure

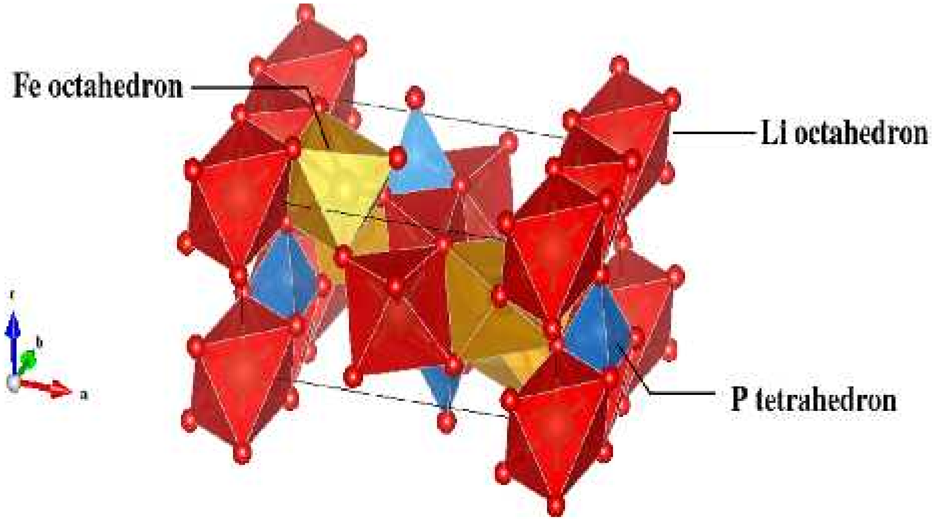
Predict Electro-chemical Properties:

i. Chemical Potential
ii. Lithium Ion Diffusion Coefficients
iii. Band Gaps in materials
iv. Structural Stability

Structure details of the materials studied



$LiMO_2$: **R-3m** , **hexagonal layered** structures and the primary unit cell contains 3 formula units (total 12 atoms per cell in completely lithiated state)



$LiMPO_4$: **Pnma**, **orthorhombic** structure and the primary unit cell contains 4 formula units (total 28 atoms per cell in completely lithiated state)

First-principles analysis

3D mapping of charge transfer happening (during charge-discharge cycle) at atomic orbital level

Helps us identify how substitution improves battery voltage and make general rule base

Density of states calculation

nature of chemical bonding

electronic conductivity

Exact d-orbital splitting energy and electronic occupation, hybridization between orbitals

directly relates the voltage to crystal structure and chemical bonding

Our Key Findings

Agreement between exptal. and DFT calculated average Lithium Intercalation Potentials

- Lithium Metal/Transition Metal Oxides (TMO)
- $LiAlO_2$, $LiCoO_2$ and $LiVO_2$

$$(x_2 - x_1)Li + Li_{x_1}MO_y \Leftrightarrow Li_{x_2}MO_y$$

$$\langle V \rangle = \frac{\left[E(Li_{x_2}MO_y) - E(Li_{x_1}MO_y) - (x_2 - x_1)E(Li_{BCC,bulk})\right]}{(x_2 - x_1)F}$$

Reported <V> in volts			CSTEP <V> in volts	
LIB Mat	Expt	LDA/NCPP	GGA/PAW	GGA+U/PAW
$LiCoO_2$	~ 4.0 – 4.2	3.75	3.48	4.26
$LiVO_2$	~ 2.55	2.81	2.54	2.59
$LiAlO_2$	-NA-	4.70	5.02	-Not Appl.-

GGA+U agrees well with experiments

Charge Transfer Analysis

Cathode Material	CSTEP (Volts)	Charge transfer			
		From Li	Onto M	Onto O	(|O/Li'|)*100
$LiAlO_2$	5.02	0.861	0.018	0.844	98.02
$LiCoO_2$	4.26	0.866	0.118	0.748	86.37
$LiNiPO_4$	5.11	0.872	0.048	0.836	95.87
$LiCoPO_4$	4.62	0.874	0.307	0.556	63.62
$LiMnPO_4$	4.28	0.881	0.305	0.548	62.20
$LiFePO_4$	3.51	0.878	0.406	0.456	51.94
$LiFeSiO_4$	4.96	0.873	-0.004	0.884	101.26

Charge Transfer to O → Battery Voltage ↑

Crystal field splitting ability of anion may provide explanation for observed trend in battery potentials in various groups of materials

Al substituted TM Oxides and Olivine Phosphates

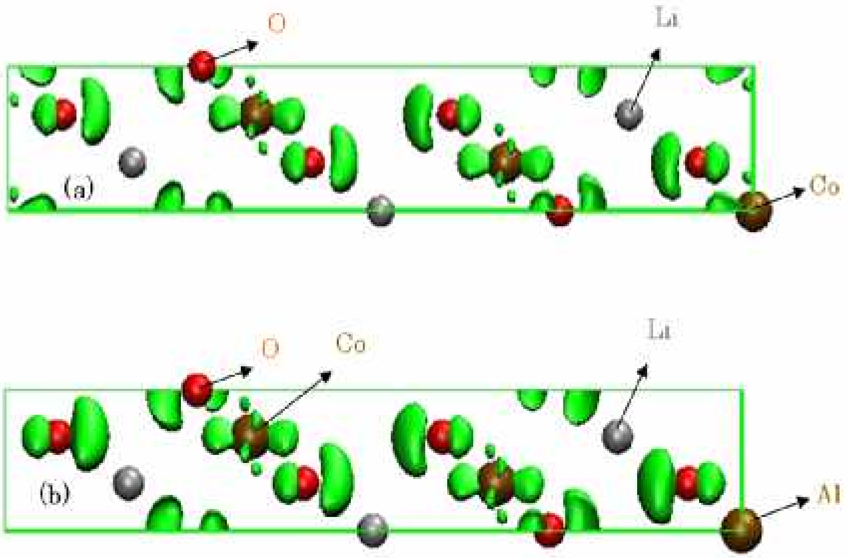
LIB Mat.	**Magnetic State**	**CSTEP** <V> in volts
Non-spin polarized calculations		
$LiCo_{0.67}Al_{0.33}O_2$	--	4.54 (4.2*)
$LiCo_{0.33}Al_{0.67}O_2$	--	4.81 (4.7*)
Collinear calculations (Spin polarized)		
$LiFe_{0.75}Al_{0.25}PO_4$	FM	2.64
$LiFe_{0.5}Al_{0.5}PO_4$	FM	1.75
$LiCo_{0.5}Al_{0.5}PO_4$	FM	2.78

* Ceder's Group Data

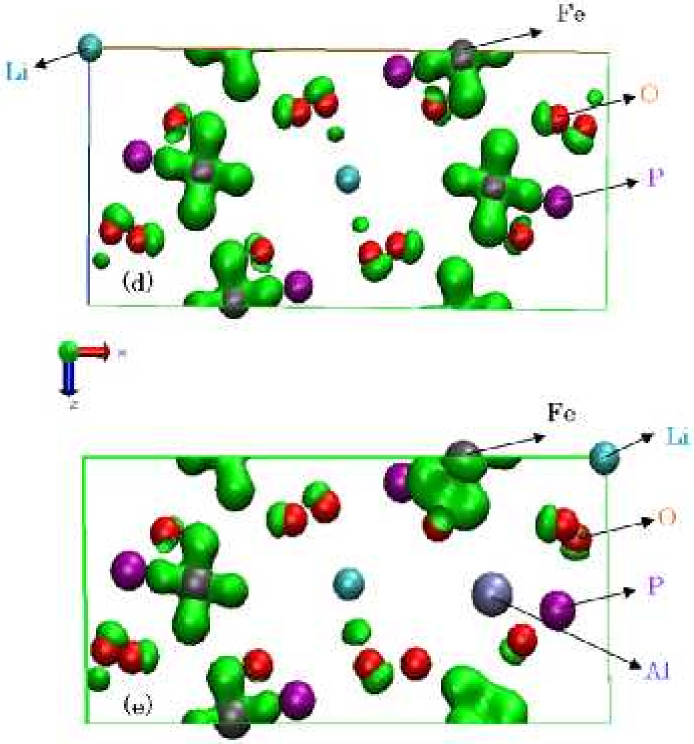
- Validation done

Al substitution improves V in TM Oxides, but not in Olivine phosphates

Results: Visualization of charge density



(a)$LiCoO_2$, $LiAl_{0.33}Co_{0.67}O_2$



(b)$LiFePO_4$, $LiAl_{0.25}Fe_{0.75}PO_4$

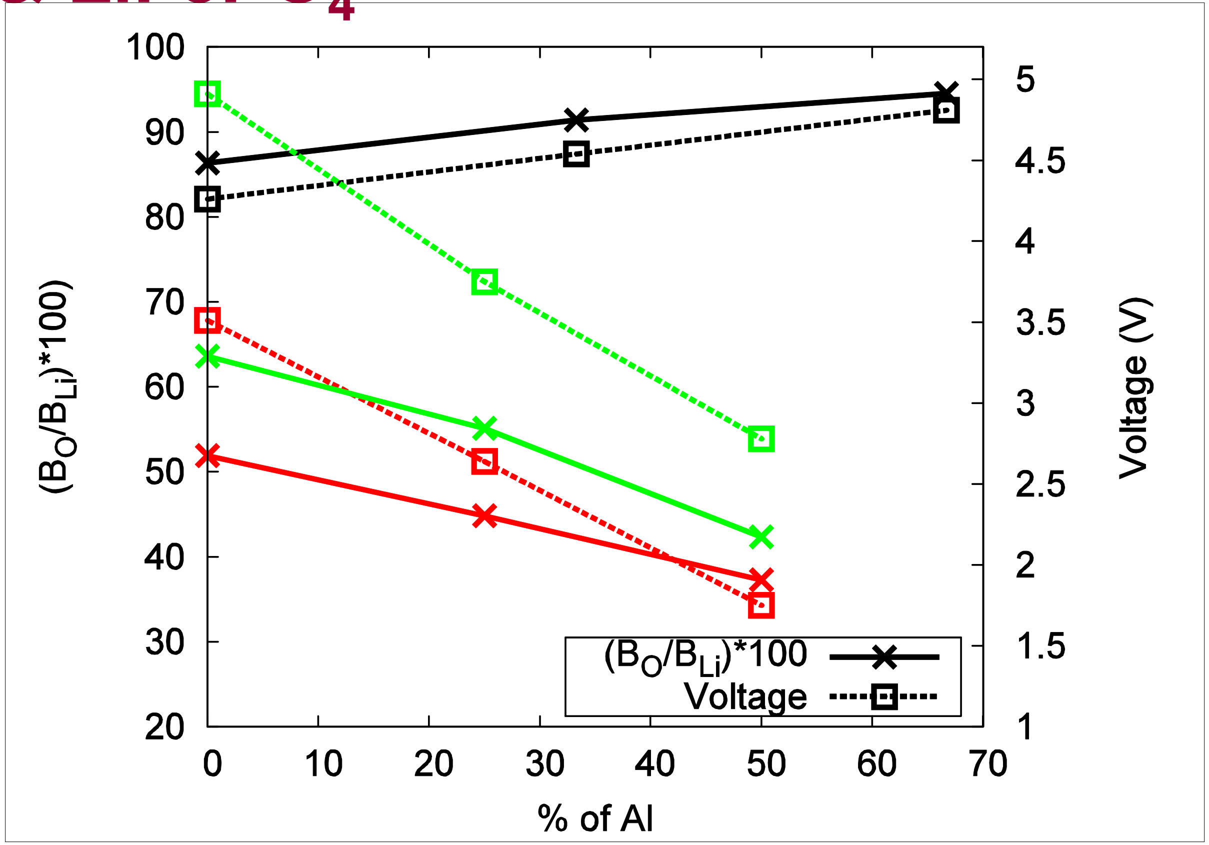
Visualization clearly indicates the different behavior in layered oxides and olivine phosphates

Bader Charge analysis for Al substitution*

Cathode Material	Voltage (V)	Fractional charge transfer per formula unit					
		From Li	Onto				$(B_O/B_{Li})*100$
			O	TM	Al	P	
$LiCoO_2$	4.26	0.865	0.748	0.117	0	-	86.37
$LiCo_{0.67}Al_{0.33}O_2$	4.54	0.863	0.789	0.069	0.004	-	91.42
$LiCo_{0.33}Al_{0.67}O_2$	4.81	0.863	0.816	0.039	0.008	-	94.55
$LiFePO_4$	3.51	0.878	0.446	0.412	0	0.020	50.80
$LiFe_{0.75}Al_{0.25}PO_4$	2.64	0.877	0.393	0.461	0.001	0.021	44.84
$LiFe_{0.50}Al_{0.\ 50}PO_4$	1.75	0.879	0.328	0.514	0.003	0.033	37.32
$LiCoPO_4$	4.62	0.874	0.548	0.315	0	0.010	62.70
$LiCo_{0.75}Al_{0.25}PO_4$	3.75	0.875	0.482	0.391	0.001	0.016	55.08
$LiCo_{0.50}Al_{0.50}PO_4$	2.78	0.877	0.389	0.477	0.002	0.026	42.37

**CSTEP publication: Accepted in Bulletin of Materials Sc*

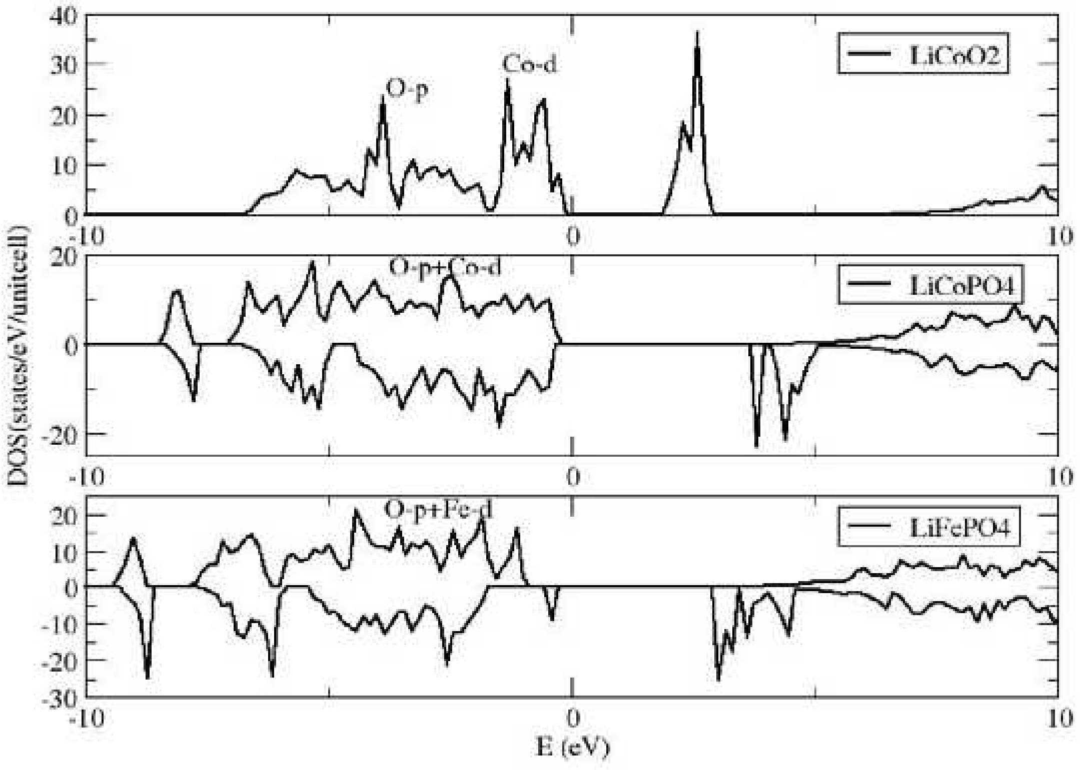
Results *: Effect of Al substitution in $LiCoO_2$, $LiCoPO_4$ & $LiFePO_4$



- •Charges are evaluated in Bader volumes compared to spherical volumes.
- •Lithium Charge transfer to other atoms shows different behavior in the three compounds

**CSTEP publication: Accepted in Bulletin of Materials Sc*

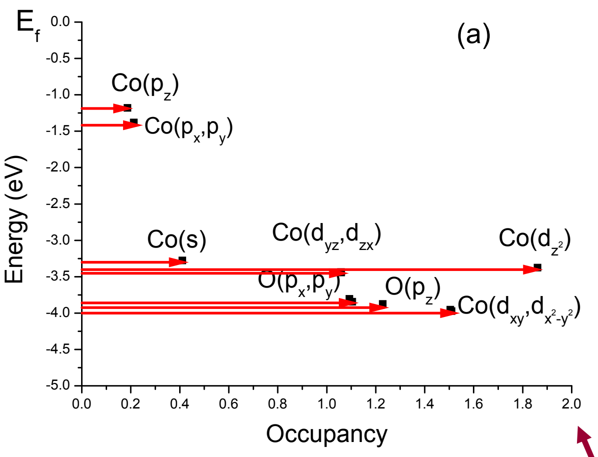
Results: Density of States analysis *



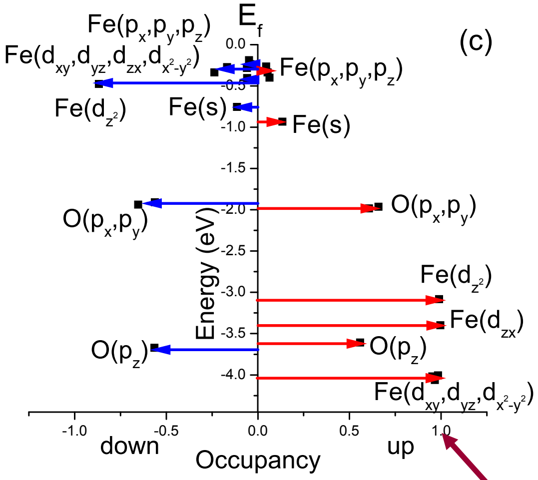
LiFe/CoPO4 has stronger co-valency between TM & O whereas in $LiCoO_2$, the TM-O bond is more ionic

** CSTEP publication: Accepted in Bulletin of Materials Sc*

Results *: Energy level & Occupancy analysis



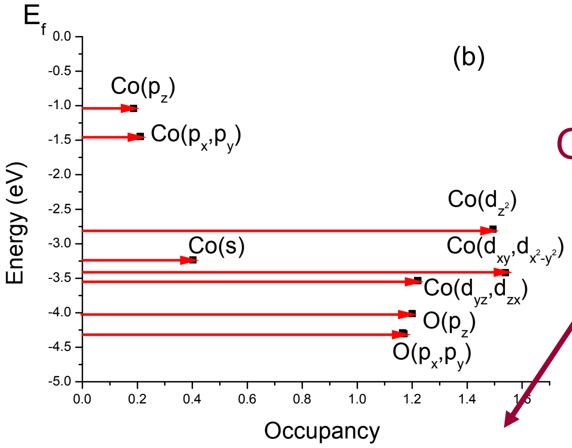
(a) LiCoO2



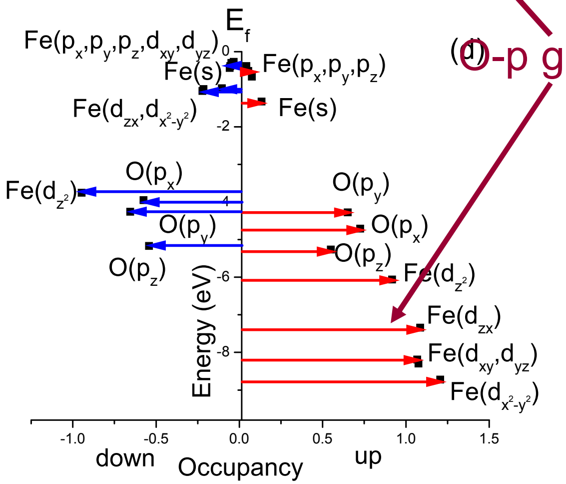
(c) LiFePO4

O-p goes down

O-p goes up



(b) LiAl0.33Co0.67O2



(d) LiAl0.25Fe0.75PO4

Shifting of energy levels with Al substitution

* *CSTEP publication: Accepted in Bulletin of Materials Sc*

Relative positions of O-p orbital & TM-d orbital in oxides & phosphates from EL analysis *

Cathode Material	Position of O-p orbital w.r.t. TM-d orbital (eV)
$LiCoO_2$	-0.195
$LiCo_{0.67}Al_{0.33}O_2$	-0.928
$LiCoPO_4$	1.176
$LiCo_{0.75}Al_{0.25}PO_4$	1.904
$LiFePO_4$	0.498
$LiFe_{0.75}Al_{0.25}PO_4$	2.111

Al substitution decreases O-p orbital energy in oxides and increases it in PO_4

**CSTEP publication: Accepted in Bulletin of Materials Sc*

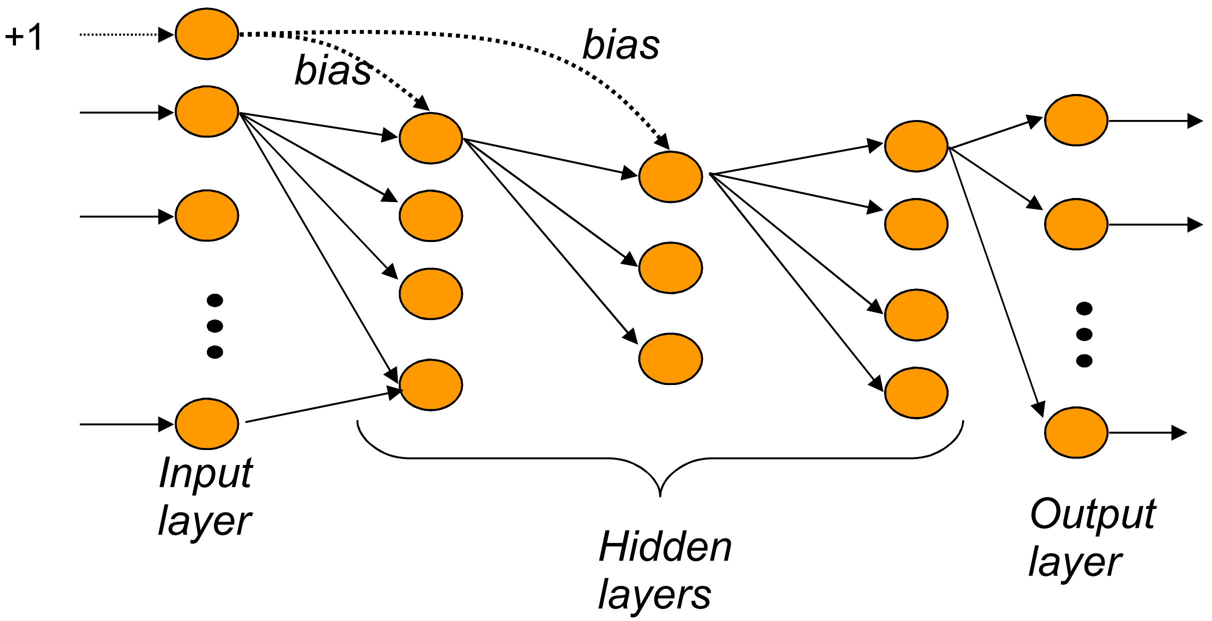
Data Mining for Battery Materials: New methods *

Traditional methods of new battery material development is very time consuming and costly.

- To utilize and build computational modeling tools for battery materials.
- To integrate materials knowledge and data mining technologies to extract new patterns and heuristics.
- Predict potential and other relevant properties based on database of known battery materials.
- Development of rule base for automatic mixing and modeling of prospective battery materials.

**CSTEP publication: in communication with Current Science*

Artificial Neural Network – Multilayer Perception



- Massively parallel structure.
- Uses train-by-example paradigm.

- Training set: Labeled samples *i.e.* both the input and output values are known.

- Test set: Only input values are known, the model gen*eralizes* to give the corresponding output values consistent with the associations learnt.

- Used for clustering, prediction and classification.

Graphical User Interface (GUI) Tool : CSTEP , CAIR (DRDO)

GUI : information and actions available to a user through graphical icons. Integration of computational tools.

- ***Artificial Neural Network (ANN)*** techniques for predicting battery performance parameter (e.g. voltage)

Helps to speed up the materials screening process

- ***Vienna Ab-initio Simulation Package (VASP)*** for Density functional theory (DFT) based calculation (like ground state energy calculation)

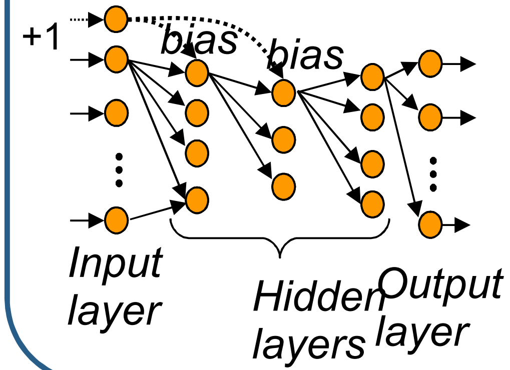
Prediction of material properties from electronic calculations

- ***Quantum Espresso (QE)*** for phonon frequency based calculation

Pre-experimental screening of materials

Materials design by combinatorial methods

Artificial Neural Network modeling



Prediction of material property through data mining

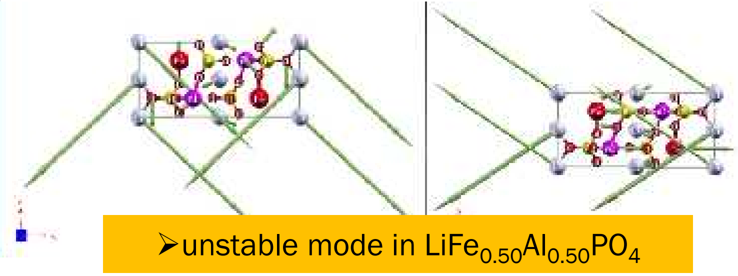
Density Functional Theory simulations

Cathode Material	Voltage (V)
$LiCoO_2$	4.26
$LiCo_{0.67}Al_{0.33}O_2$	4.54
$LiCo_{0.33}Al_{0.67}O_2$	4.81
$LiFePO_4$	3.51

Voltage calculation

Charge transfer analysis

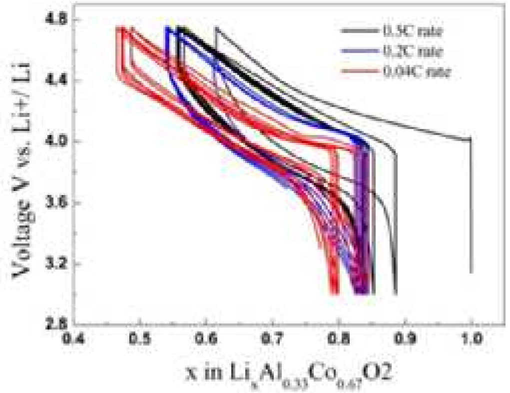
Vibrations and stability PHONONS



➢unstable mode in $LiFe_{0.50}Al_{0.50}PO_4$

Crystal structure stability check for proposed new materials to evaluate **feasibility of synthesis**

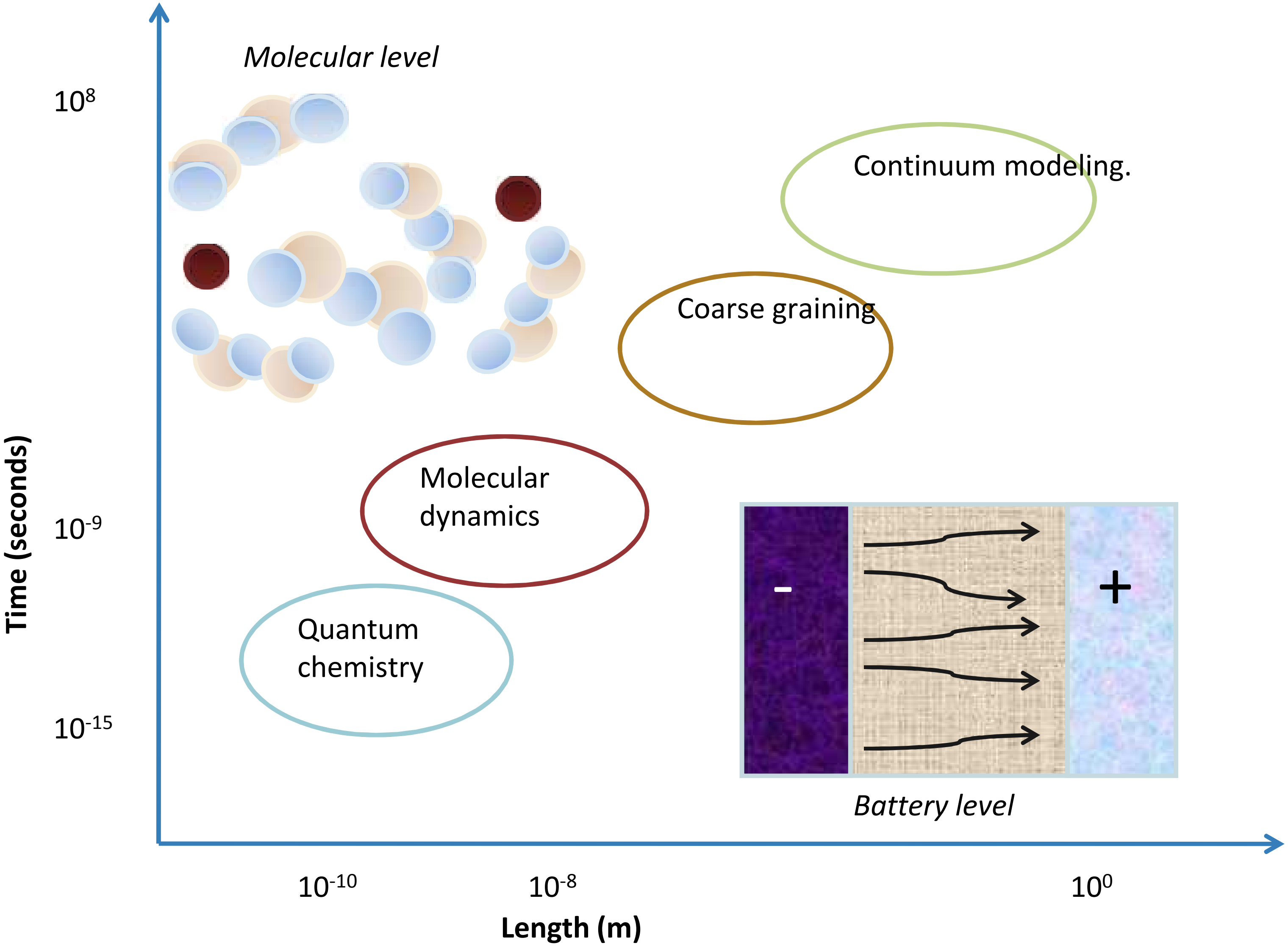
Experimental Validation*



Voltage from
DFT: 4.6 V
ANN: 4.38 V
Exp: 4.74 V

***Expt courtsey: CECRI, CSIR campus, Chennai**

Simulation tools



Way forward

☐Identification of present state of energy storage technologies for grid level applications .

☐Comparative analysis of storage technologies including technical parameters such as round-trip efficiency, self-discharge rate, cycle life, specific energy, specific power, energy density and economic parameters including power cost, energy cost, power conversion cost, capital cost and O&M fixed cost.

☐ Develop innovative methodologies to discover next generation battery materials

Thank You