Development and Challenge of Vanadium flow Battery Technology

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Energy storage division

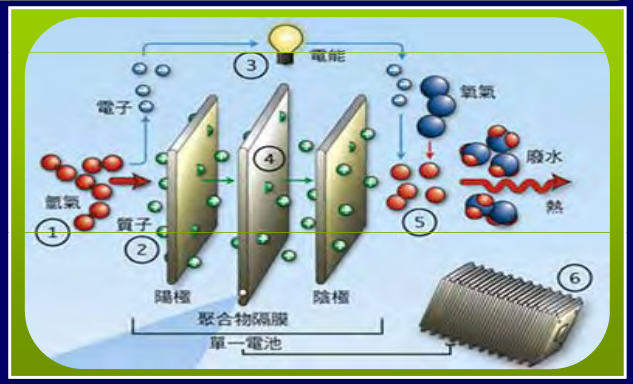
Dalian National Lab for Clean energy

Around 30 staffs
20 graduate students

Division of Energy storage

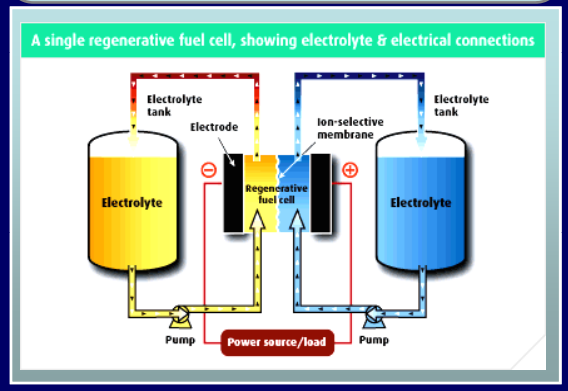
Division Head:
Prof. Huamin Zhang

PEMFC & flow battery testing, evaluation



- Materials (Catalyst, membranes)
- MEA
- Test and standardization

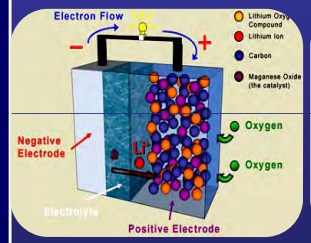
Materials and technologies For flow batteries



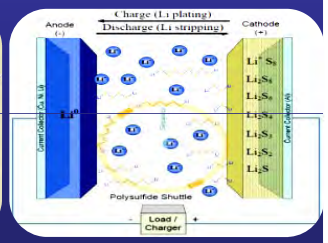
- Materials
- Stacks
- System integration

High energy density Li battery

Li-Air



Li-S



- Materials
- Components

Rongke Power at a Glance

Rongke Power is a leading VFB manufacturer :

- **Innovative materials & components development and production**
- **Integrated energy storage solutions from engineering to finished turn-key systems.**

- **Company own 16,000 m^2 manufacturing and R&D facilities**
- **150 employees**
- **Manufacturing Facilities: Stack annual capacity of 30MW/Y , Electrolyte annual capacity of 300MWh/ Y**
- **Certified ISO9000/14000 and GB/T28001**
- **R&D Center for Flow Battery Energy Storage authorized by National Energy Administration**

Stacks and System Assembly Facilities

Materials Manufacturing Facilities

Technology Innovation Centre

Why energy storage?

Non-controllable

Too "random" to be connected to the grid for widely use.

Energy Storage

Energy Storage

Affected by weather

Energy Storage

Energy Storage

Smart grid

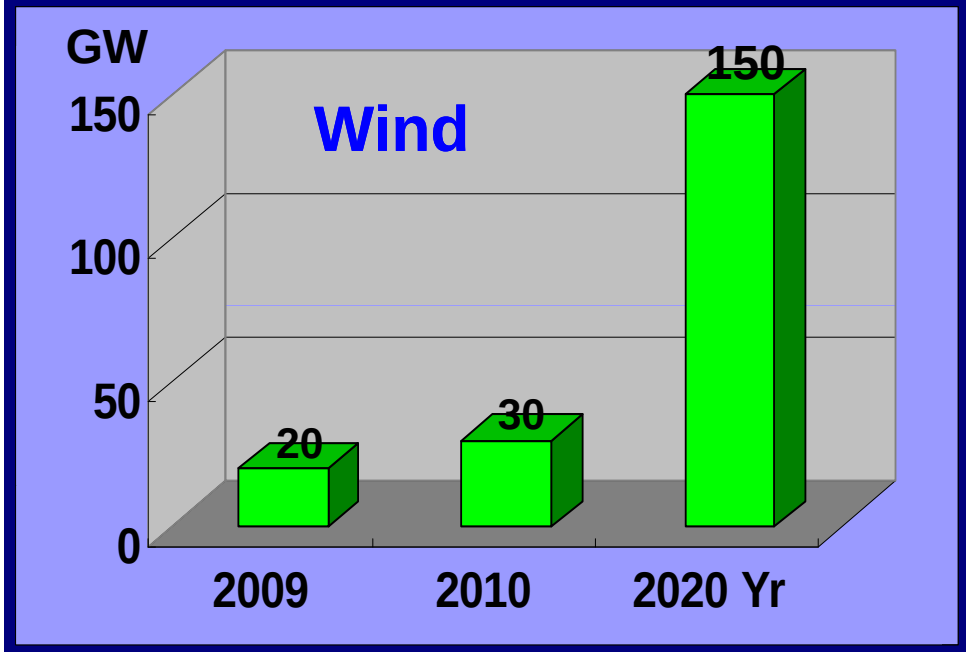
Solutions: to combine renewable energies with energy storage technologies

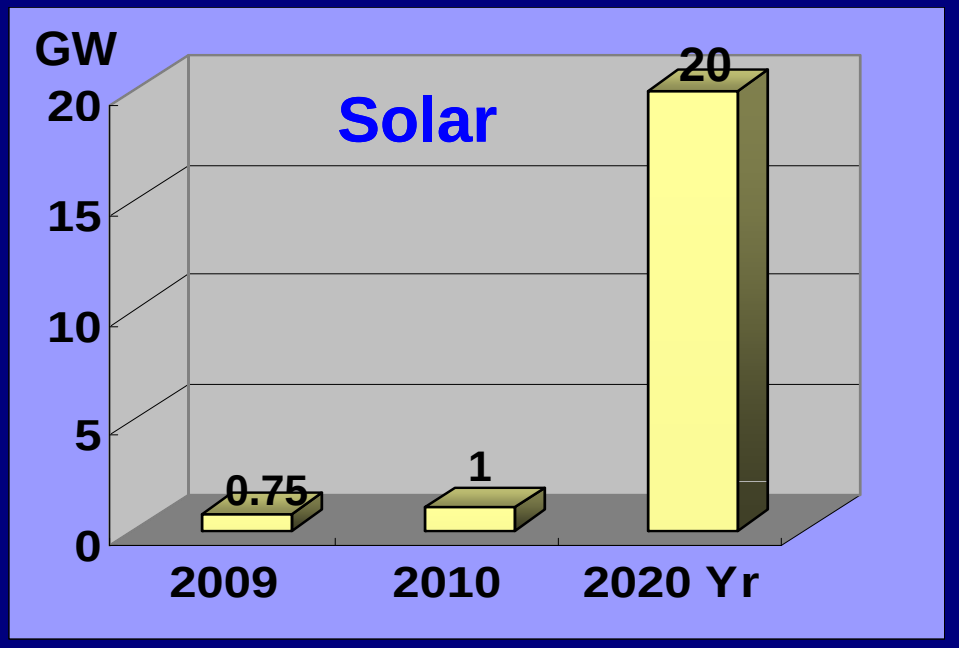
Solar and wind power application target of China

《Renewable Energy Revival Plan of china》

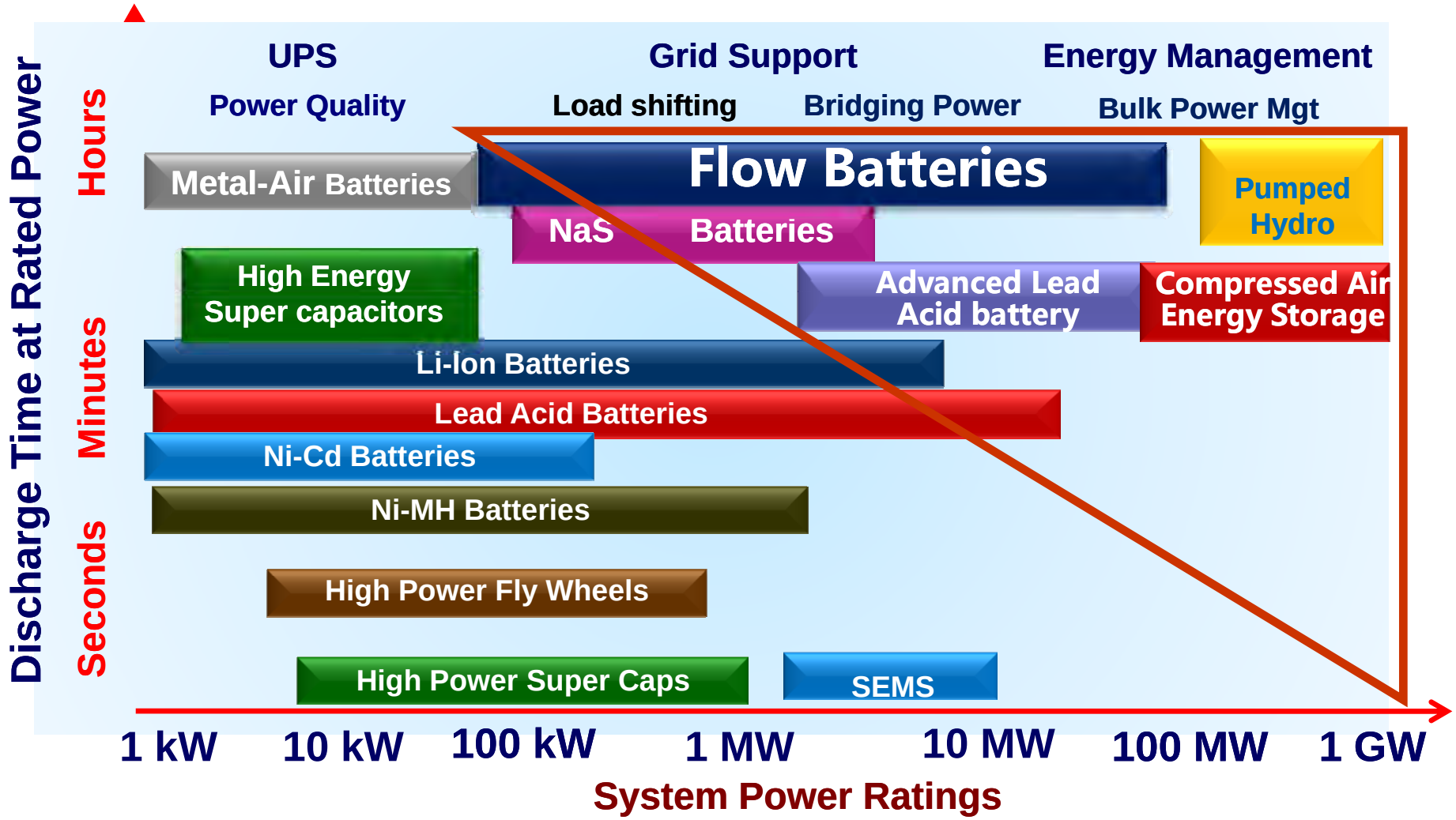
Target: By 2020, 15 % of all consumption energy is to come from RE

Installation Capability	Wind	Solar
2009 yr (GW)	20	0.75
2010 yr (GW)	30	1
2020 yr (GW)	150	20





Characteristics of Different Energy Storage Techniques



Rastler, D. Electricity Energy Storage Technology Options: A White Paper Primer on Applications, Costs and Benefits; EPRI: Palo Alto, CA, 949 2010; p 1020676.

Our work focus on Vanadium Flow Battery Energy Storage Technique

Requirements for large-scale energy storage technology

- Safety
- Higher Performance-to-price ratio of life cycle
- Lower Environmental load of life cycle

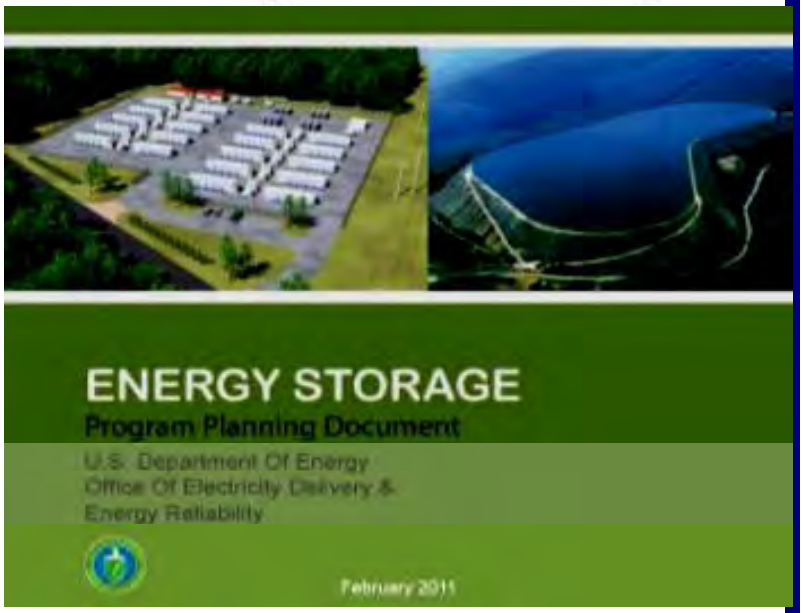
For large-scale energy storage, the harm and loss resulting from safety accidents are serious because of its large power and capacity. Thus, the primary requirement for large scale energy storage is safety.

Formulation of the research program on energy storage from the US energy department in 2011

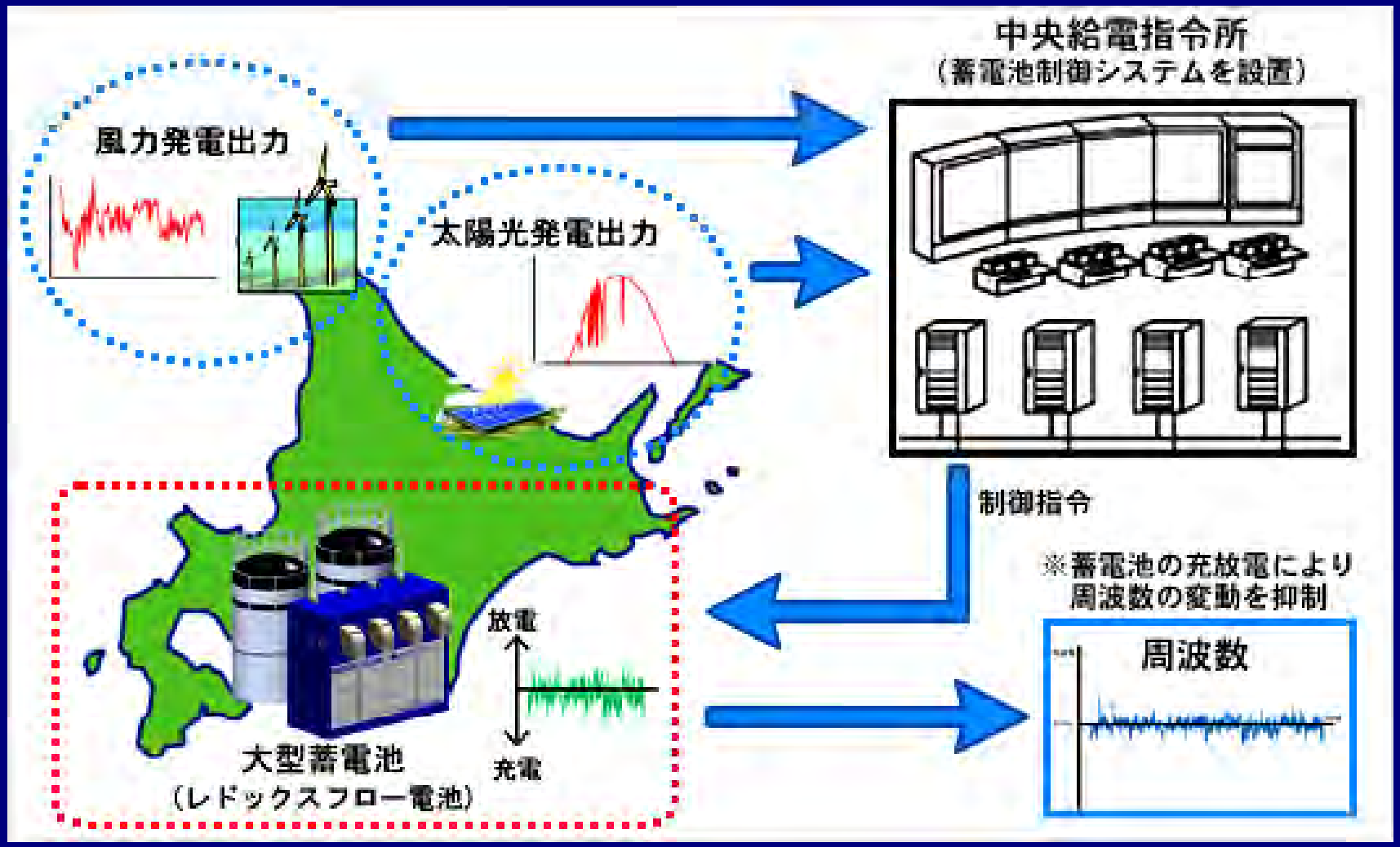
3.2. The Research & Development Component of the Program

The Research & Development (R&D) component of the Program currently aims to understand the performance promise of multiple technologies. The Program takes this view because the likely needs of different technologies for varied stationary markets that have different requirements in performance, costs, siting, etc. Also at this time it is too early in the industry's maturity to focus on one or two "selected" technologies. The discussion that follows highlights the technologies—and the challenges—that are the focus of the R&D component of the Program:

- Redox flow batteries
- Sodium based batteries
- Lithium-ion batteries
- Advanced lead-acid batteries
- Compressed air energy storage
- Flywheel storage



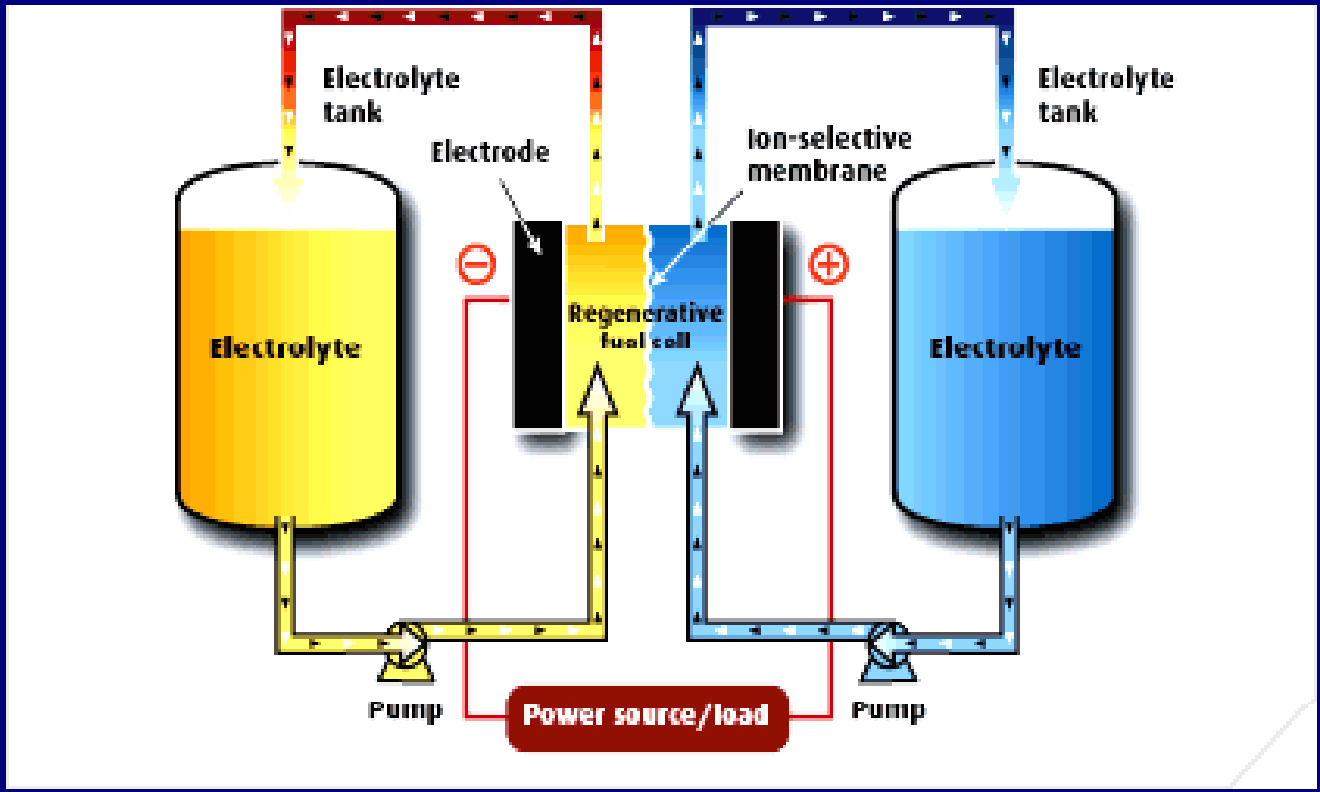
Japan is building a large-scale (15MW/60MWh) VFB energy storage system in Hokkaido



Output Smoothing, frequency modulation, and Power Prediction generation for renewable energy

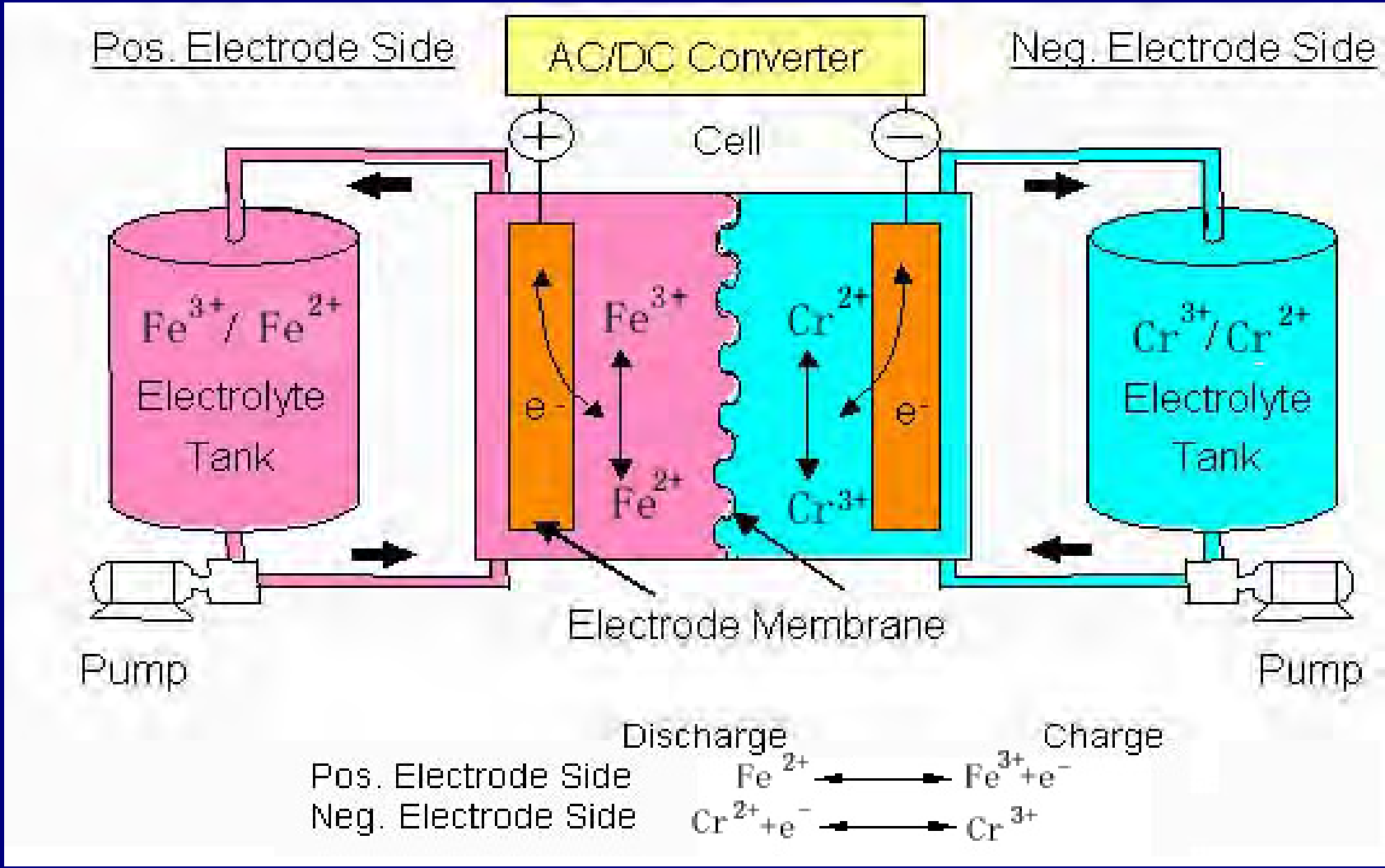
Principle of the flow battery

Flow battery electrochemically store/release electricity by the valence change of the species in the electrolyte that circulate through the anode and the cathode, which are separated by an ion exchange membrane.



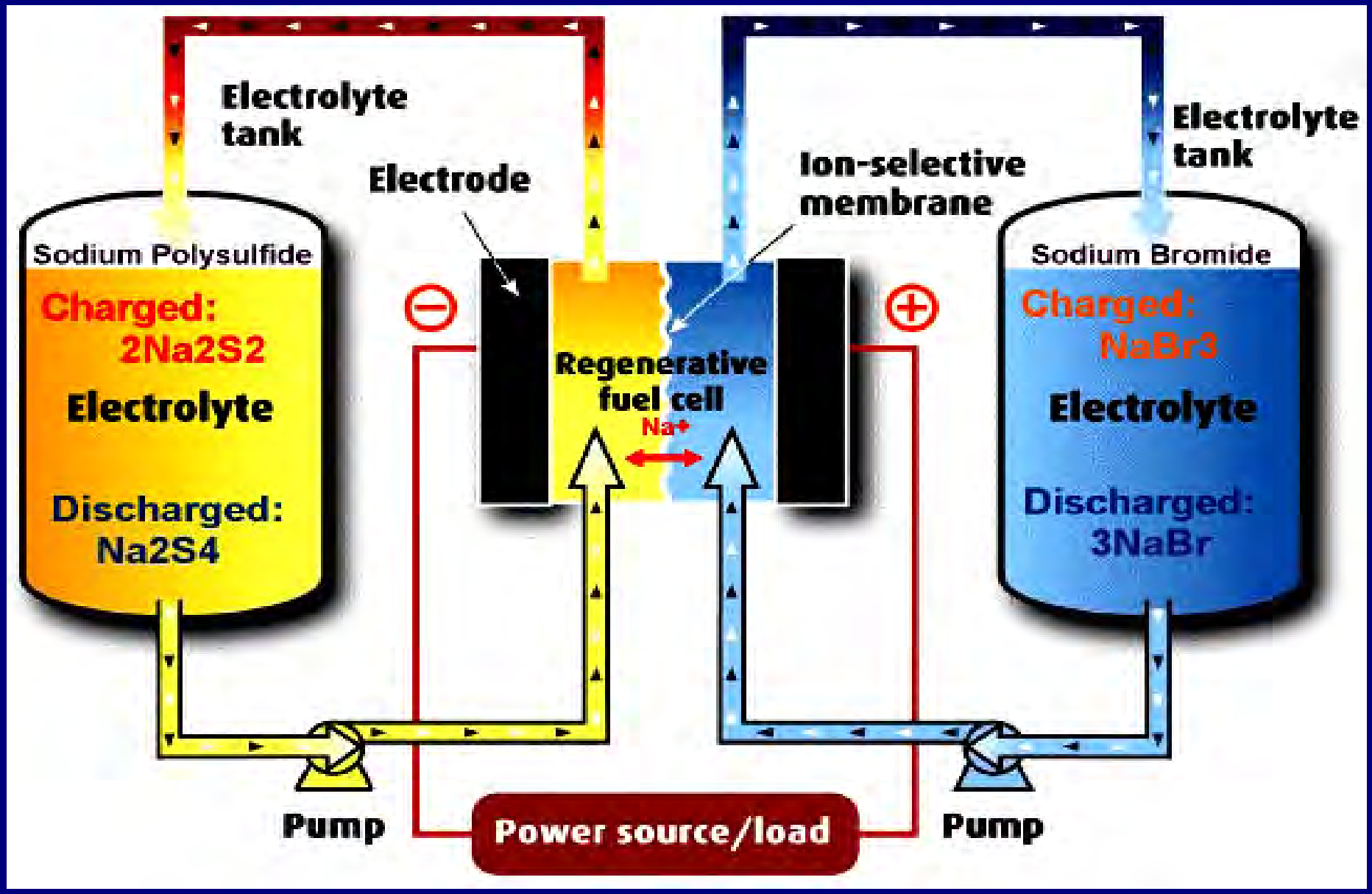
Principle diagram of flow battery

Cr/Fe Flow Battery

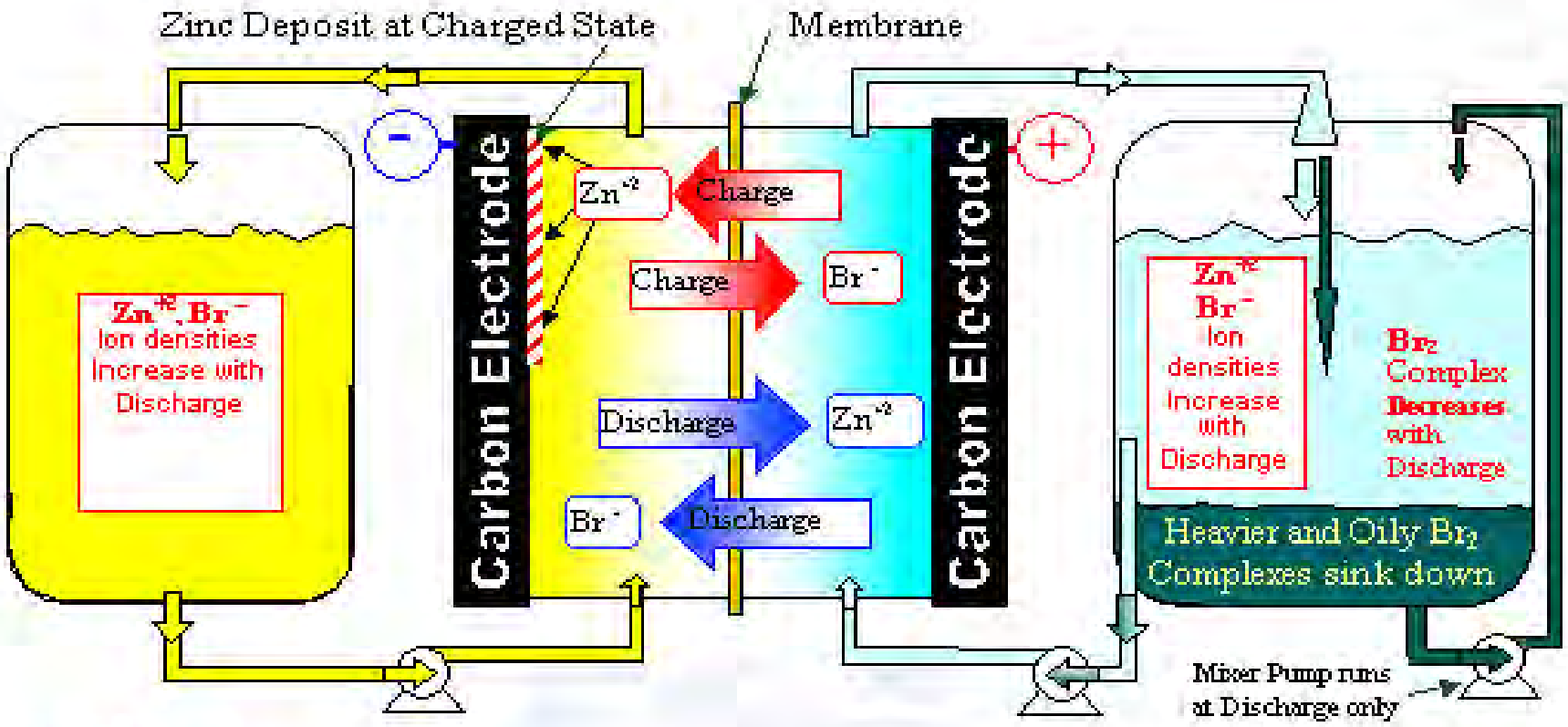


Serious hydrogen evolution, capacity loss, low energy efficiency

Sodium Polysulfide /Br flow battery



Zn-Br flow battery



At Charge:

Neg. electrode side: $Zn^{2+} + 2e \Rightarrow Zn^0$ (Zn plated on neg. electrode)

Pos. electrode side: $2Br^- \Rightarrow Br_2\,(aq) + 2e$

(Br, complexed into a thick, oily sludge, is stored in a separate location inside container)

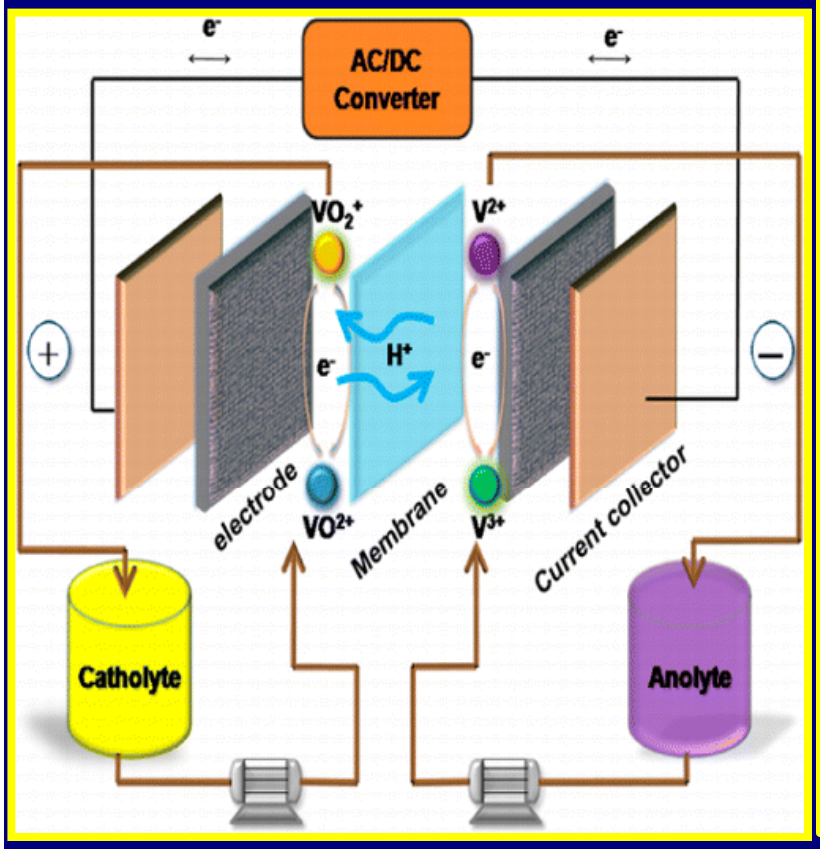
At Discharge:

Neg. electrode side: $Zn^0 \Rightarrow Zn^{2+} + 2e$ (Zn ions dissolved in **both** electrolytes)

Pos. electrode side: $Br_2\,(aq) + 2e \Rightarrow 2Br^-$ (Br ions dissolved in **both** electrolytes)

Vanadium flow battery (VFB)

VFB electrochemically store/release electricity by the valence change of the Vanadium ions in the electrolyte that circulate through the anode and the cathode, which are separated by an ion exchange membrane.



Vanadium Flow Battery (VFB)

Anode:

$$VO^{2+} + H_2O - e \leftrightarrow VO_2^{+} + 2H^{+}$$

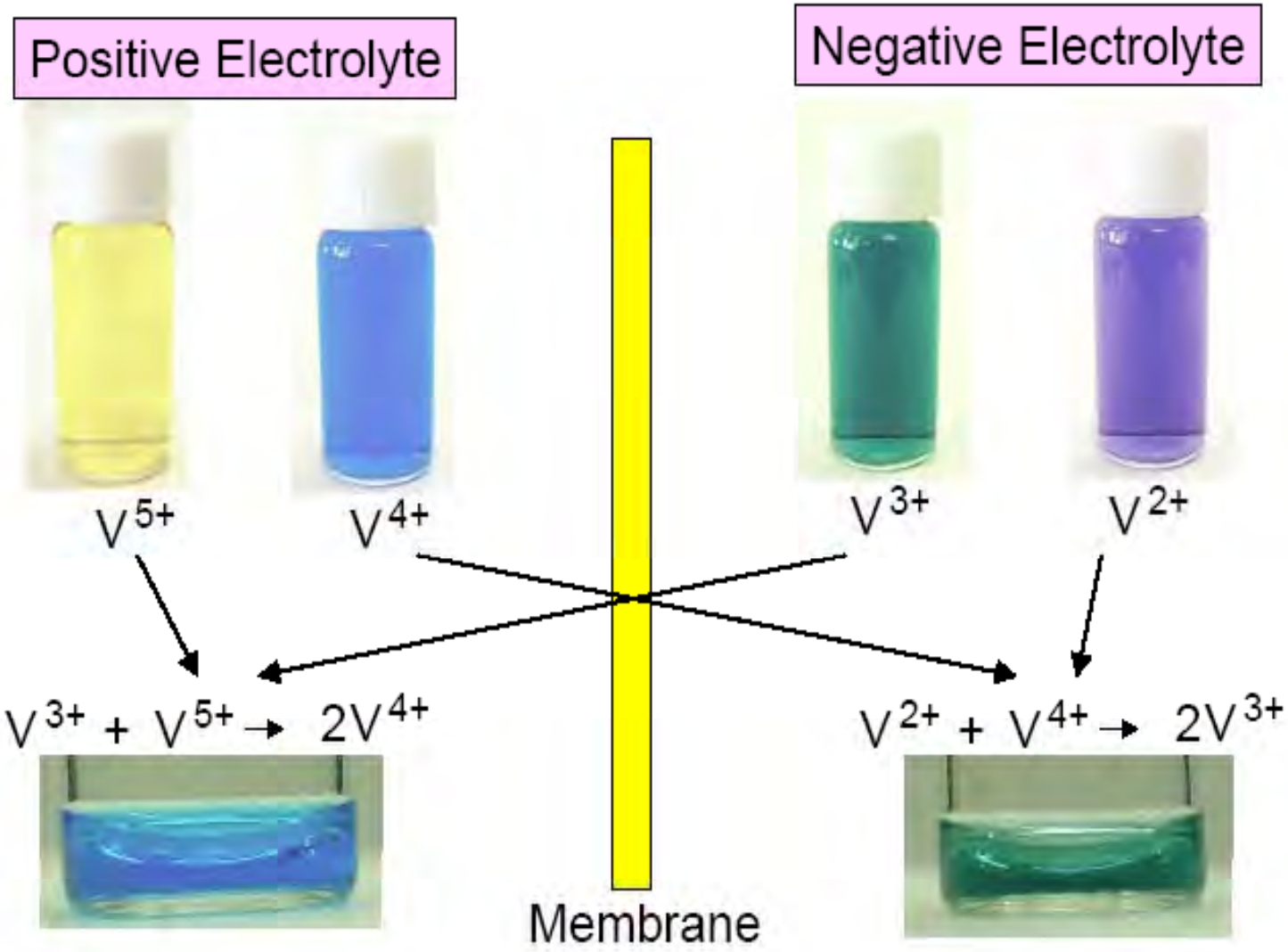
Cathode:

$$V^{3+} + e \leftrightarrow V^{2+}$$

Total reaction:

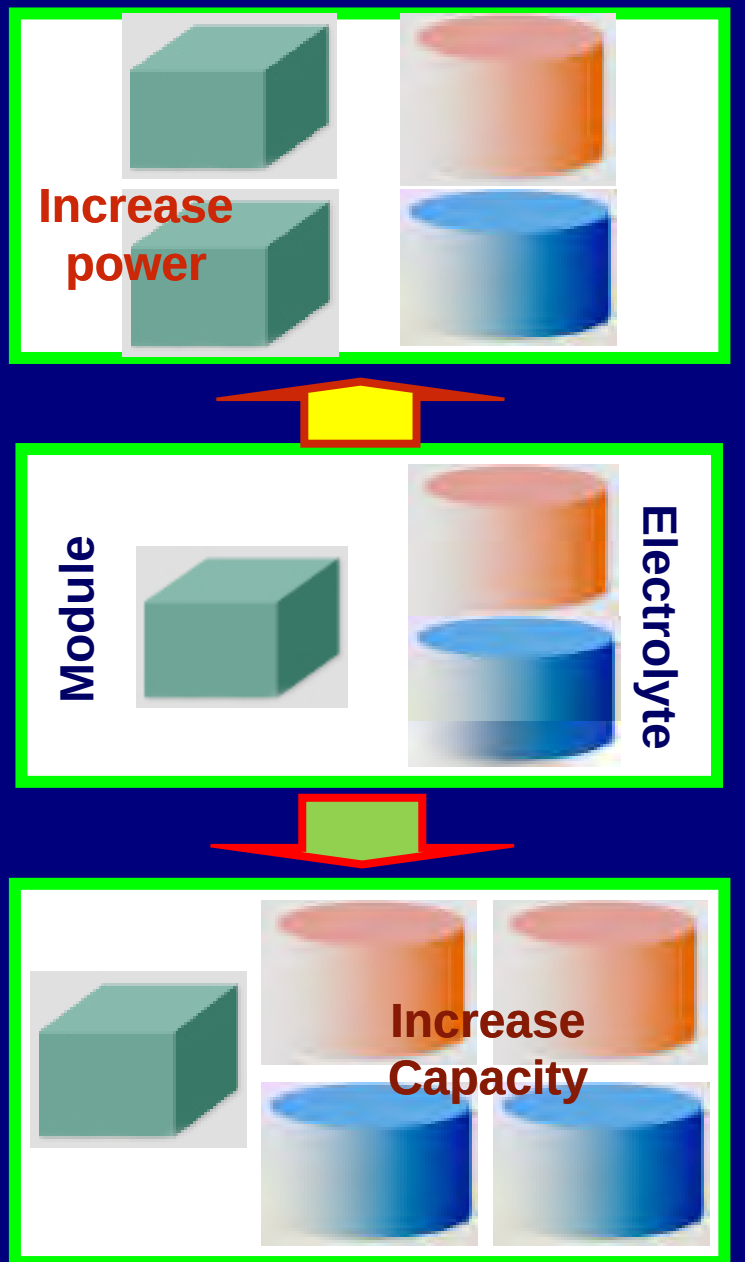
$$VO^{2+} + V^{3+} + H_2O \leftrightarrow VO_2^{+} + V^{2+} + 2H^{+}$$

Electrolytes of Vanadium Flow Battery

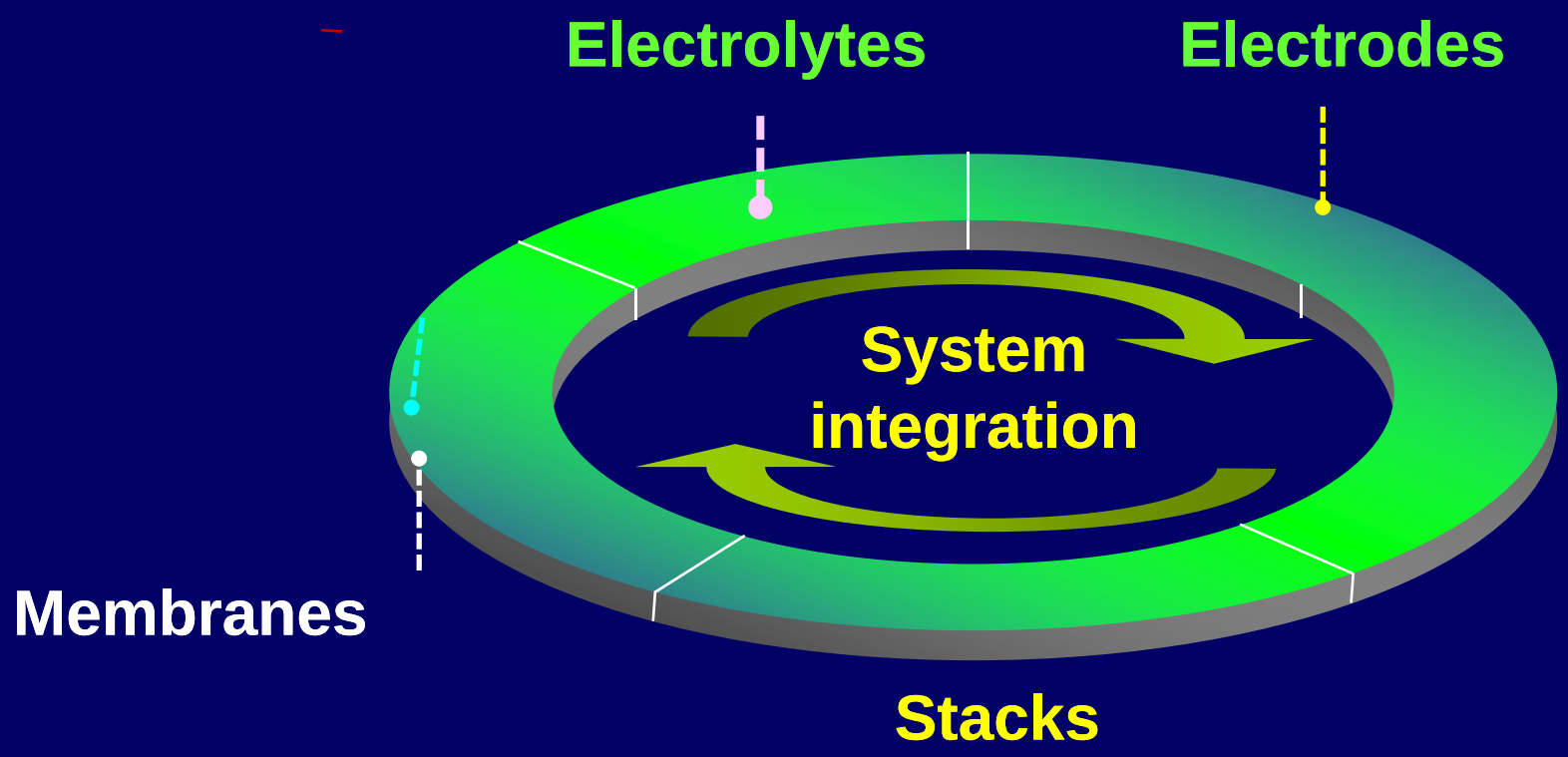


Advantages of VFB

- Independent system design for power and capacity
  - Output Power Range: kW-MW;
  - Energy Storage Capacity : kWh-10MWh
- High energy efficiency (>75%)
- Long change/discharge lifetime
- Deep discharge ability
- Low self-discharge, fast response
- Environmental friendly
- Operation safety



Key materials and technology of flow battery

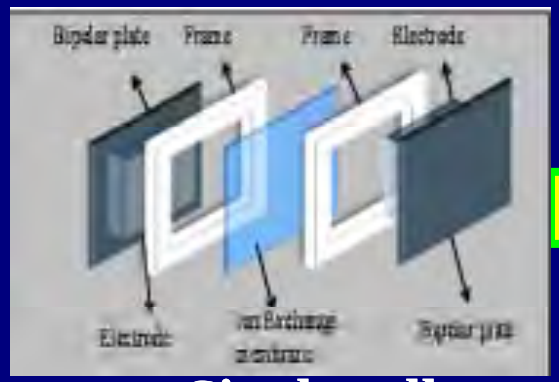


The main target is to improve the power density and decrease the cost of VFB by exploring high performance materials and optimizing stack structure (membranes with high selectivity, stability and conductivity, electrode with high conductivity and activity, electrolytes with high stability and solubility).

Challenges of VFB key materials for improving performance and cost down

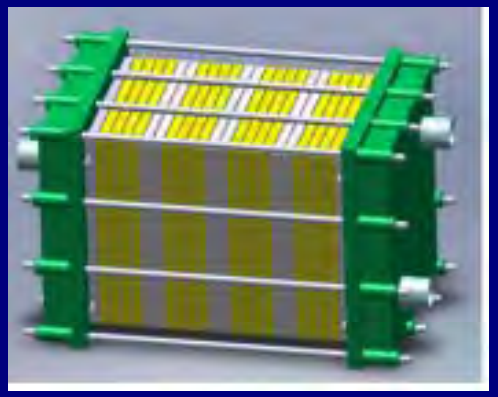
The performance of the materials used determines the performance of the VFB

$VOSO_4$ Electrolyte	Ion membrane	Electrode/Bipolar plate
➢ Stability ➢ Solubility	➢ Stability ➢ Durability ➢ Selectivity ➢ Cost	➢ Activity ➢ Electrical conductivity ➢ Anti-oxidation ➢ Cost



Single cell

Cells



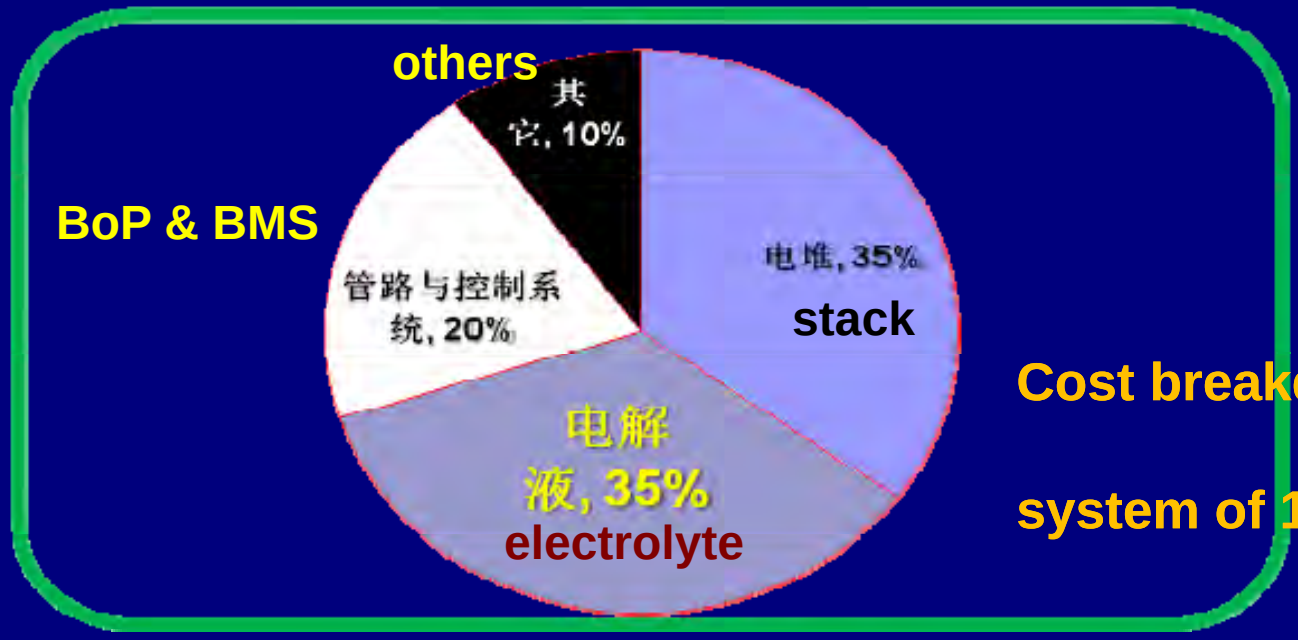
Stacks

Challenges of VFB for commercialization

- poor electrolyte stability and less solubility lead to low energy density.
- Low selectivity to the vanadium ions of memberan lead to the Unbalance of vanadium ions and Water, and the capacity degradation after long operation time.
- Low rated operation current density lead to higher material cost.
- High cost of the ion exchange membrane.

Limited the VFB practicability seriously

Challenges to VFB industrialization



Cost breakdown with a system of 1MW/5MWh

Challenges

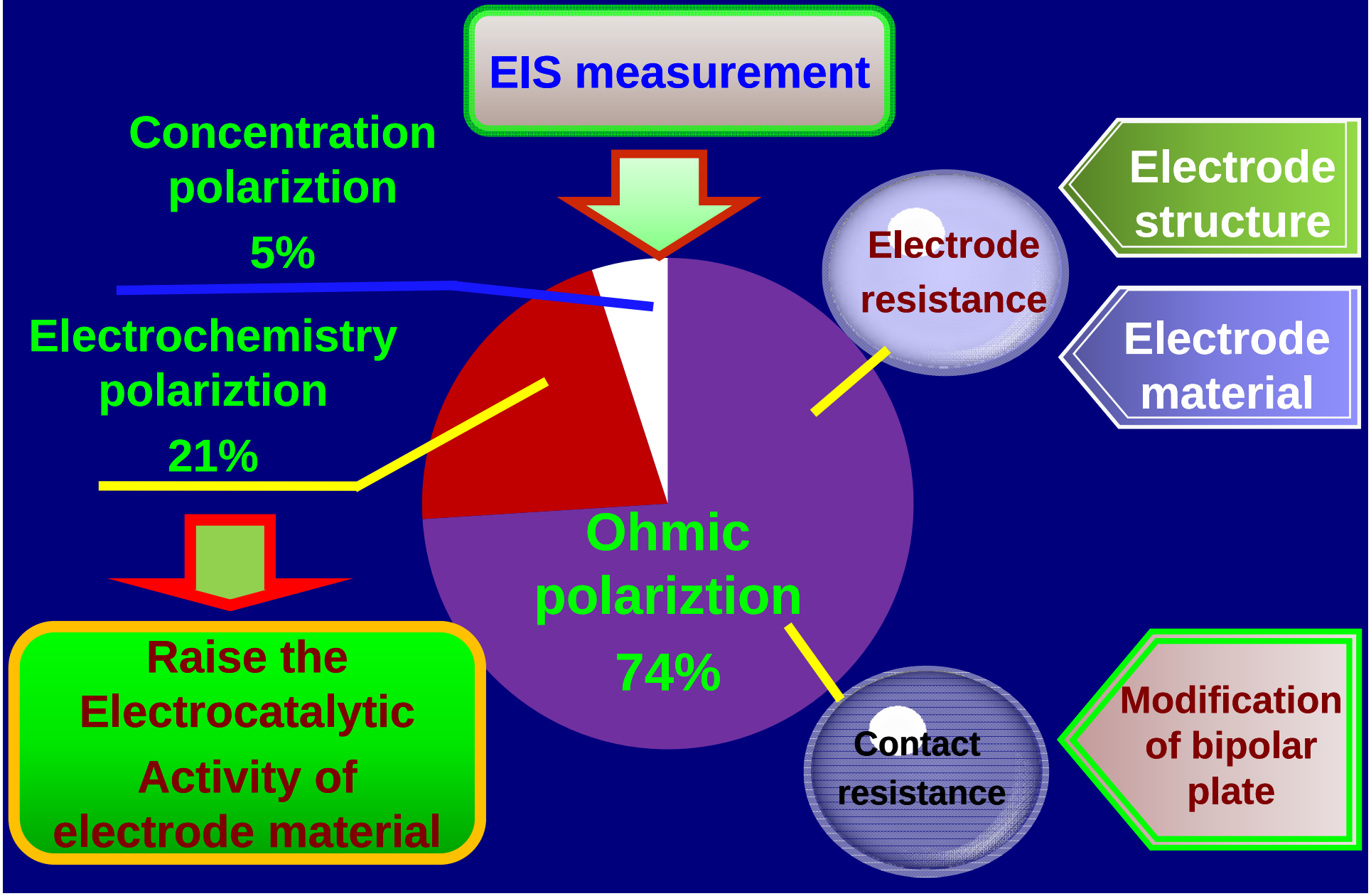
Lower power density,

high material cost !

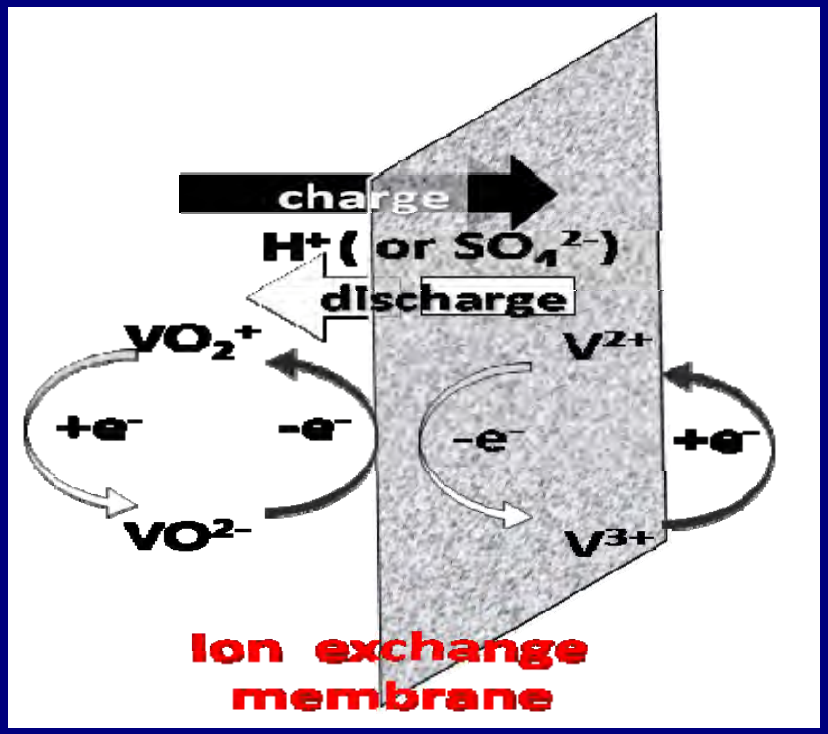
Cost Target: 3000RMB/kWh

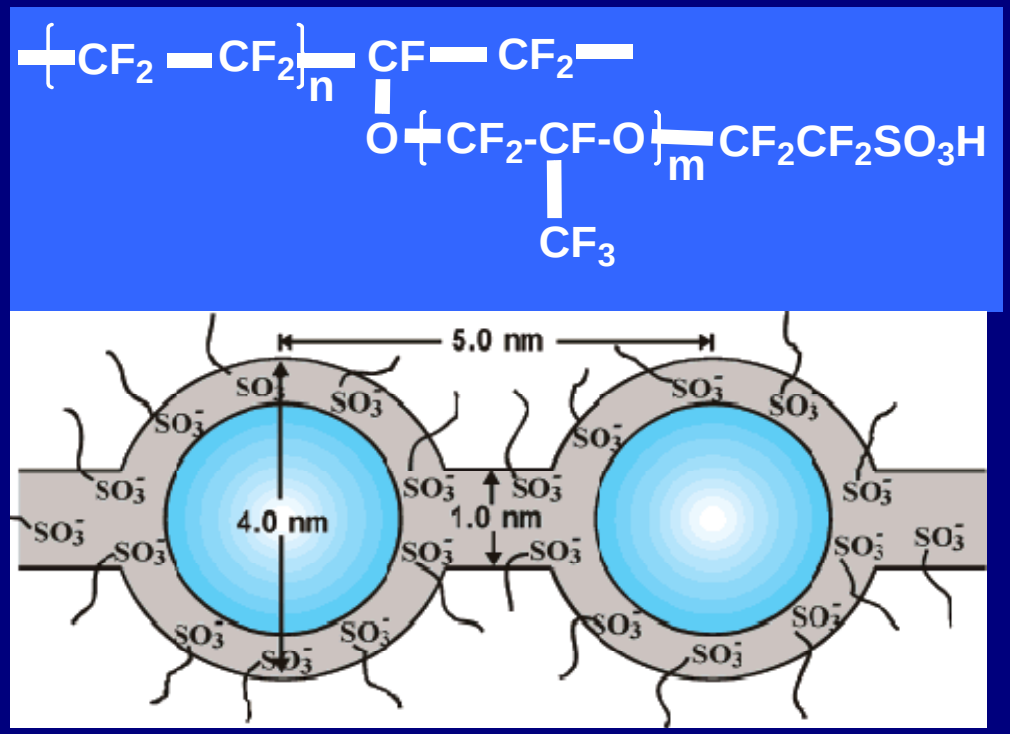
- High perfomance, low cost materials
- new stack with high power density
  - Rated current density should be improved from 80mA/cm2 to 200mA/cm2 and even higher
- Container system design

Polarization analysis of VFB



Membranes: Key materials to push VFB commercialization





Perfluorosulfonic acid membranes
(Larger continuous clusters Structure)

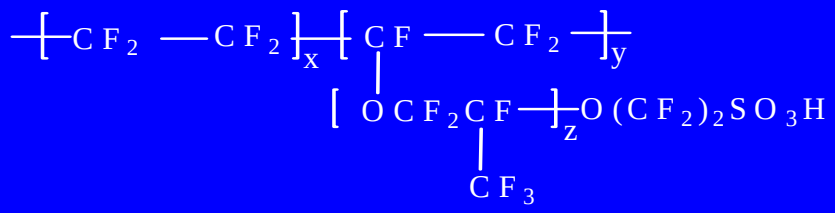
Function

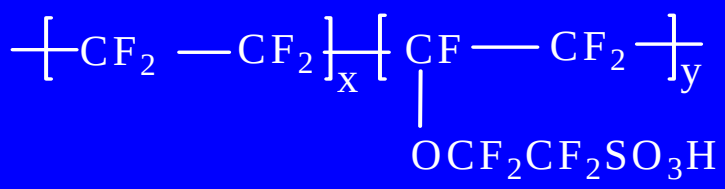
- Isolate electrolytes
- transport H^+ or SO_4^{2-}

Disadvantage

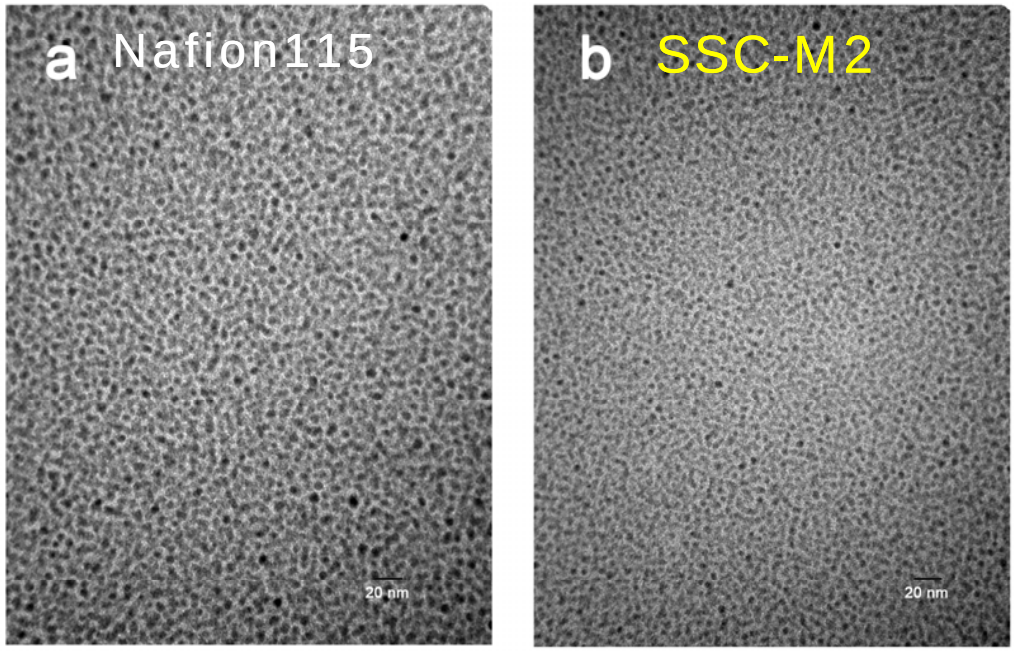
- High cost (600-800 $/m^2) → 100 $/m^2)
- Low ion selectivity (Vanadium crossover)

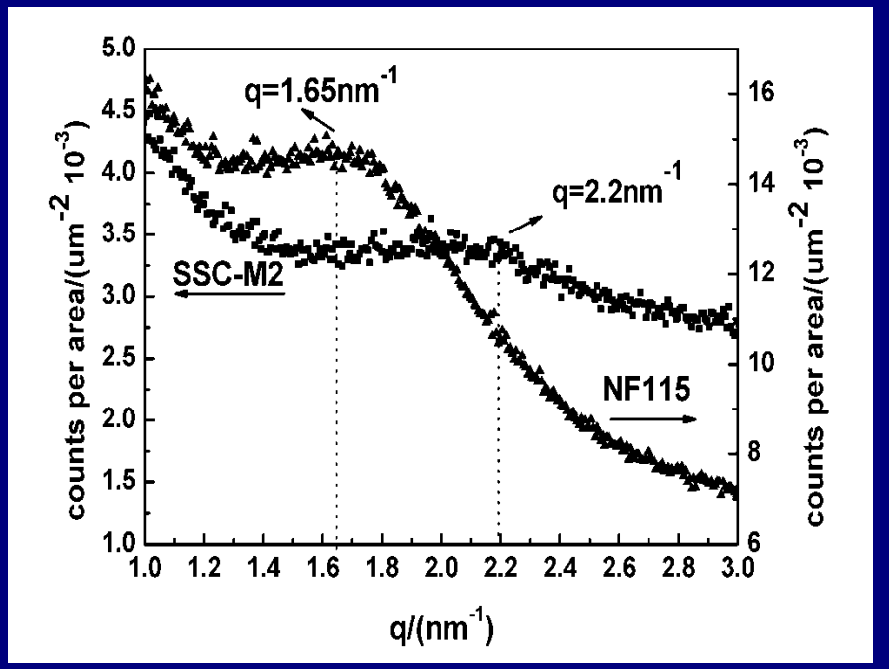
Morphology of Perfluorosulfonic acid membranes





Nafion 115 with long side chain SSC with short side chain (Solvay)

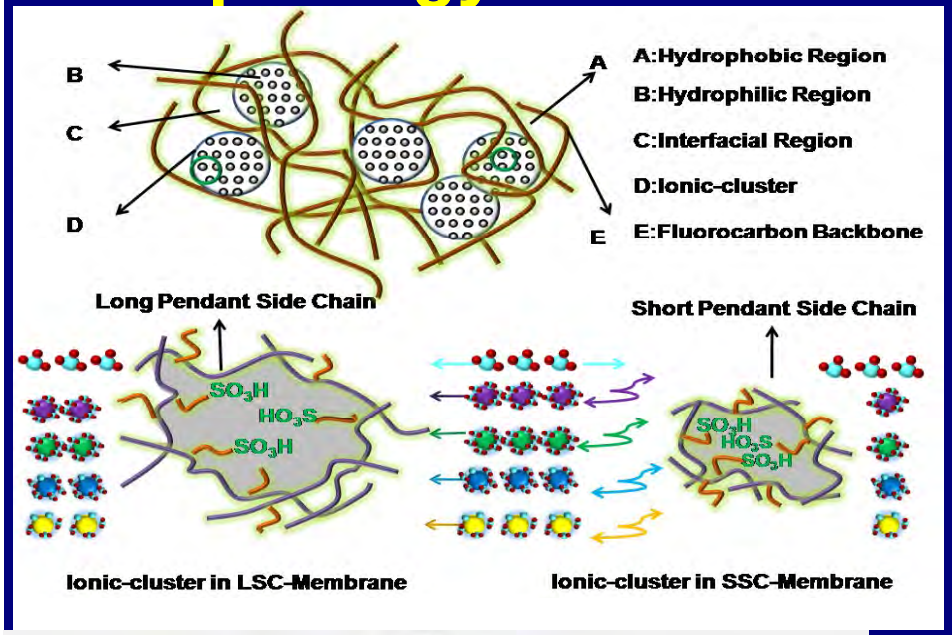


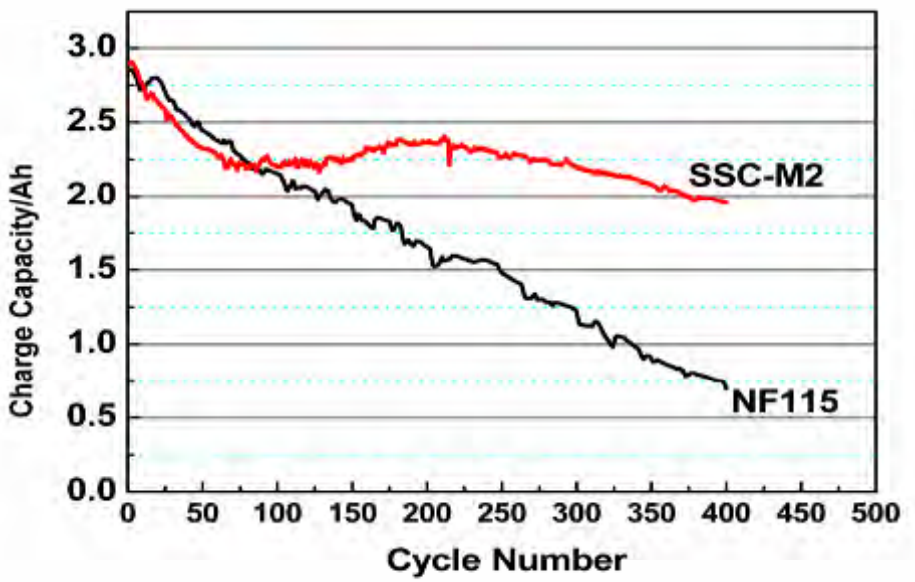


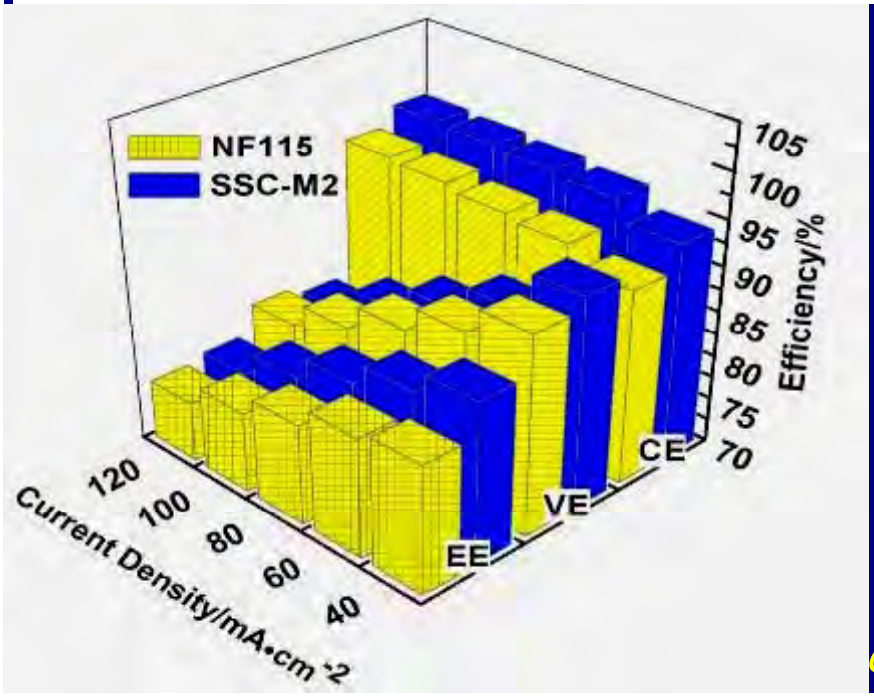
Morphologies of hydrophilic domain recorded by TEM and SAXS.

Membranes with short side chain shows smaller and more discontinuous clusters, expecting higher selectivity

Morphology of Perfluorosulfonic acid membranes



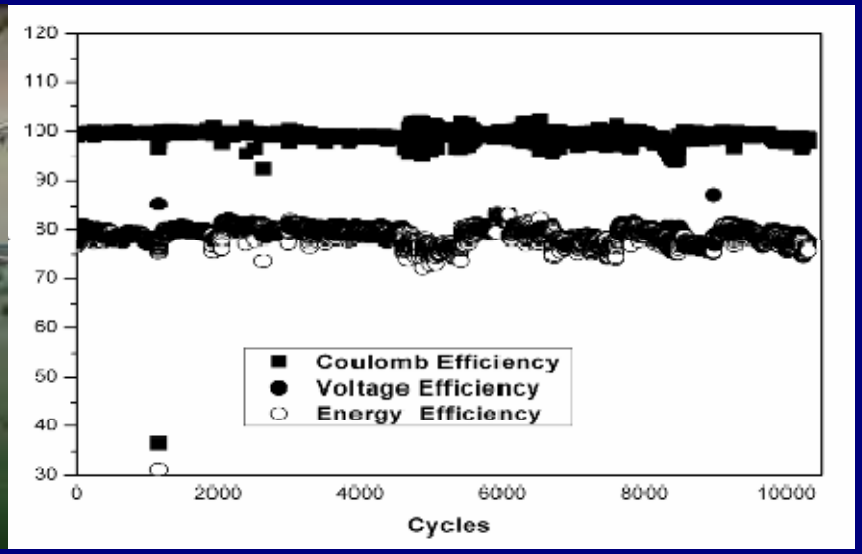




SSC-M2 exhibited higher coulomb efficiency and similar voltage efficiency and much slower capacity fading than that of NF115. The results indicate that membrane with short side chains is proved to be one of the ideal options in fabricating high-performance VFBs with low capacity reduction.

ChemSusChem 2013, DOI:10.1002/cssc.201300014.

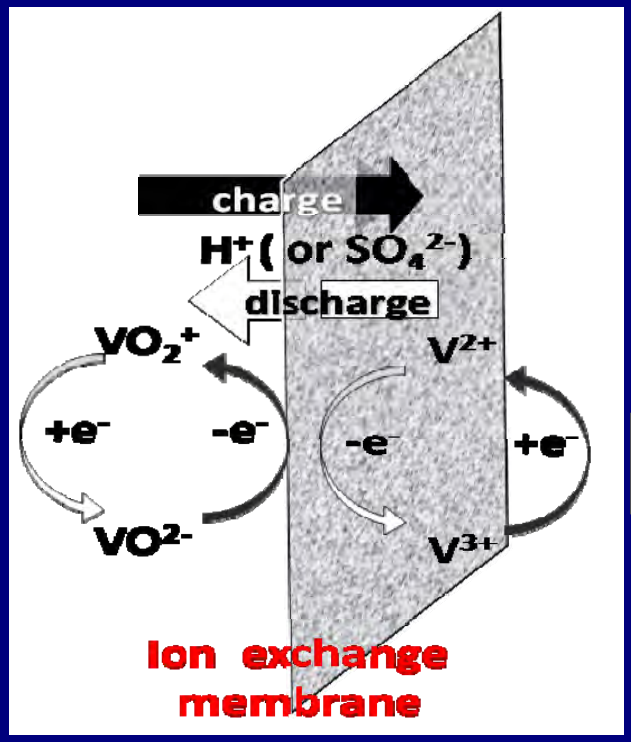
Non-Fluoride IEMs Developed by DICP



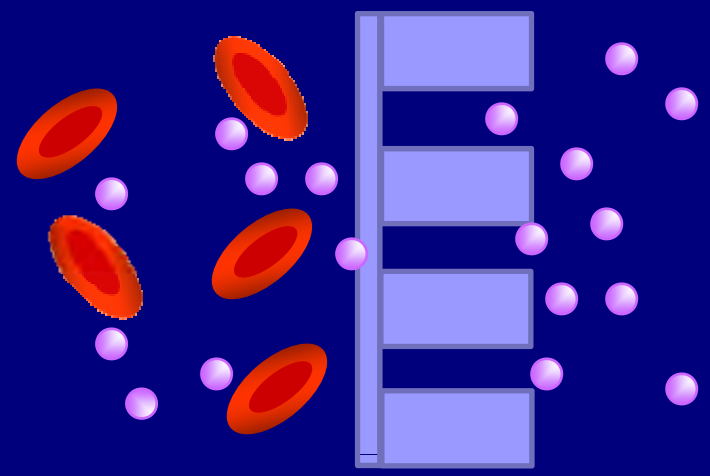
	Nafion-115	DICP
CE (%)	95	97.6
EE (%)	80	84%
Life (cycles)	>13000	>10000
Cost ($/m^2)	650	100

The cycle life of DICP-2 membranes was investigated. The performance kept stable after running more than 12 months. The battery has finished more than 10,000 cycles up to now.

Porous membranes as VFB separators



Larger molecules unable to pass



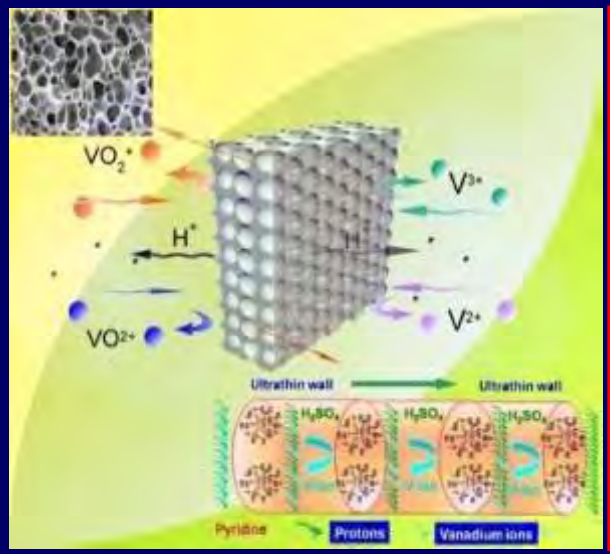
Smaller molecules/ solvent pass through.

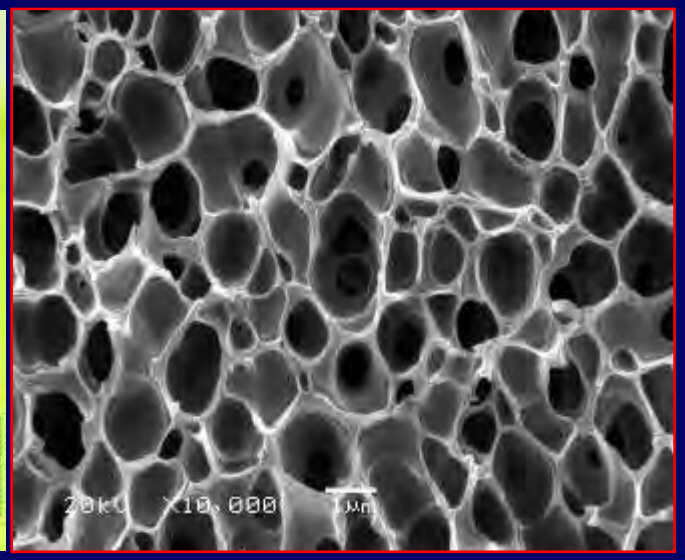
Membrane

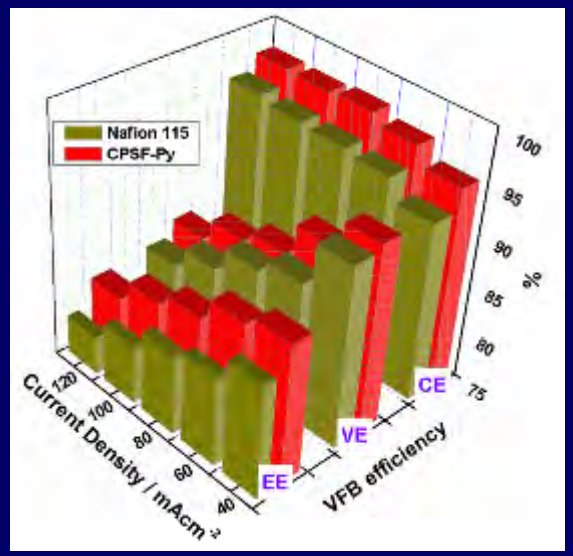
Can porous separation membranes be next generation separator for VFB?

Energy & Environmental Science, 2011, 4, 1676–1679

Porous membranes for VFB application







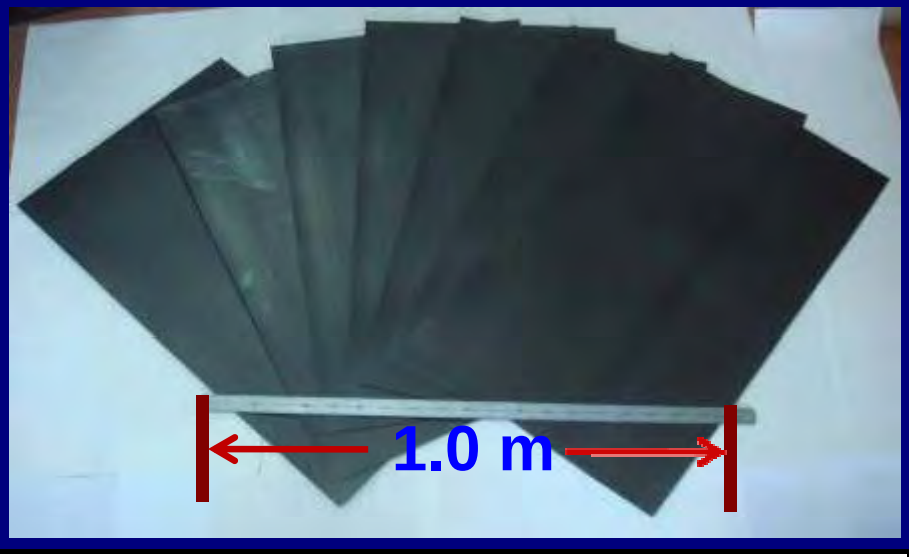
After optimization, membranes very high ion conductivity and ion selectivity were successfully explored and show excellent performance (Better than Nafion 115) under VFB operating condition.

Energy & Environmental Science,6 (2013); 776, 4 (2011) 1676; 5 (2012) 6299

The Mass Production of Electrolyte

A produce line with capacity of 200MWh/year was successfully assembled. The produced electrolytes show very good stability and high performance.

Carbon Plastic Bipolar Plate



Bulk resistance	< 0.17 Ω.cm
Bending strength	>28 MPa
Corrosion resistance	<0.7 uA.cm^{-2}
Thickness	1 mm
Cost	<100 RMB/m^2
Yield	10,000 m^2/year

Carbon/plastic plates showed similar properties with commercial graphite plates, while the cost almost the 1/10 of the graphite plates. It has been used in stacks for demonstration widely.

Mass production of 22kW Flow Battery Stack

Stack assemble line

Production capacity 15MW/Year

352kW VFB module for MW class system

22kW Stack

352 kW VFB system module

Energy efficiency (EE) of stacks	>80%
352 kW subsystem (EE)	>75%
90% Charge ↔ 90% discharge conversion time	<90ms

A wind/solar/VFB joint power supplying system for intelligent residence (2009)

energy storage Delegation of US DOE visit my home

A “BIPV-VFB” Demonstration in Rongke Power Co. Ltd. (Dec. 2009)

Solar-VFB-Diesel Engine Power Supply System for An Isolated Island

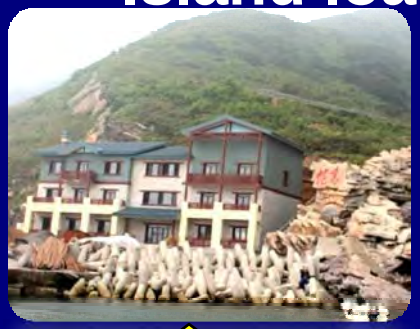
(Sep. 2011)

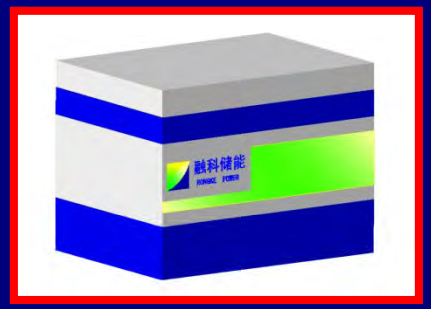
Solar Cell 20kW

PV controlor

Inventor

Island load





VFB 10kW/200kWh

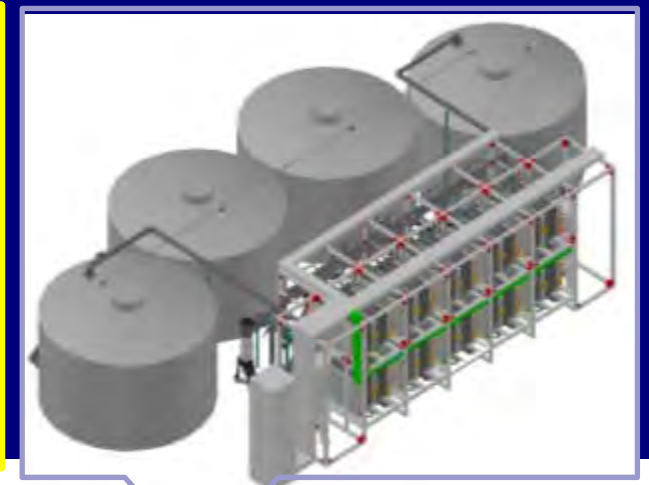
Charger

Diesel Engine

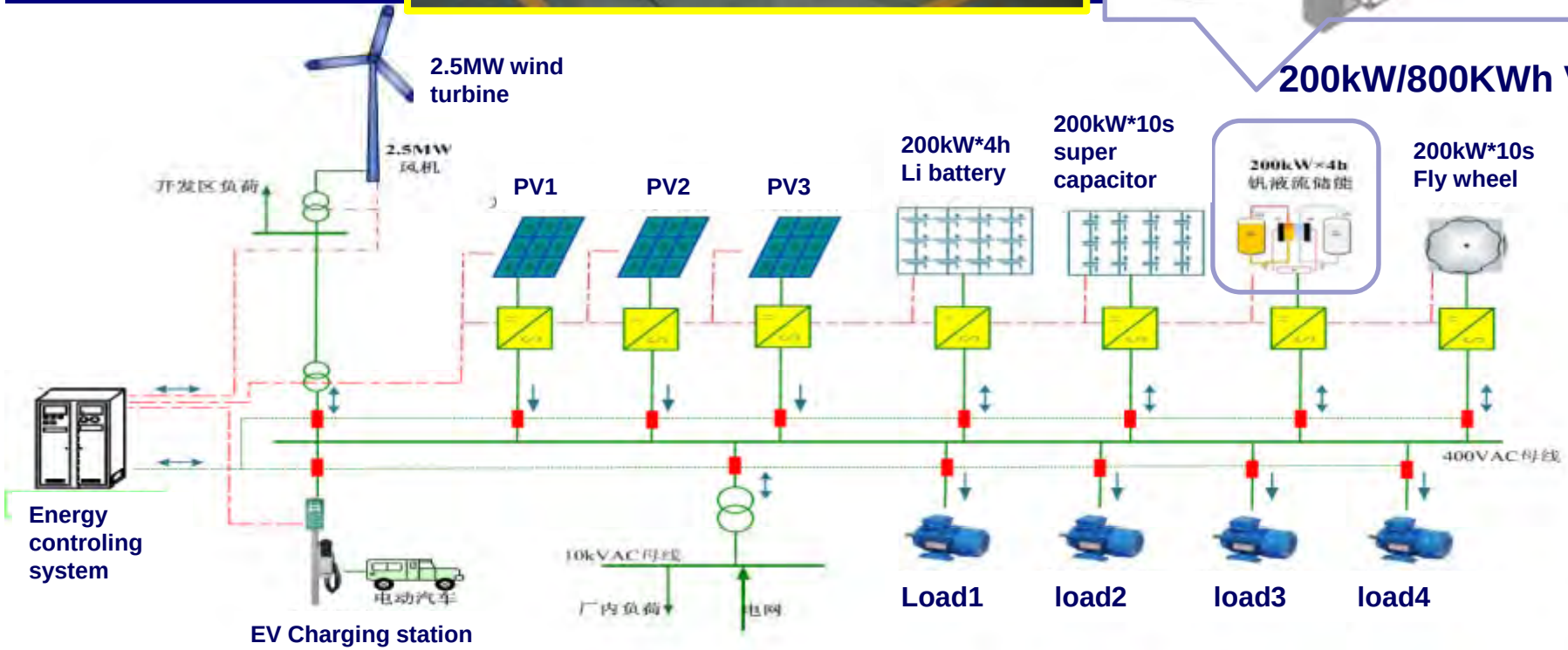
Distributed Energy Storage

Micro-grid Power Supply System

200kW/800kWh VFB for a micro grid



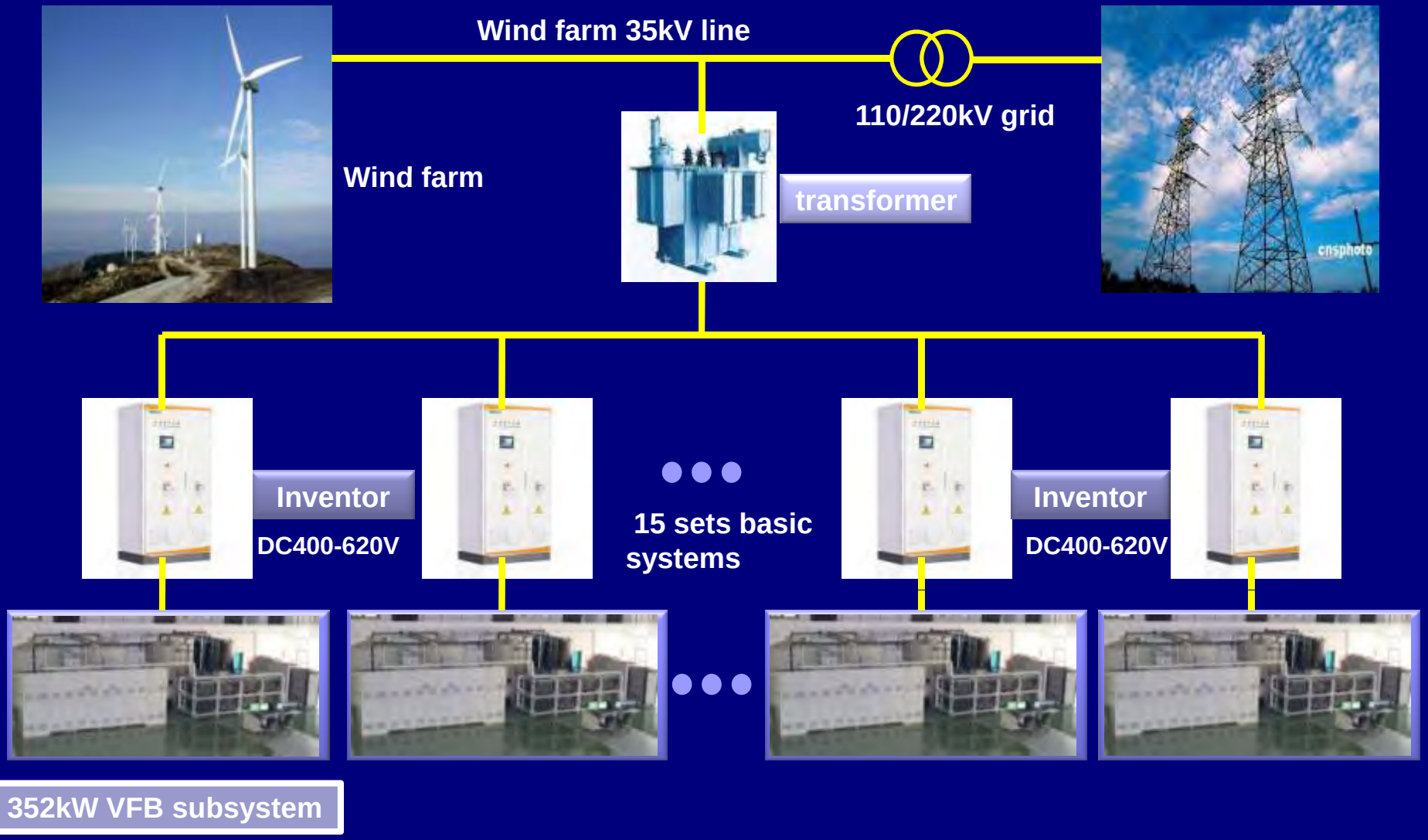
200kW/800KWh VFB



200kW/800kWh VFB for Micro grid

Items	Parameter
Rated Power	200 kW
Capacity	800 kWh
DC Voltage	250-390 V
Rated Current	DC 640A
Stack	20kW * 10 5 serials, 2 parallel
Temp.	-20℃ – 40℃
Size	12.5m×7.2m×2.5m

5MW/10MWh VFB for a 50MW Wind Farm (Since Oct. 2012)



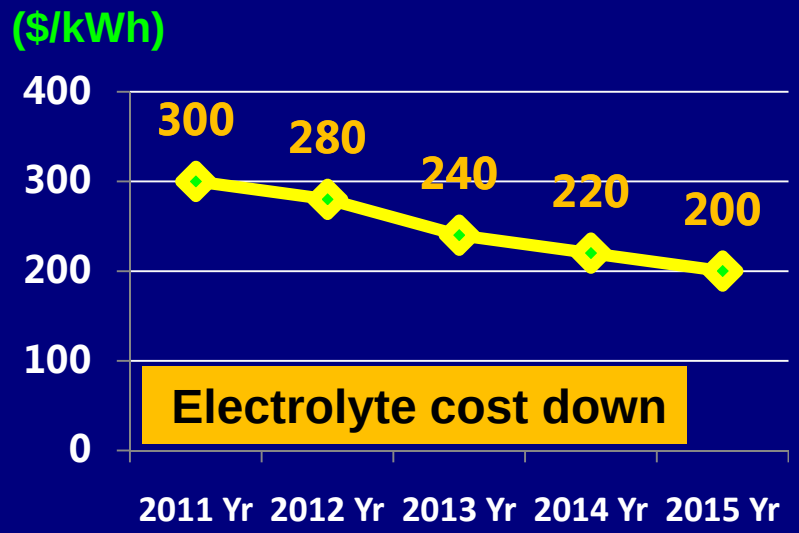
Demonstration project of the world’s largest scale VFB system of 5MW/10MWh in the wind farm

5MW/10MWh VFB for a 50MW Wind Farm

A 5MW/10MWh VFB system was successfully installed recently by Rongke Power and Dalian Institute of Chemical Physics. This is the largest VFB system up to now in the world, the system is combined with a 50 MW wind farm to ensure the smooth output of the wind power. This demonstration was located in Liaoning Province, China.

Cost Reduction Roadmap

Costdown map of RKP



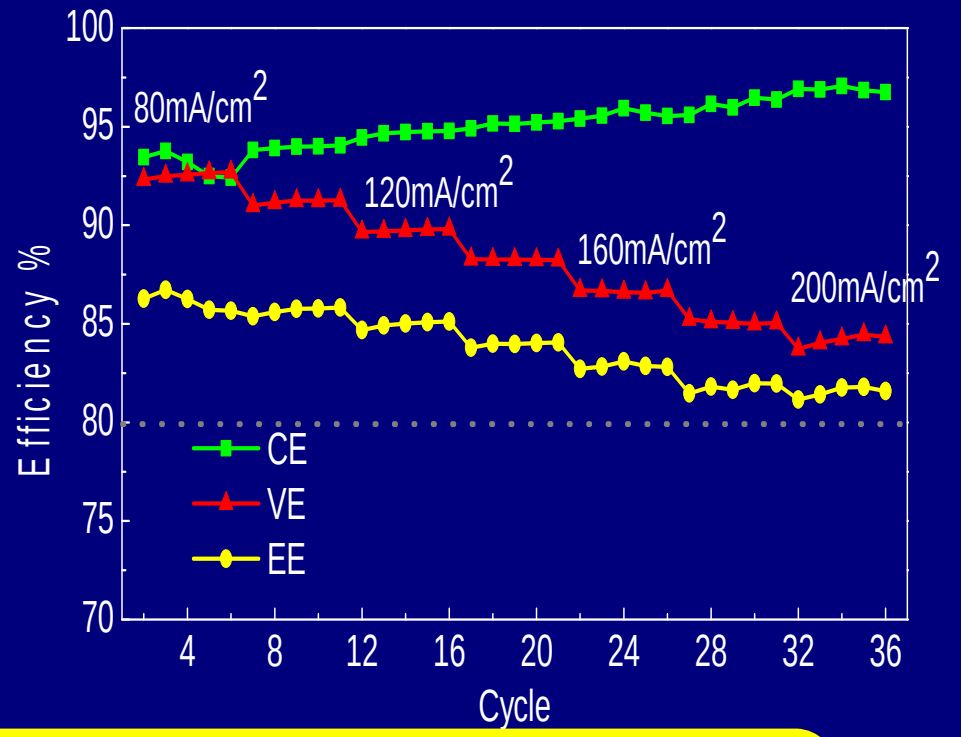
The cost of 1MW/5MWh-class VFB system is expected to be cost down to 400 $/kWh in the year of 2018-2020 via innovation of materials and battery technologies.

High Operation Current Density

- Decrease the inner resistance of VFB
- Increase the conductivity of membrane
- Improve the electrocatalytic activity of electrode

→ High performance

Current density (mA/cm^2)	CE (%)	VE (%)	EE (%)
80	93.8	92.5	86.7
120	94.7	89.7	85.0
160	95.7	86.6	82.9
200	97.1	84.2	81.8



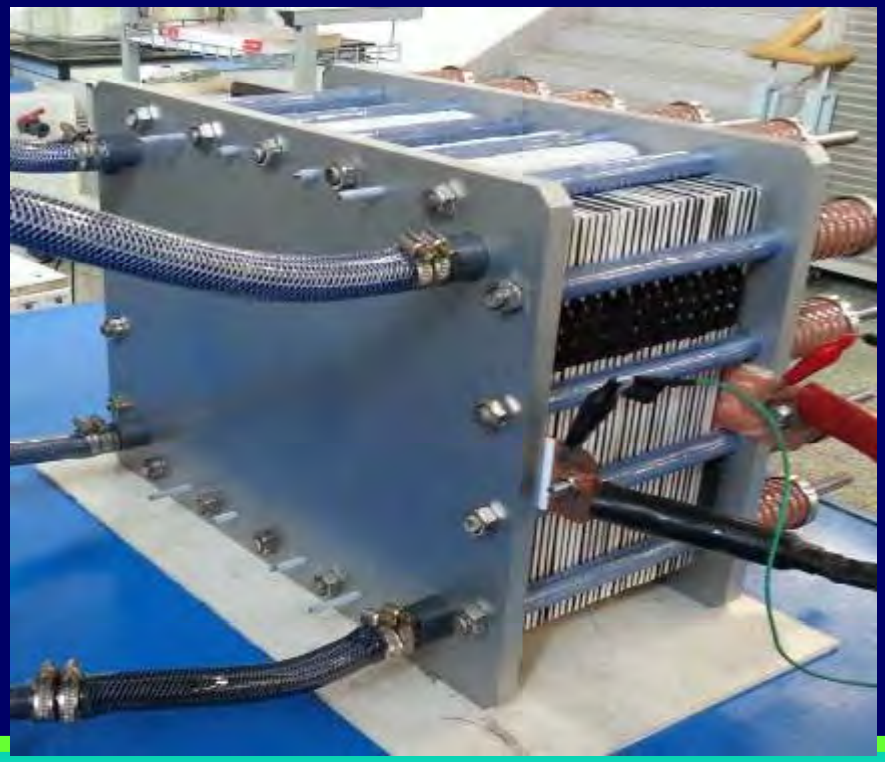
By employing the new electrode , bipolar plate and **improved the conductivity of membrane** , VFB single cell can keep the energy efficiency above 80% under the current density of 200 mA/cm^2.

Development of High Power Density VFB Stacks

Materials and structural optimization

The operating current density increased from 80 to 160 mA/cm^2

Current density (mA/cm^2)	CE (%)	VE (%)	EE (%)
80	97.4	90.1	87.8
100	98.2	88.0	86.4
120	98.5	85.9	84.6
140	98.7	83.9	82.8
160	98.9	81.9	81.0



Dramatically lower the stack cost can be obtained by the doubled increased operating current density.

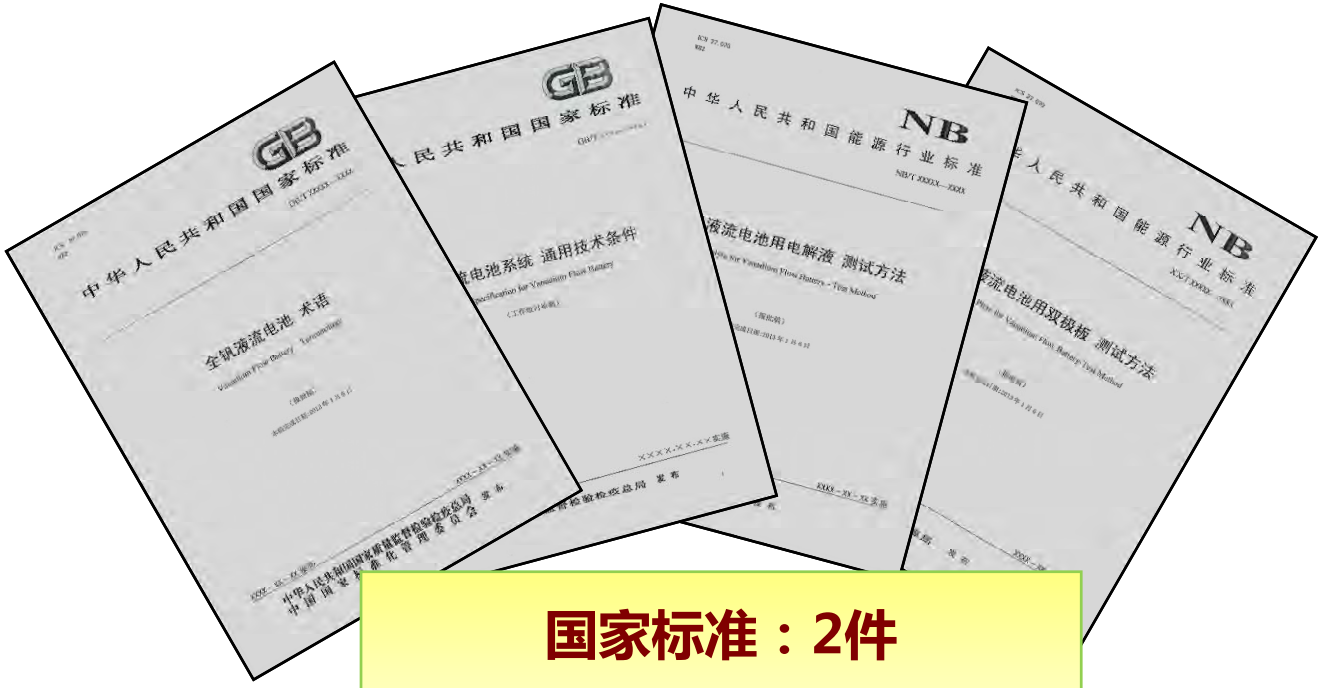
领军国家及国际液流电池标准制定具有重要的影响力和话语权

国家能源液流电池技术标准委员会主任委员单位

应欧洲标准化组织CEN&CENELEC邀请，全面参与欧洲液流电池标准制定,多次参加欧洲液流电池标准化会议

入选国际电器工业协会（IEC）TC105液流电池标准战略研究专家组，全面参与国际液流电池标准战略的制定

领军液流电池技术相关国家标准和行业标准制定



国家标准：2件

行业标准：2件 已颁布实施

	标准名称	类型	标准号/计划号	状态
1	全钒液流电池 术语	国标	20111001-T-604	报批
2	全钒液流电池通用技术条件	国标	20111001-T-XXX	形成讨论稿
3	全钒液流电池用电解液 测试方法	行标	NB/T 42006-2013	颁布实施
4	全钒液流电池用双极板 测试方法	行标	NB/T 42007-2013	颁布实施

全面参与欧洲液流电池标准化工作

应欧洲标准化组织CEN&CENELEC邀请，参加欧 洲液流电池标准化5个工作组中的3个，其中为第3工作组的牵头

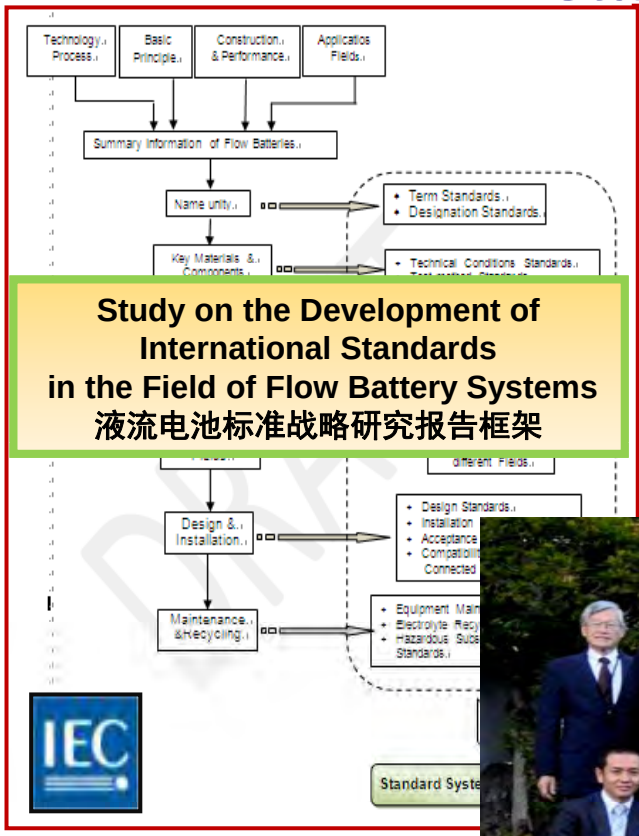
WG (# of Members)	WHO	COORDINATOR	WHEN
WG1 (5)	**HORNE** Craig/Enervault **FERRAIRA** Summer/SNL **N.N**/Cellstrom **CUTHBERT** Sean/LR **ZHANG** Huamin /DICP	**HORNE** Craig/Enervault	Week of January 23rd
WG2 (5)	**GARCIA LORENS** Vicent/IronFlow **VISWANATHAN** Vilayanur/PNNL **HORNE** Craig/Enervault **GARCIA** Alberto/Tecnalia **MEINERT** Lewerenz/Next energy	**GARCIA LORENS** Vicent/IronFlow	
WG3 (10)	**ZHANG** Huamin /DICP **SCHREIBER** Martha/Cellstrom **SCHNEIDER** Dirk/SGL **N.N**/PNNL **FERRAIRA** Summer/SNL **NOACK** Jens/Fraunhofer **DENNEMOSER** Martin /Fraunhofer **HORNE** Craig/Enervault **MENICTAS** Chris /NSIP **MEINERT** Lewerenz/Next energy	**SCHREIBER** Martha/Cellstrom	
WG4 (3)	**WANG** Xiaoli/Rongke **ADAMS** Bret/Enervault **ZHOU** Hantao (Hunter)/Linyang OTHERS TO BE ADVISED	**WANG** Xiaoli/Rongke	
WG5 (5)			

欧洲 液流电池标准化各工作组成员名单

积极推进国际液流电池标准制定

➢参与完成首个液流电池标准国际指导文件。

（Flow batteries - Guidance on the specification, installation and operation ）



Study on the Development of International Standards in the Field of Flow Battery Systems
液流电池标准战略研究报告框架

代表中国向IEC提出成立液流电池分标委提案，已提交到 IEC/TC105

出席国际标委会IEC/TC105年会

Acknowledgments

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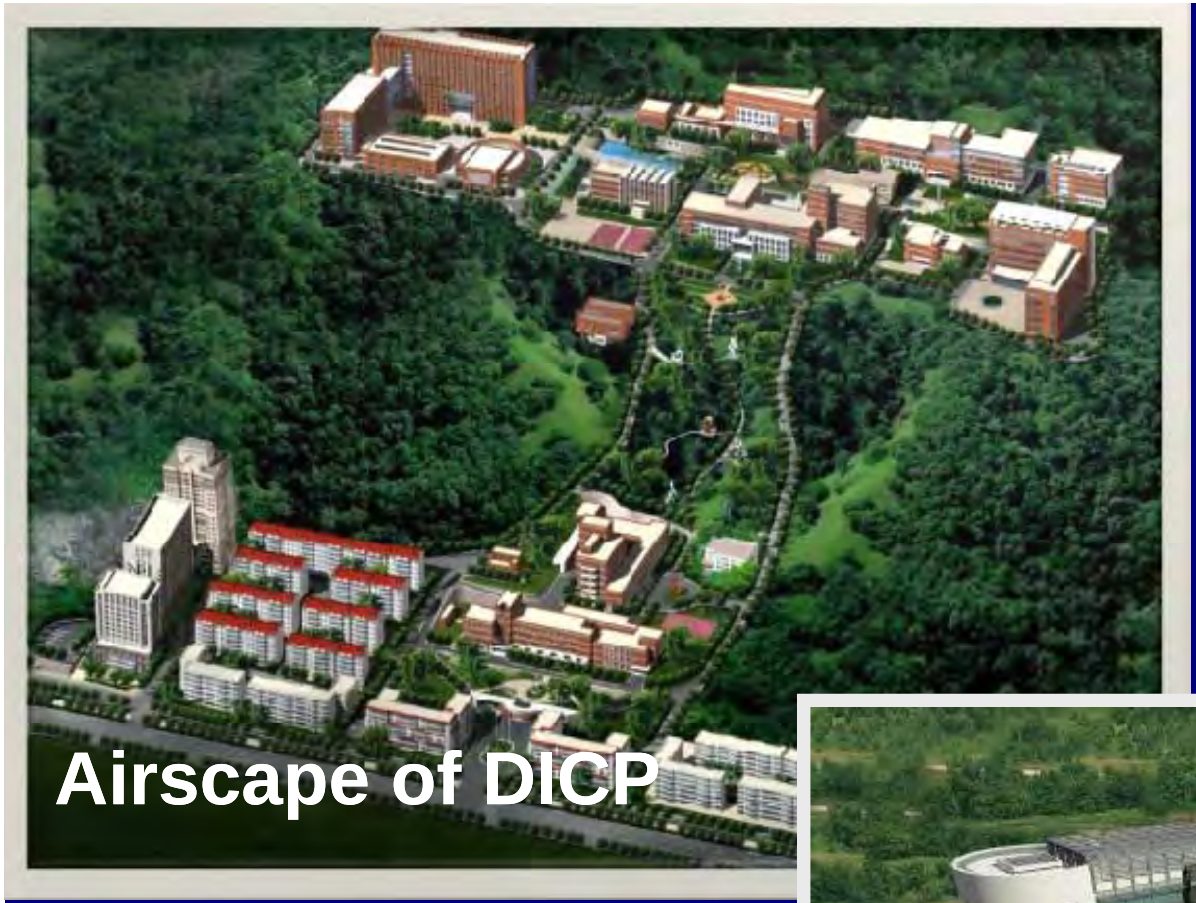
中国科学院大连化学物理研究所
DALIAN INSTITUTE OF CHEMICAL PHYSICS, CHINESE ACADEMY OF SCIENCES

Dalian Institute of Chemical Physics (DICP)



zhanghm@dicp.ac.cn

Thank you for your attention.