MAChE Talk 5/2023

ESS Batteries & VRFB

Aug 2023

Nyunt Wai, ChE (1982)

Senior Scientist & Program Manager, ERI@N

wnyunt@ntu.edu.sg

NANYANG TECHNOLOGICAL UNIVERSITY SINGAPORE

Energy Research Institute @ NTU

What is ESS?

- Energy storage system (ESS) stores energy at one point for use at later time.

Energy storage in various forms

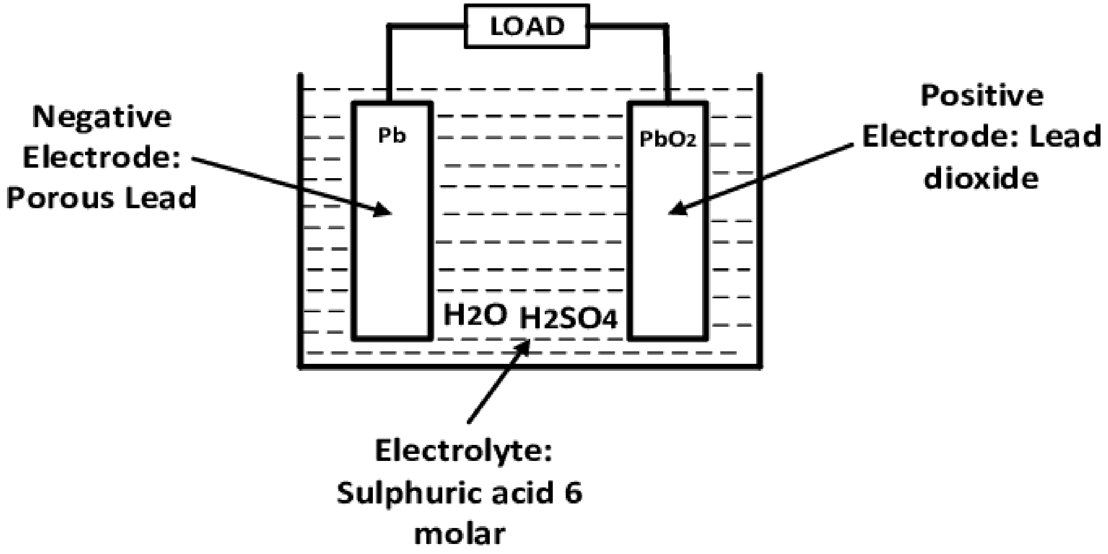
Type of Energy Storage System	Examples
Mechanical storage	Pumped Hydro Storage (PHS); Compressed Air Energy Storage (CAES); Flywheels
Thermal storage	Hot water; Cold water; Molten salt; Phase change material
Electrical storage	Super-capacitors; Superconducting Magnetic Energy Storage (SMES)
Electrochemical storage	Batteries - PbA, Ni-Cd, MH, LiB, NaB, NaS, RFB (Fe-Cr, Fe-Fe, Zn-Br, VRFB, Organics, …), Metal-air, Solid state, etc.
Chemical storage	Hydrogen storage; Power-to-gas

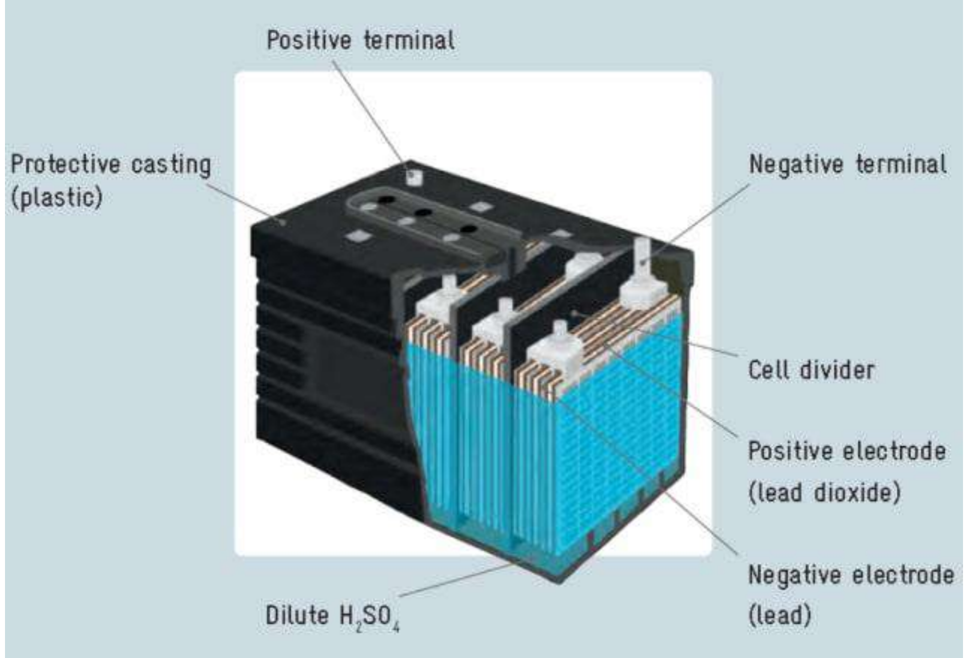
ESS Batteries

- Lead Acid Battery (PbA): Most matured technology
- Ni-Cd, MH Batteries: Dry Cells, matured technology
- Lithium Ion Battery (LiB): High energy density, fire safety is a concern, a number of variants for improving energy density, efficiency, safety, high C-rating, reducing cost.
- Sodium Ion Battery (NaB): Alternative to LIB, lower cost owing to abundance of Sodium, but lower capacity, compared to Lithium
- Sodium Sulphur Battery (NaS): Molten-salt battery, high operating temperature (300-350 ^{0}C), energy density similar to LIB
- Redox Flow Batteries (RFB) (Fe-Cr, Fe-Fe, Zn-Br, VRFB, Organics, …),
- Metal-air batteries, Solid state batteries, etc.: developing, low TRL

Lead Acid Battery (PbA)

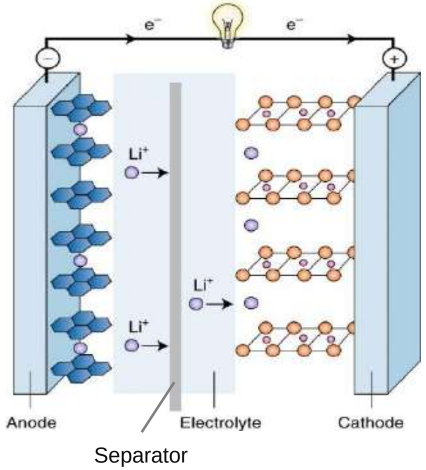
- Uses lead-based electrodes and sulphuric acid as electrolyte
- Mature technology
- Low CAPEX
- Moderate efficiency
- Low energy density
- Low lifetime, leading to high LCOS
- Lead is toxic, not environment friendly (could be partly recycled)
- Initial key applications were Automobile starting, ignition, lighting, UPS, etc.
- Sealed lead-acid battery for deep discharge





Lithium-ion battery (LIB)

- Li^+ travel from cathode to anode through electrolyte & separator during charging process, and back when discharging



- Intercalated lithium compound as positive electrode and typically graphite at the negative electrode
- High Efficiency; High Energy Density
- Moderate Lifetime; High C-rates possible
- High CAPEX
- Fire safety concerns in many variants (thermal runaway)
- Key applications are portable electronics – phones, laptops etc. and electric vehicles

Cathode

$$LiCoO_2 \underset{d}{\overset{c}{\rightleftarrows}} Li_{1-x}CoO_2 + x\,Li^+ + x\,e^-$$

Anode

$$C_n + x\,Li^+ + x\,e^- \underset{d}{\overset{c}{\rightleftarrows}} C_n\,Li_x$$

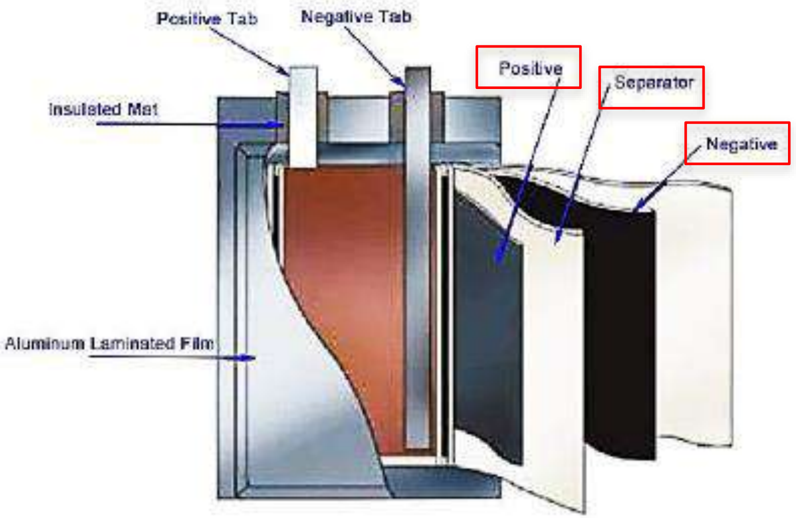
Basic Components of LIB

Cathode (positive)
Normally as source of Li ions, determine energy stored, e.g. $LiCoO_2$, $LiFePO_4$, NMC, NCA, $LiMnO_4$.

Anode (negative)
Store and release Li ions from cathode side, e.g. Graphite, LTO, Silicon

Separator
Prevent contact between anode and cathode, porous membrane, e.g. PE or PP

Pouch Cell



Electrolyte
Medium for movement of ions within the cell; Majority of electrolyte is non-aqueous, e.g. 1.0M $LiPF_6$ in ES/DEC=50/50 (v/v)

Current Collector
Conducts electricity to the outside circuit, e.g. Copper (anode current collector) and Aluminium (cathode current collector)

Casing
Housing for the Cell, Al laminated film (for pouch cell) protect system within the cells from direct contacting with air and moisture.

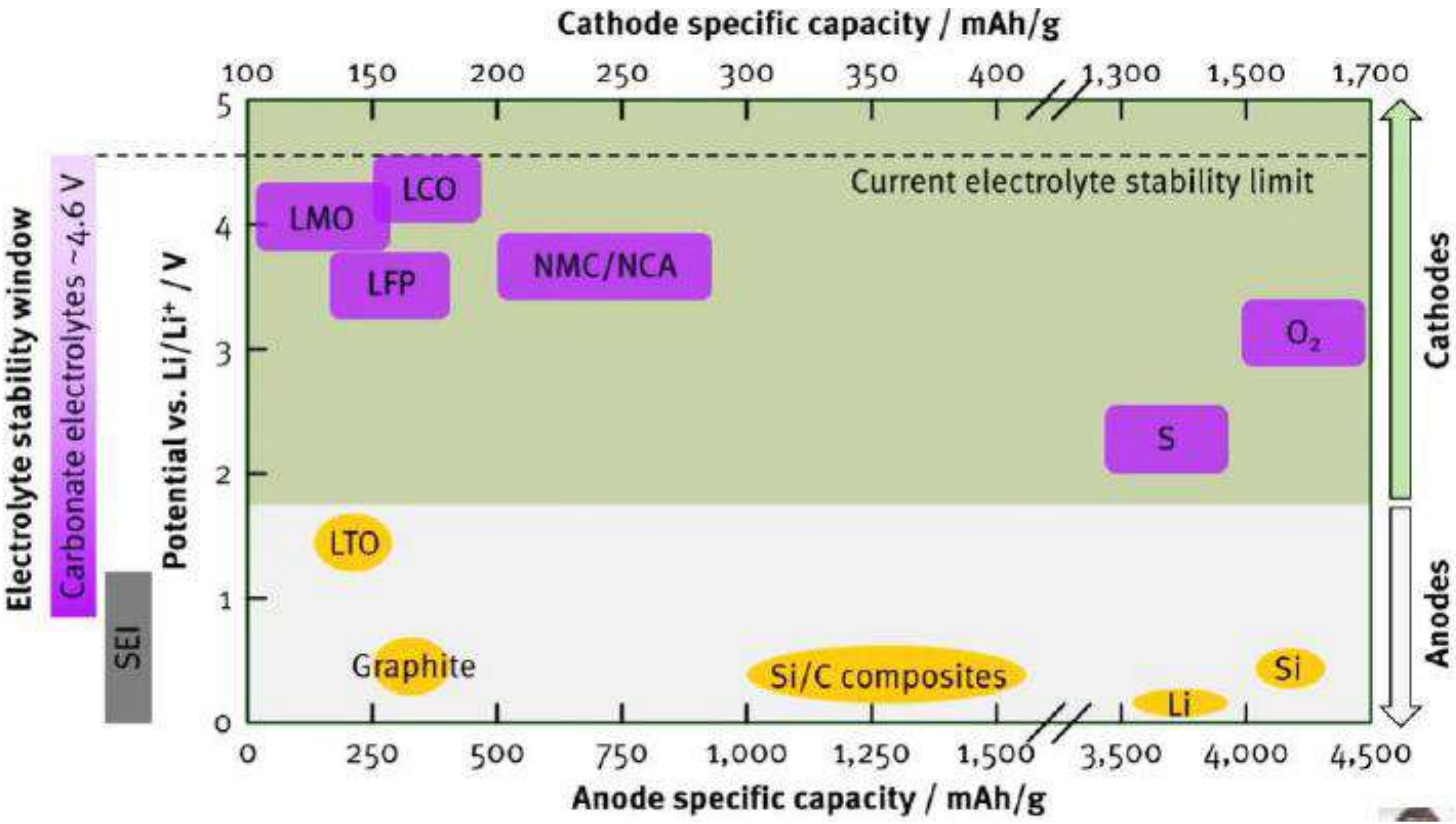
Forms: Coin cell, Cylindrical cells, Pouch Cells, Prismatic Cells

Common Cathodes and Anodes in LIB

Anode
High capacity and low voltage

Cathode
High capacity and high voltage

Electrolyte
Large stability window



Electrolyte is a medium with Li salt in organic liquid solvent

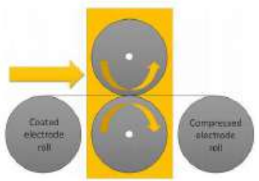
Processes in manufacturing a LIB cell

Mixing

Mix active materials (graphite, NMC) with conductive carbon and binder (solvent) to form homogeneous slurry.

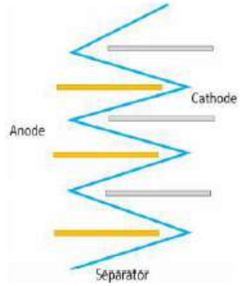
Coating

Coat slurry:
Cathode on Al foil
Anode on Cu foil



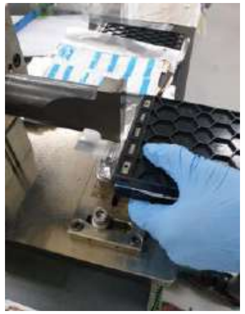
Calendaring

After drying, press Electrodes to desired thickness.



Stacking

Electrodes stacking
(Anode + Separator + Cathode)



Welding

Tab lead connection by U.S.W

Filling Electrolyte

Fill / inject Electrolyte into Electrodes in a pouch / cylindrical container in dry room

Sealing

vacuum-seal the cell and send to pre-charge

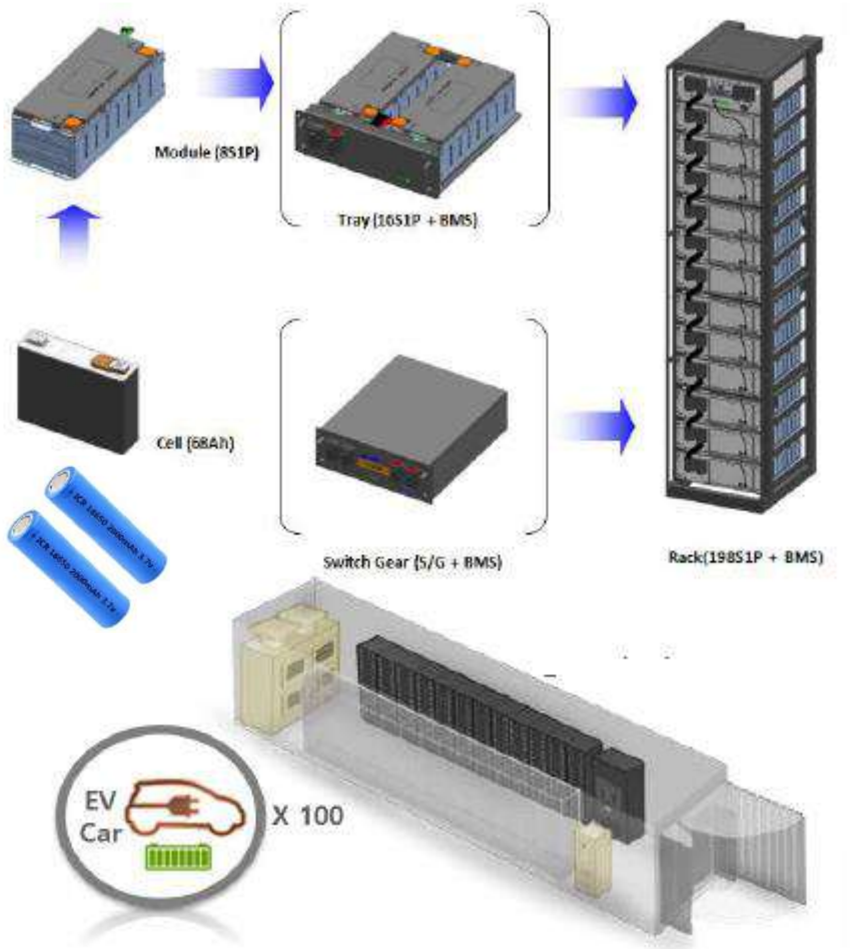
Testing

After pre-charge, degassing and 2nd sealing, test and grade the cells

Pouch Cells

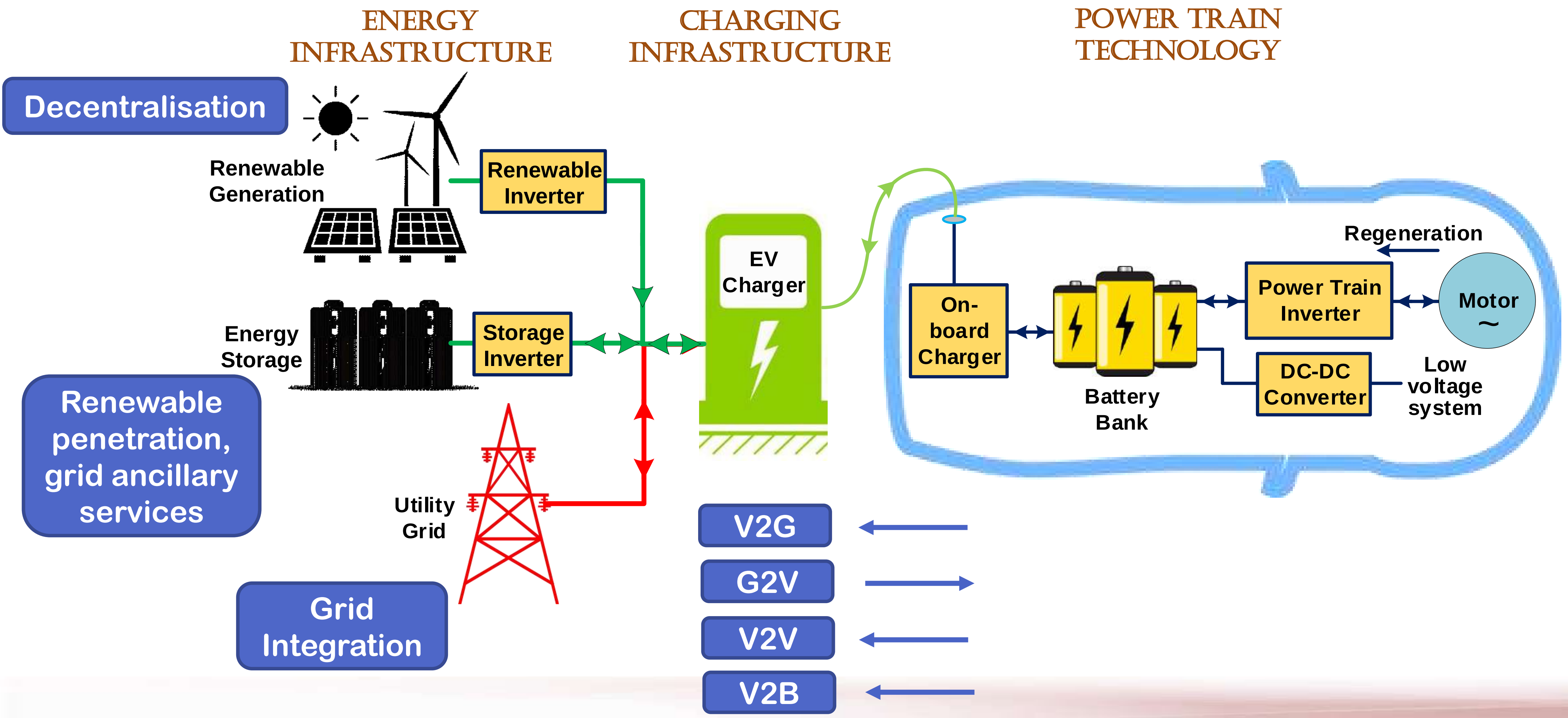
Terminology: Cell → Module → Tray→ Rack→ Container

- Different levels of battery integration
- Multiple cells are arranged together to form a module
- Multiple modules are assembled to obtain a Tray
- Multiple trays are stacked to get a Rack
- Multiple racks are housed inside a Container.
- For EV applications the terminologies slightly vary as cell, module and pack.
- Battery packs are installed typically underneath the chassis of EV.



Courtesy: HYOSUNG

BEV Architecture



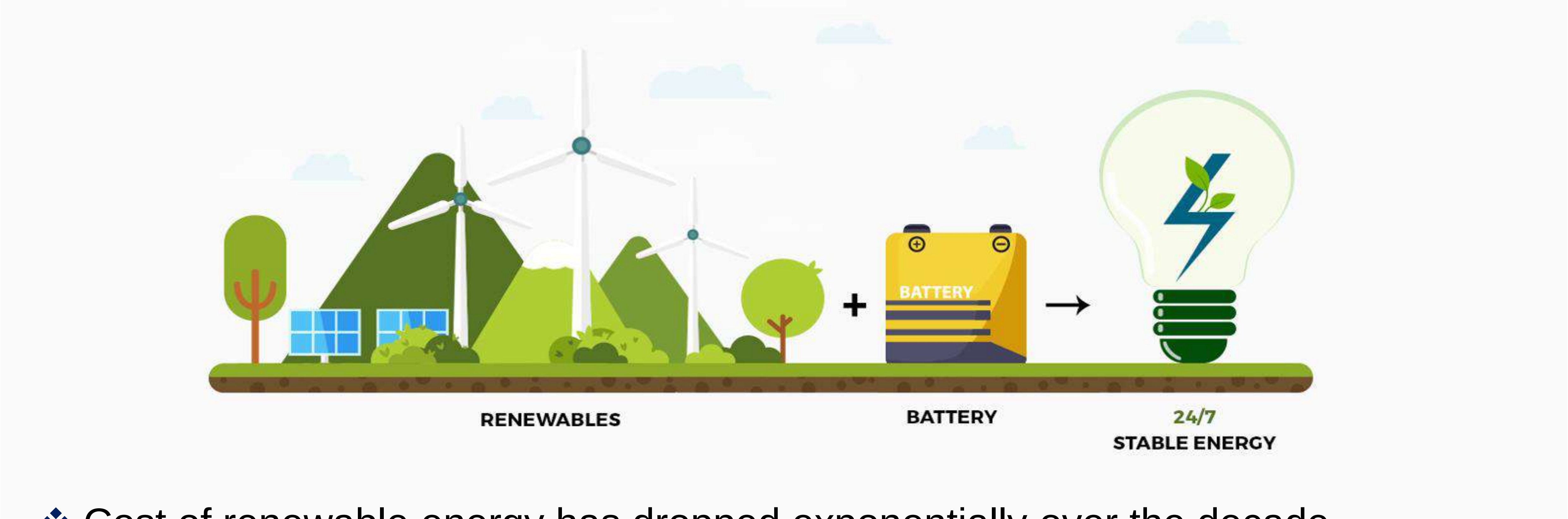
Vanadium Redox Flow Battery Development in NTU

Aug 2023

Nyunt Wai, ChE (1982)

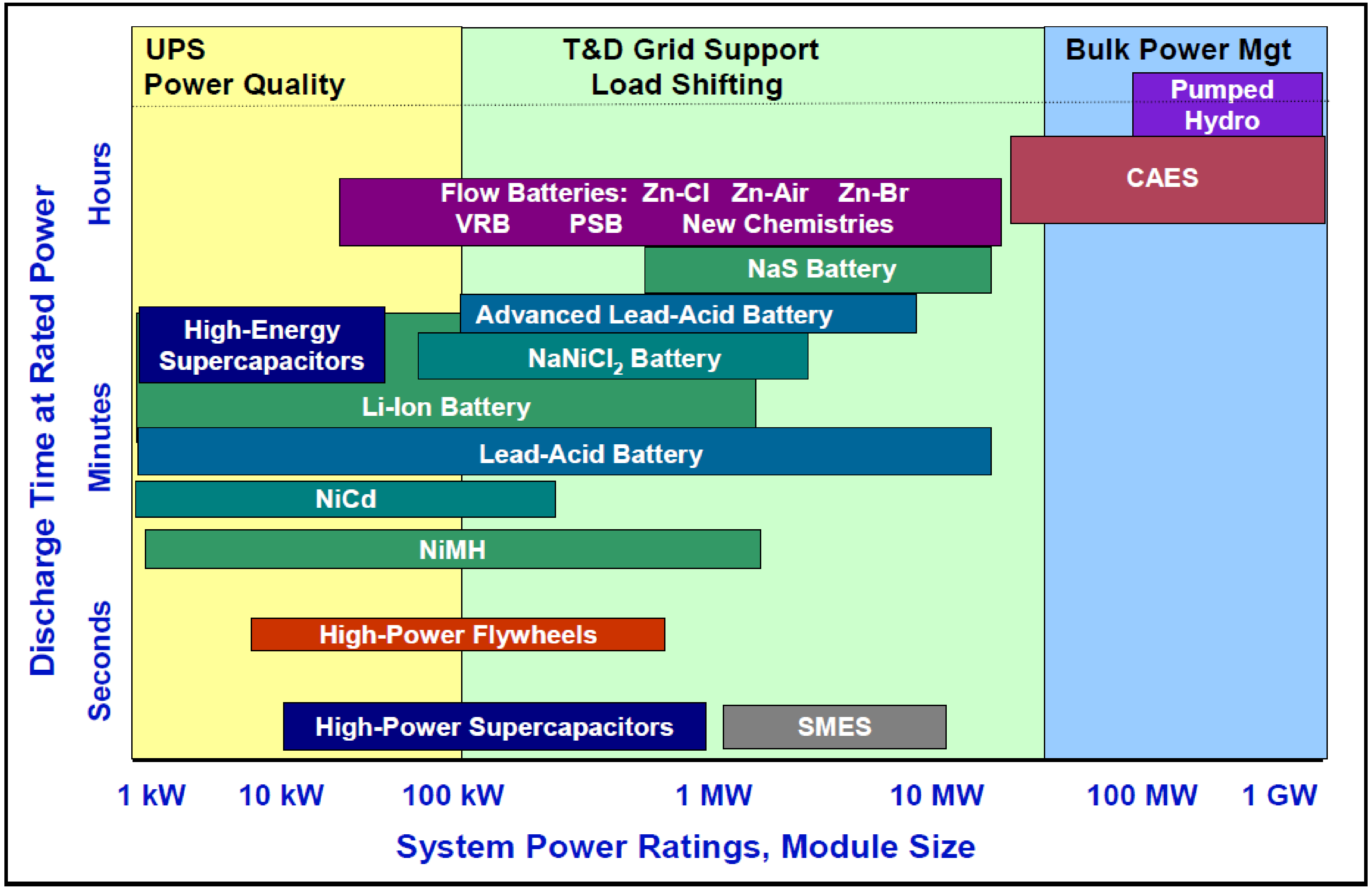
wnyunt@ntu.edu.sg

Renewable Energy is the Future!



- Cost of renewable energy has dropped exponentially over the decade
- Policy makers drive toward clean and green energy to reduce carbon emission
- Urgent need for long duration energy storage to drive the renewable demand further

Position of Energy Storage Technologies

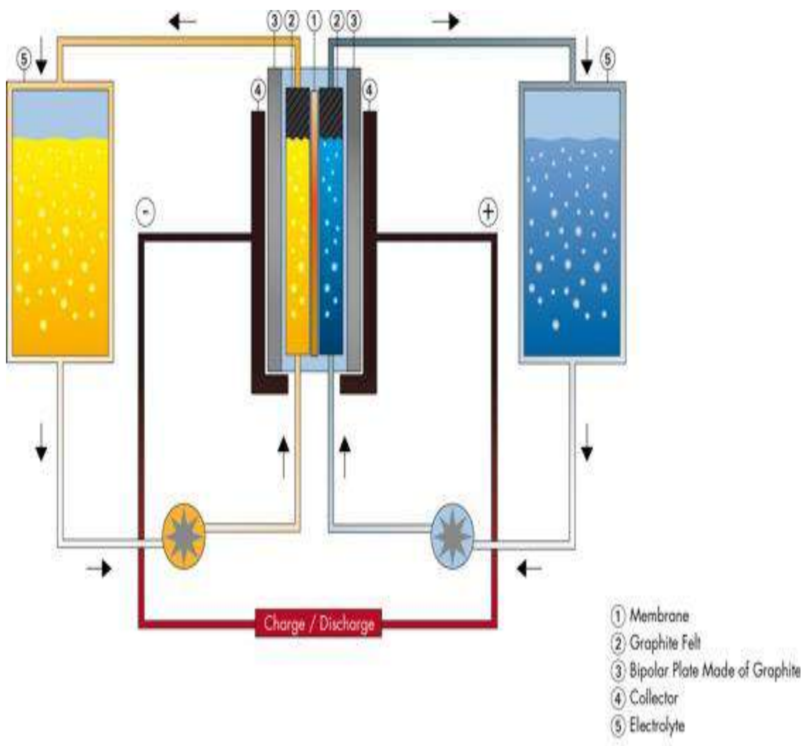


Source: Electric Power Research Institute (EPRI) White Paper on Energy Storage December 2010

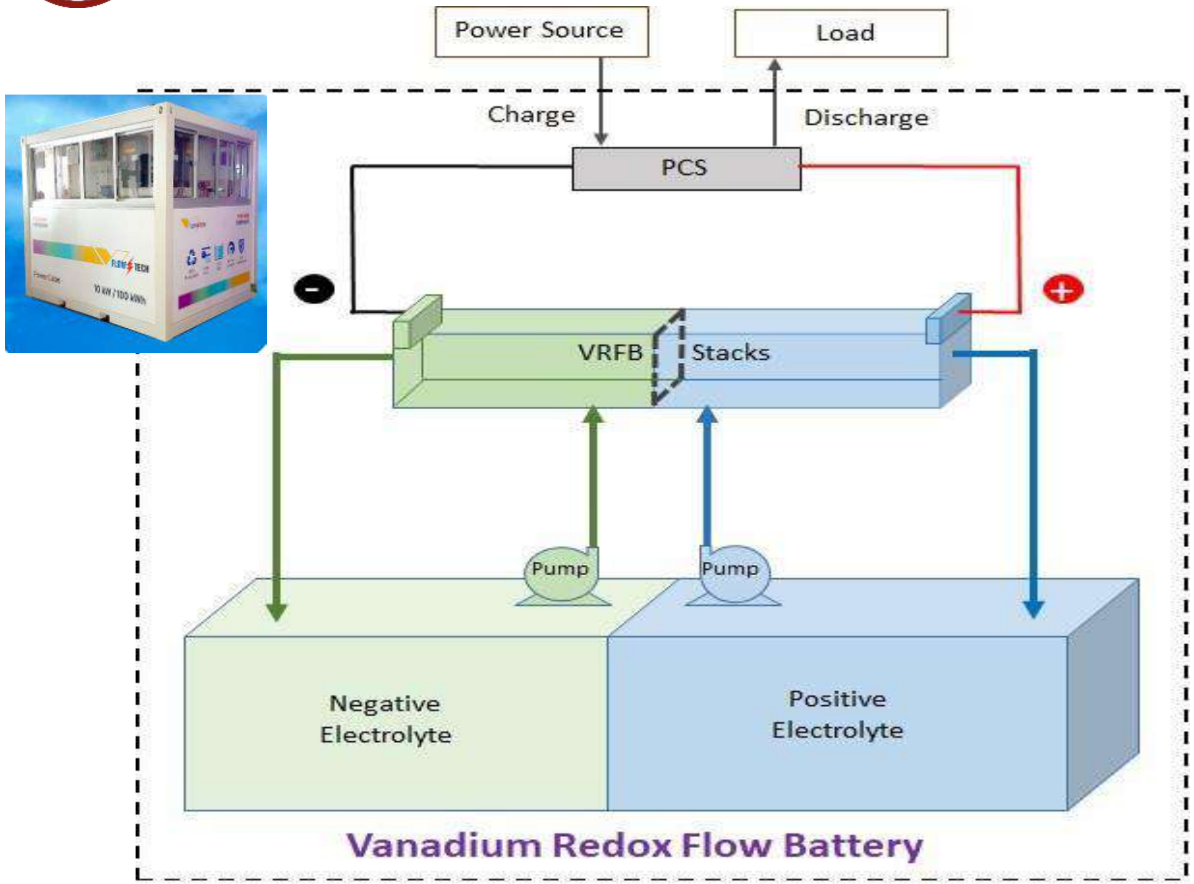
- Lead-Acid and Li-ion batteries are good for high power but short duration energy storage (minutes to 2 hours).
- Li-ion battery, due to its high energy density, the development is more focusing on mobile applications.
- Supercapacitors are good for high power for few seconds.
- Redox flow batteries are suitable for large scale energy storage - high power (kW to MW) and backup time (hours to days), for stationary applications.

Flow Batteries

- The flow batteries are the most suitable candidates for storing large-scale electrical energy (kWh to MWh scale).
- The energy is stored in separate electrolyte tanks. The battery stack is a power converter.
- The components such as electrodes, membrane, electrolyte, etc., in the flow batteries play a crucial role and determine the battery performances and cost.
- Energy storage is based on different oxidation-reduction potentials of redox couples.
- Some developed redox couples: Fe-Cr, Fe-Fe, Zn-Br, V-V, Metal-air, Organics, etc.



Vanadium Redox Flow Battery



Anode: $VO^{2+} + H_2O \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} VO_2^{+} + 2H^{+} + e^{-}$ $\quad E^{o} = 1.00\ V$

Cathode: $V^{3+} + e^{-} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} V^{2+}$ $\quad E^{o} = -0.26\ V$

Overall: $VO^{2+} + V^{3+} + H_2O \leftrightarrow VO_2^{+} + V^{2+} + 2H^{+}$

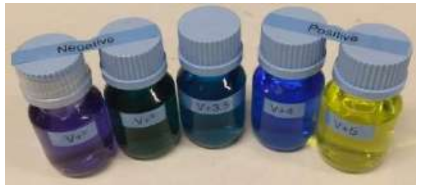
OCV : **1.4 V at 50% SOC to 1.6 V at 100% SOC**

Pros

- Good for Large-scale energy storage (kW to MW power and hours to days back-up)
- Power and Energy decoupled & independent
- V-Electrolyte in both half-cell (V-ions in dilute S.A.)
- High energy efficiency; 100% DOD capable
- Long lifetime (>10,000 cycles); High residual value
- No fire hazard; Low pollution, fully recyclable

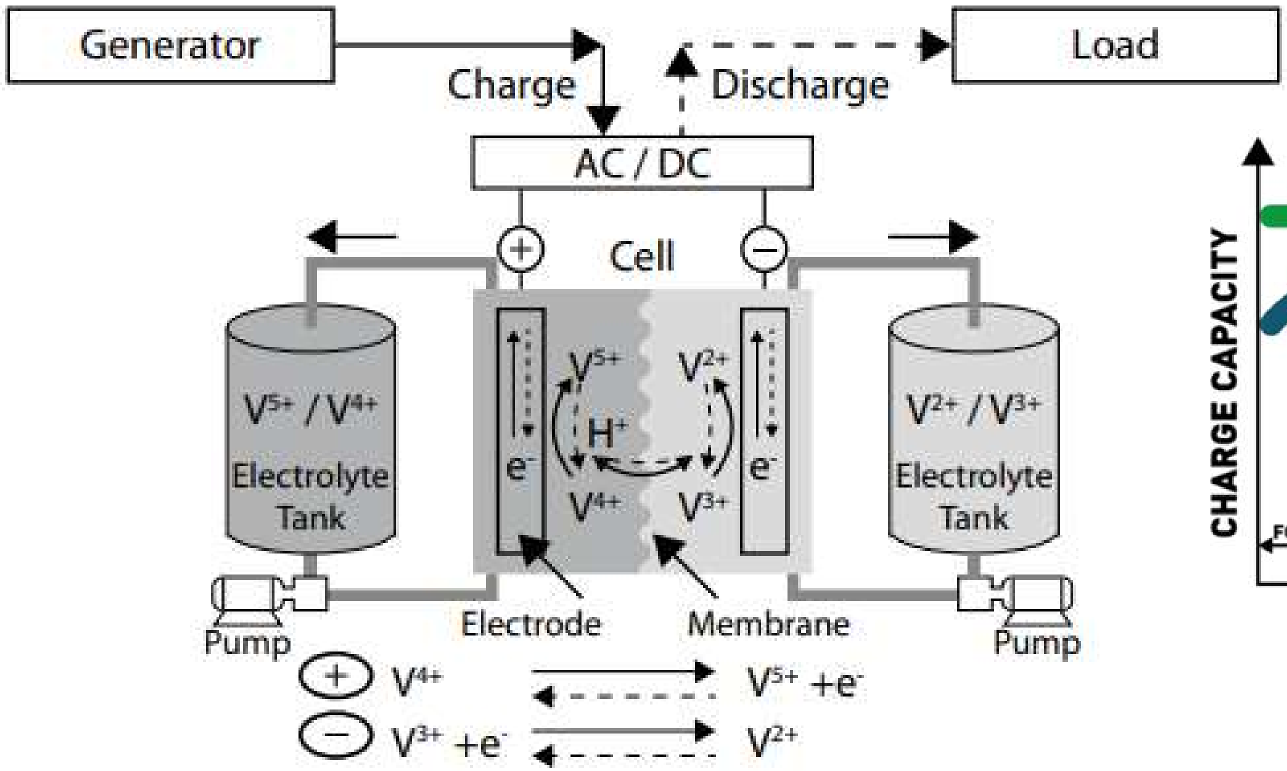
Cons

- Low energy density (compared to LIB)
- Limited Temp. window operation (-10 to 50 C)

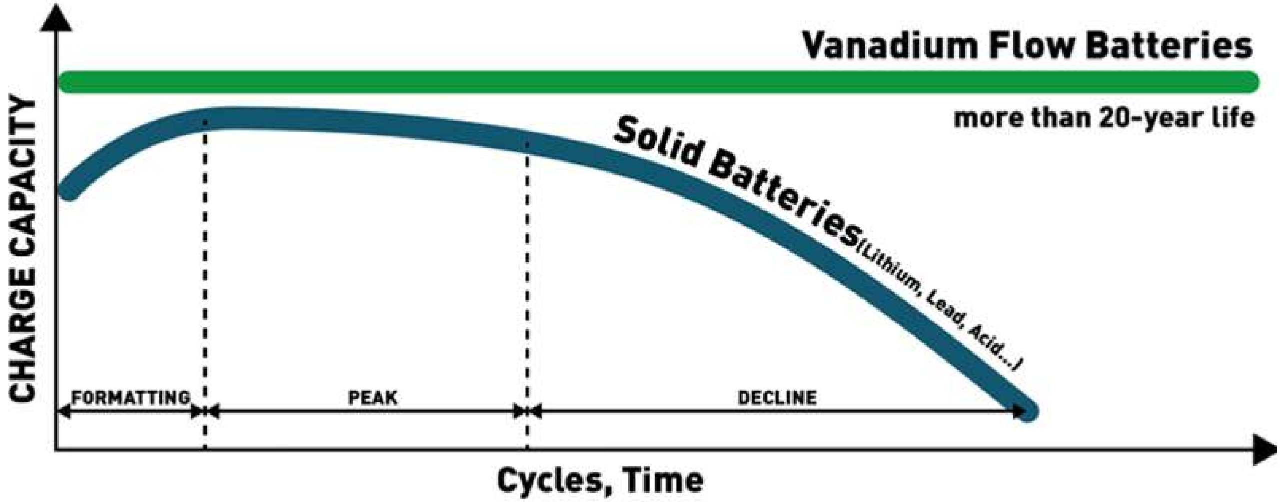


Chemistry: (2M) $VOSO_4$ in (5M) H_2SO_4

Vanadium Redox Flow Battery



Working mechanism



No degradation


Safe to use

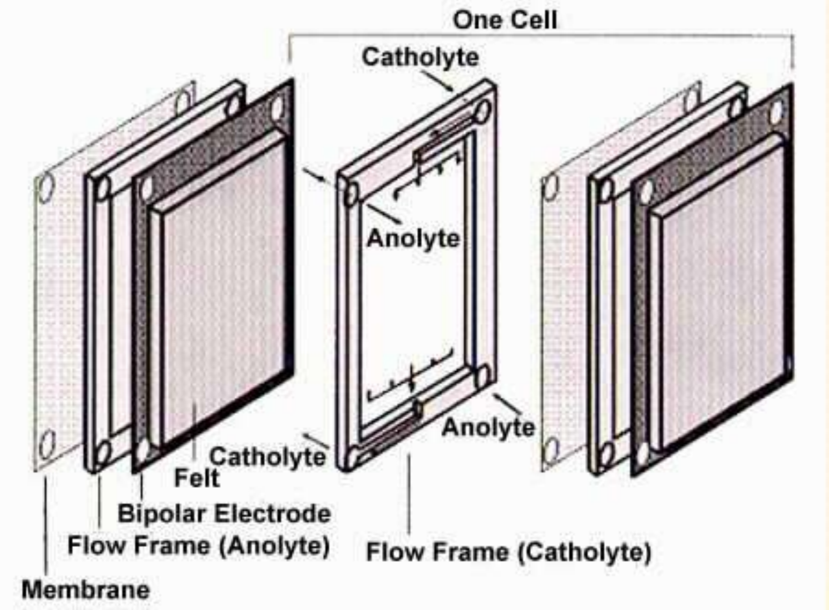

100% Recyclable

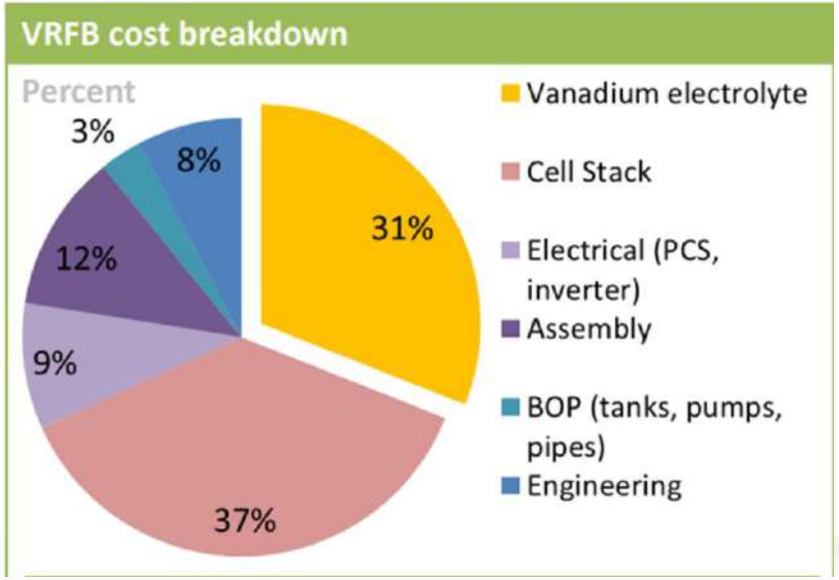

25-year Life


100% DOD


Long hour

Key Components of VRFB





Bipolar Electrode

- Activity
- Surface Area
- Conductivity
- Chemical Stability
- Mechanical Strength
- No Permeability
- Cost

IX Membrane

- Selectivity
- Conductivity
- Stability (Chemical, Mechanical)
- Mechanical Strength
- Lifetime
- Cost

Electrolyte

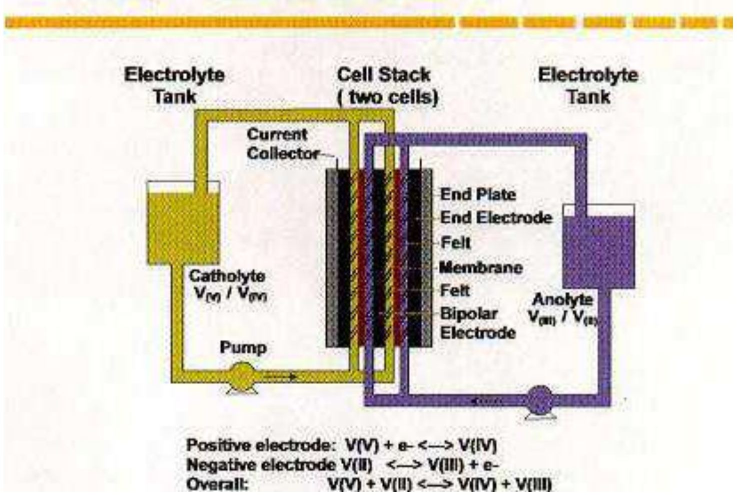
- Energy Density
- Stability
- Electrochemical activity
- Cost

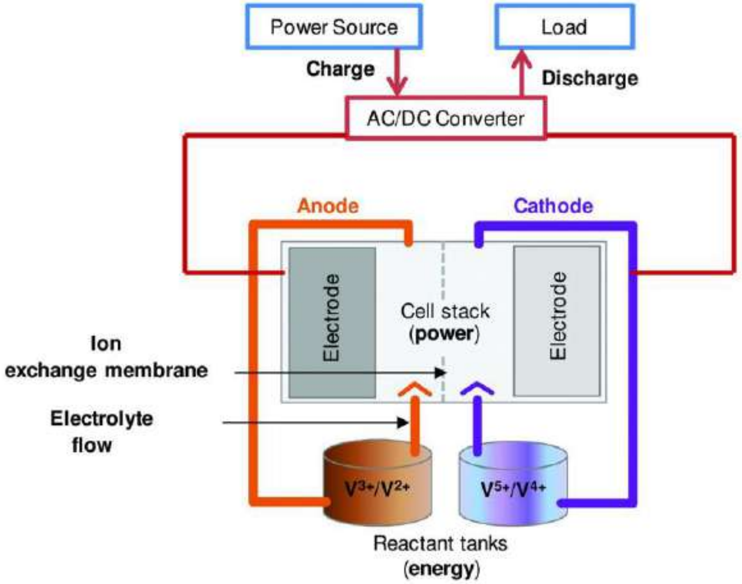
Flow Frame / Stack

- Flow Distribution
- Pressure Drop
- Power Density
- Cost

VRFB Electrolyte Development

VRFB System Schematic





G1 Electrolyte: $VOSO_4$

Anode: $VO_2^+ + 2H^+ + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} VO^{2+} + H_2O$ $E^o = 1.00\ V$

Cathode: $V^{3+} + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} V^{2+}$ $E^o = -0.26\ V$

Overall: $VO^{2+} + V^{3+} + H_2O \leftrightarrow VO_2^+ + V^{2+} + 2H^+$

OCV = 1.4 V at 50% SOC to 1.6 V at 100% SOC

G2 Electrolyte: V/Br

Anode: $Br^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Br^{3-} + 2e$ $E^o = 1.07\ V$

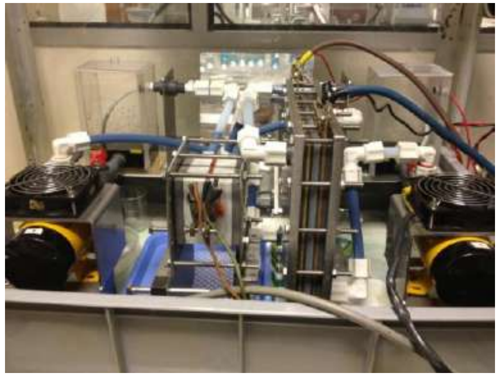
Cathode: $V^{3+} + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} V^{2+}$ $E^o = -0.26\ V$

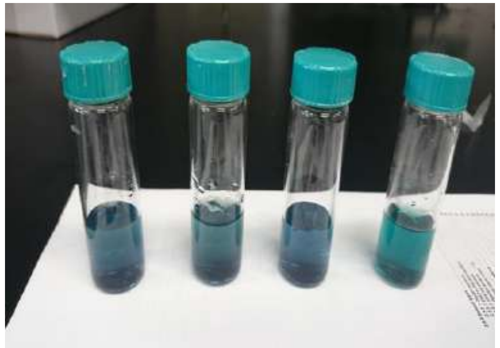
Overall: $3Br^- + 2V^{3+} \leftrightarrow Br_3^- + 2V^{2+}$

- Energy density increased to 50Wh/kg (from 25Wh/kg in G1)
- Developed novel Br_2 complexing agent
- Developed low cost SPEEK ion exchange membrane

VRFB Electrolyte Thermal Stability Improvement

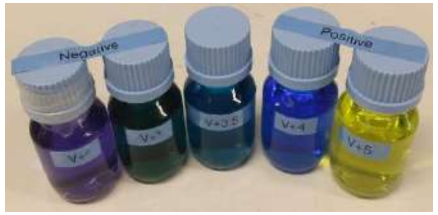
- Development of a novel halide-free, higher temperature stable electrolyte formulation
- Precipitation test at different temperature
- Screening and testing of various additives
- Study of precipitation hindrance mechanism
- Optimize electrolyte formulation
- Test long-term stability of new electrolyte in laboratory scale 1 kW stack
- Efficient operation of flow battery system in the tropical environment
- TD/283/16 Novel combined additives enhancing thermal stability of electrolyte to more than 50 degree C





V – recovery from Fly Ash

VRFB Electrolyte

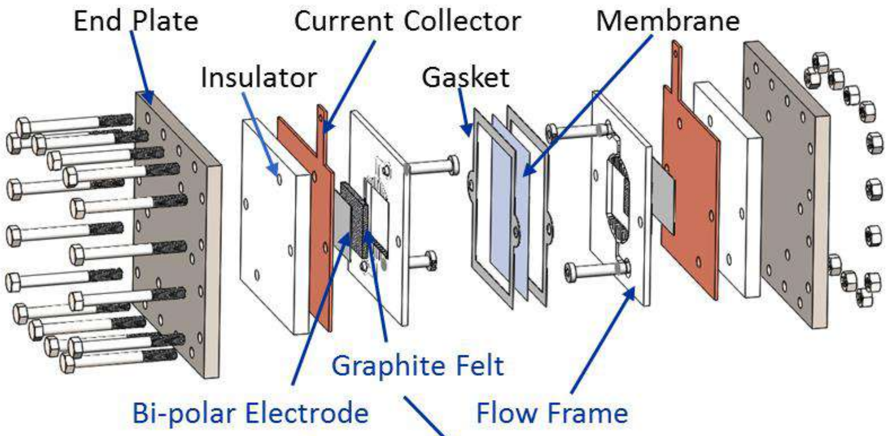


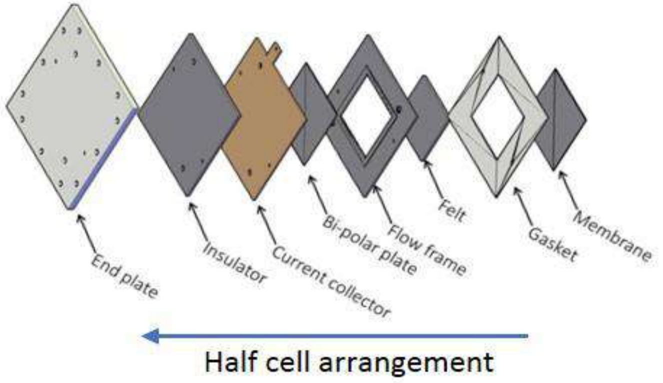
Raw Materials

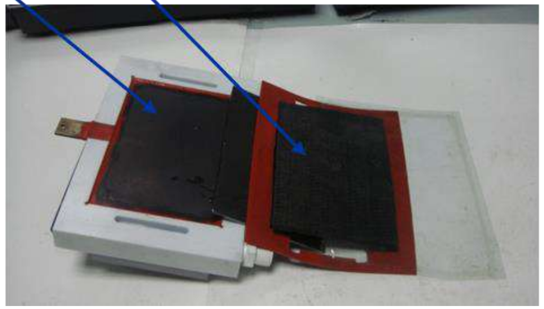
- Vanadium Oxide
- Sulphuric Acid

- Vanadium in VRFB electrolyte is mostly used in steel industry; Vanadium price increased 10 years high in 2018.
- Fly ash samples from one refinery shows V content of >2% in weight.
- Recovery processes:
  - High temperature smelting – formed Ferro Vanadium (FeV) slug
  - Acid leaching – most of the metal oxide dissolved in acid; difficult to remove Fe & Ni from the dissolved acid solution
  - Alkaline leaching – Ni dissolved at low pH, Al and V dissolved at high pH; Al can be removed by selected precipitation
- V dissolved in alkaline solution in VO_4^{3-} : V(V) form, then slowly formed $Na_2V_6O_{16}.3H_2O$.
- Dissolve it in H_2SO_4 with SO_2 bubbling to get V-electrolyte solution.
- Targeted electrolyte cost <$3/litre (1.6-2.0M V in 5M H_2SO_4).

VRFB - Development of Electrode and Stack







Electrode Improvement

- Ex-situ material characterization and modification
- Electrochemical characterization
- Half cell, single cell and stack measurements
- Durability test, novel electrode configuration
- Electrode from c-based waste materials

Stack Design

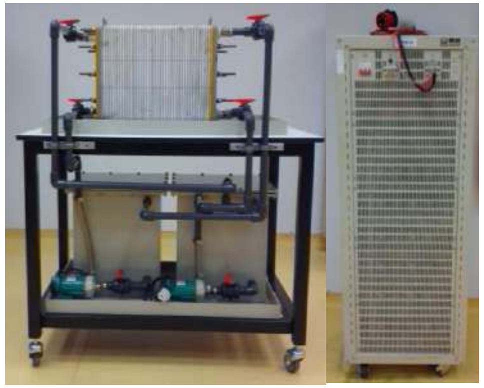
- Modelling: Porous electrodes, single cell
- Laboratory scale stack design (1kW)
- Testing components and system
- TD/171/17 Design of FF and Channel Cover & methodology on making modules for the assembly of RFB

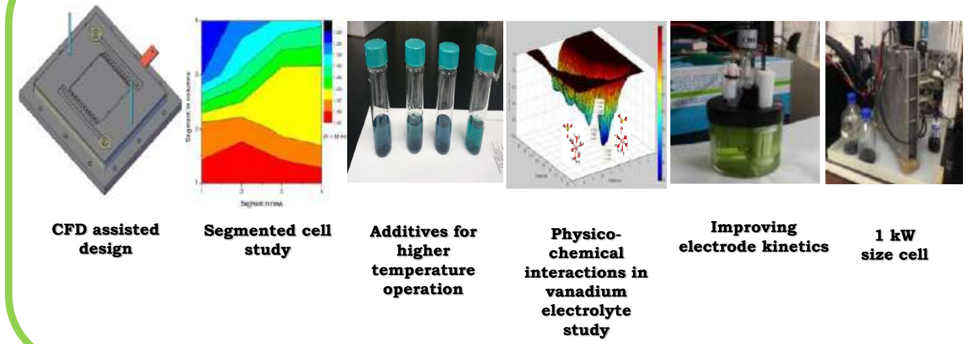
- Flow-field design in bipolar plates and electrodes for high-power density stack development

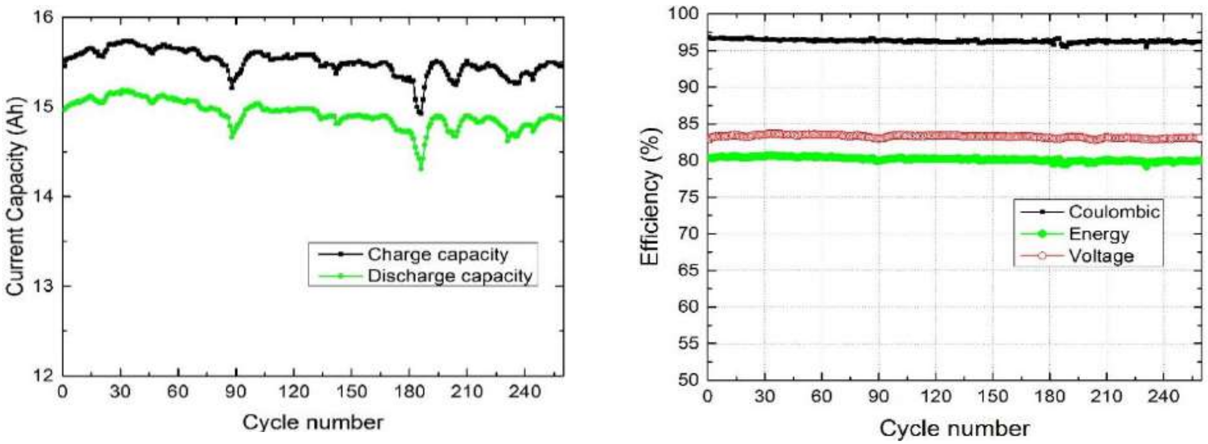
VRFB System Level Development

- Improvement of carbon-based electrode materials
- Modelling, cell and stack design, performance evaluation and improvement
- Development of a halide-free, thermal stabilized electrolyte
- Characterizing electrode and electrolyte interactions at molecular level
- Development of energy efficient modular 1-2.5 kW stack and system


1kW-1kWh VRFB


2.5kW-10kWh VRFB





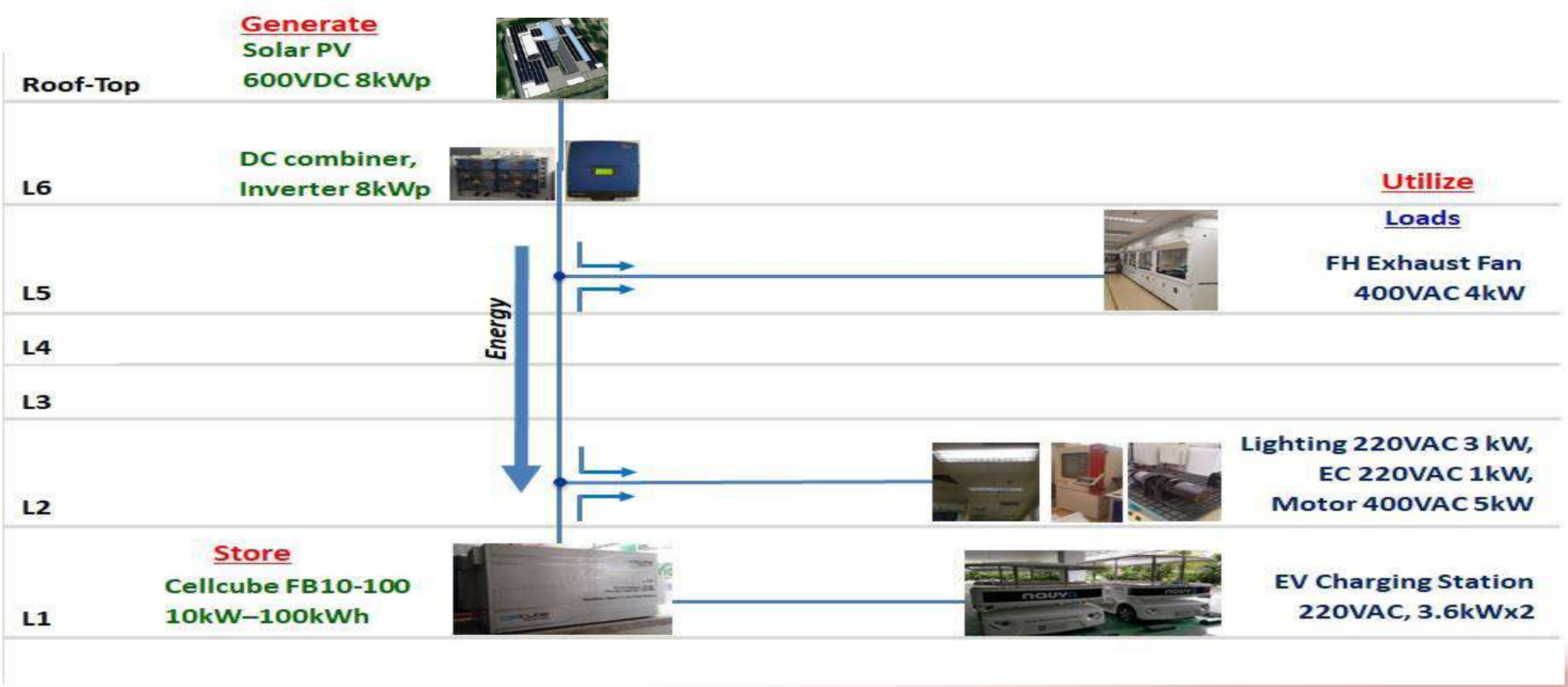
Test Cycles Results

Test-bedding of VRFB in a Building Micro-Grid

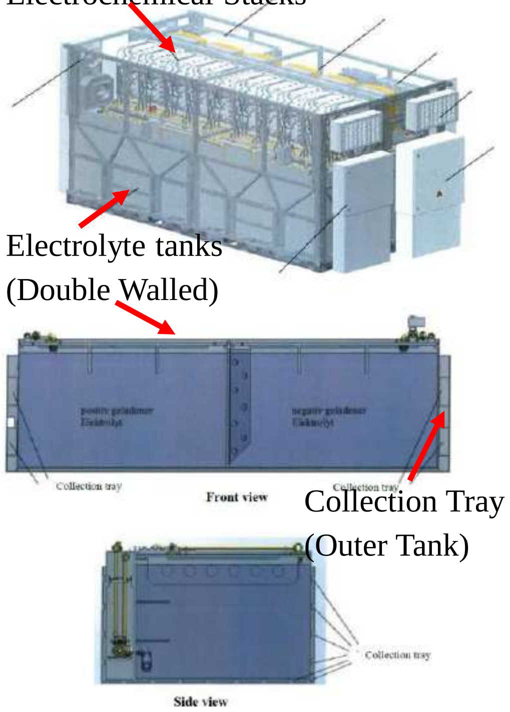
- Generate: Solar PV on roof-top with PV Inverter
- Storage: VRFB10kW-100kWh at generator room
- Loads: Lightings, fume hood and EV charging station

Test-bedded on:

- Impact of solar intermittency, Energy security
- Energy trading (arbitrage) application



Safety measure in VRFB installation



Double Walled Electrolyte Tank for Spillage Control

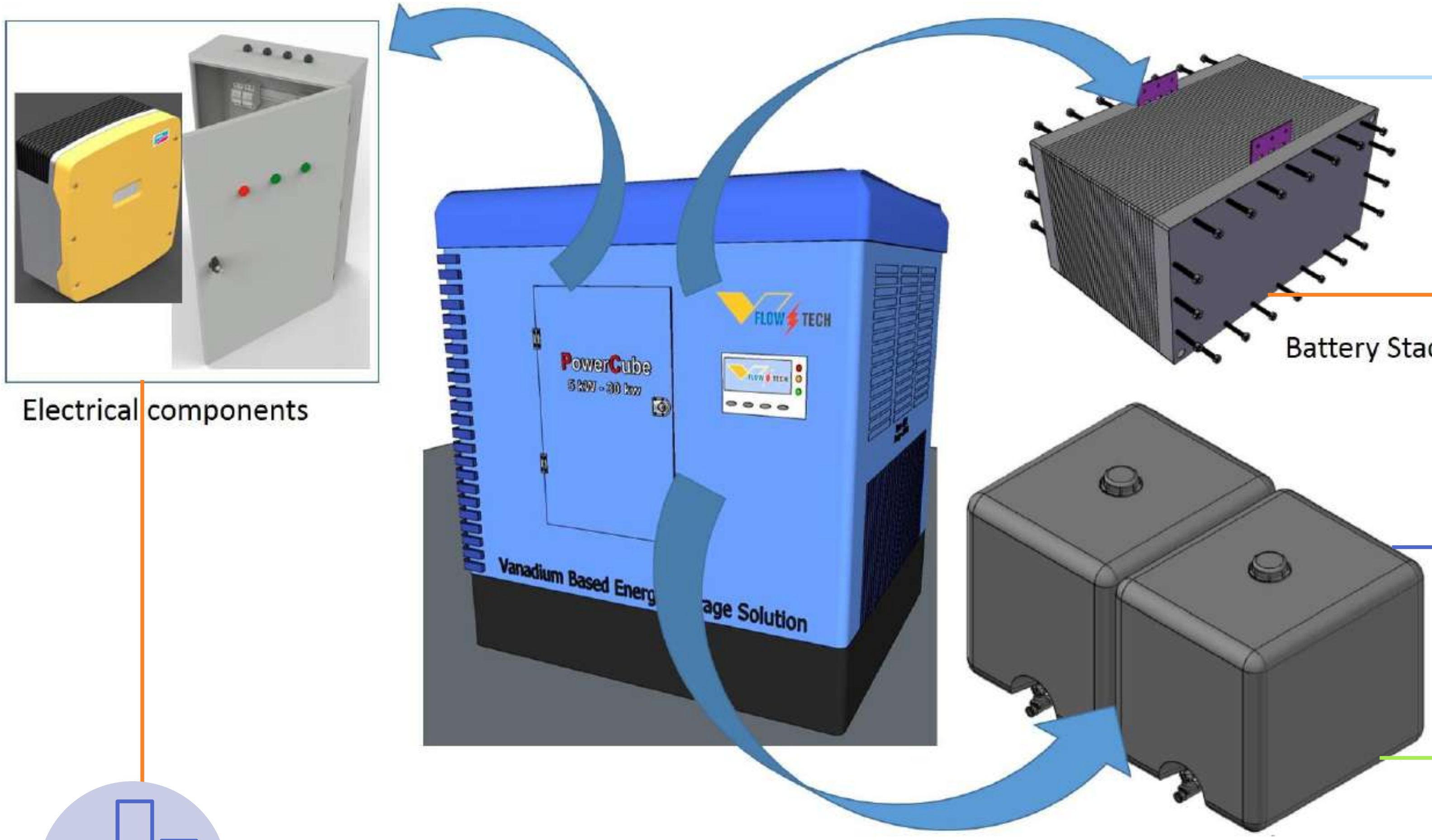
Tertiary Containment on site for Spillage Control

- Electrolyte: 1.6-2M Vanadium Sulfate in 5M Sulfuric acid
- SDS shows no fire hazard
- Fitted with leakage sensors, alarm and control
- Stacks installed above the electrolyte tank
- Double-walled electrolyte tank, outer tank functioned as a collection tray
- As a tertiary containment, an epoxy coated concrete dyke with a sump constructed for spillage control to the ground
- At the latest installation, 2-hour fire rated partition installed between the battery and generator
- Approval received: SCDF, NEA, JTC

1

Technology Innovation in VRFB

V-Flow Tech is a spinoff from NTU, Singapore commercializing vanadium redox flow batteries with key IPs and know-how to deliver energy storage solution (ESS)



Innovative Stack design
Compact and scalable design

Reduced parasitic losses
High and stable efficiency & capacity

Novel Chemistry
Allows better thermal window

Higher solubility of vanadium
25% Higher energy density

Proprietary BMS and EMS
>IOT and Load management capabilities

& Lower cost

V-Flow Product-Application Matrix

Product	Application	Customer	Use Case V-Flow
 5 kw/30 kWh	telecom tower Home application Solar tracker	SOLARIN my very own power plant STAY·ON UNLIMITED ENERGY BROADCAST & COMMS Scorpius Trackers RESOURTIUM INTERNATIONAL ers	❖ Anti-theft is important criteria for remote operation in telecom tower ❖ Idea for solar homes ❖ DC system with Solar Tracker
 10 kW/100 kWh	C&I Off grid application Diesel Genset	RIGHT PEOPLE RENEWABLE ENERGY FOURTH PARTNER ENERGY CleanTech GLOBAL RENEWABLES CANOPY POWER	❖ Safe operation for house hold and industry application ❖ UPS ❖ Long hour operation (>4 hours) ❖ Micro-grid and DG replacement ❖ Solar peak shifting
 125 kW/500 kWh	Solar and wind farm Grid Balancing Large Industry	BANPU Vopak NEPAL ELECTRICITY AUTHORITY SUNSEAP Shinoda Co., Ltd.	❖ Higher temperature operations ❖ Diesel replacement ❖ Solar peak shifting/Frequency ❖ Load levelling and peak shaving ❖ Energy Transport

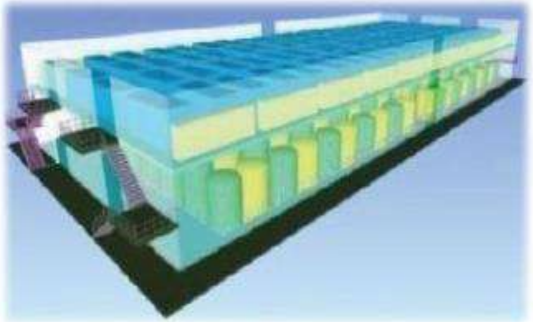
Large-scale VRFB ESS Projects (Examples)

Sumitomo

- Hokkaido, Japan
- Capacity 60 MWh
- Power 15 MW (30 MW max)
- Grid application for short and long term use cases
- Earthquake resistant

VRB Energy

- Hubei Zaoyang, China
- 3MW / 12 MWh Phase 1
- 10 MW-40MWh total
- Solar photovoltaic integration



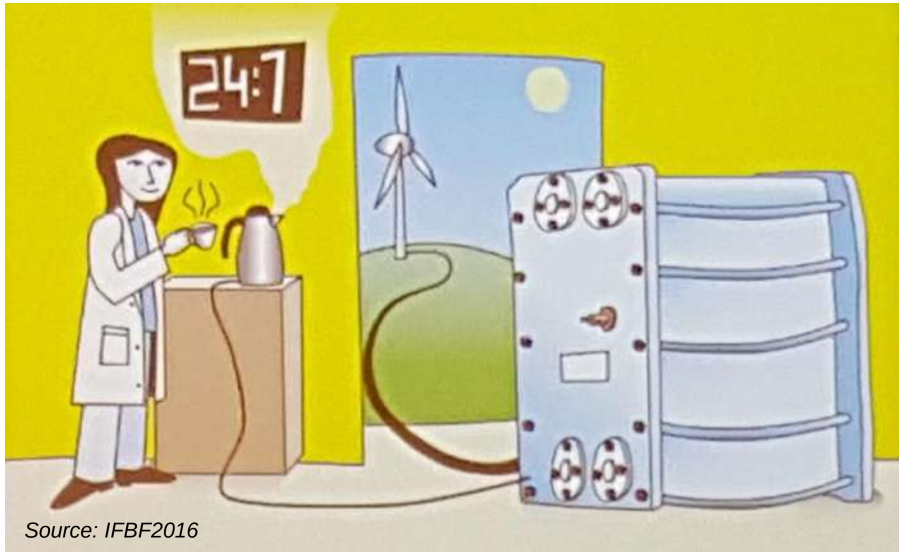
Rongke Power

- Dalian City, China
- Plan 200MW / 800 MWh
- Peak Power, Grid Support, black-start
- 8% of Dalian's peak power

UET / Rongke

- Snohomish County, WA, USA
- 2MW / 8 MWh
- Modular construction
- Grid application with Public Utility

Thank you!



Source: IFBF2016

Q & A