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

# Flow Batteries for Stationary Energy Storage

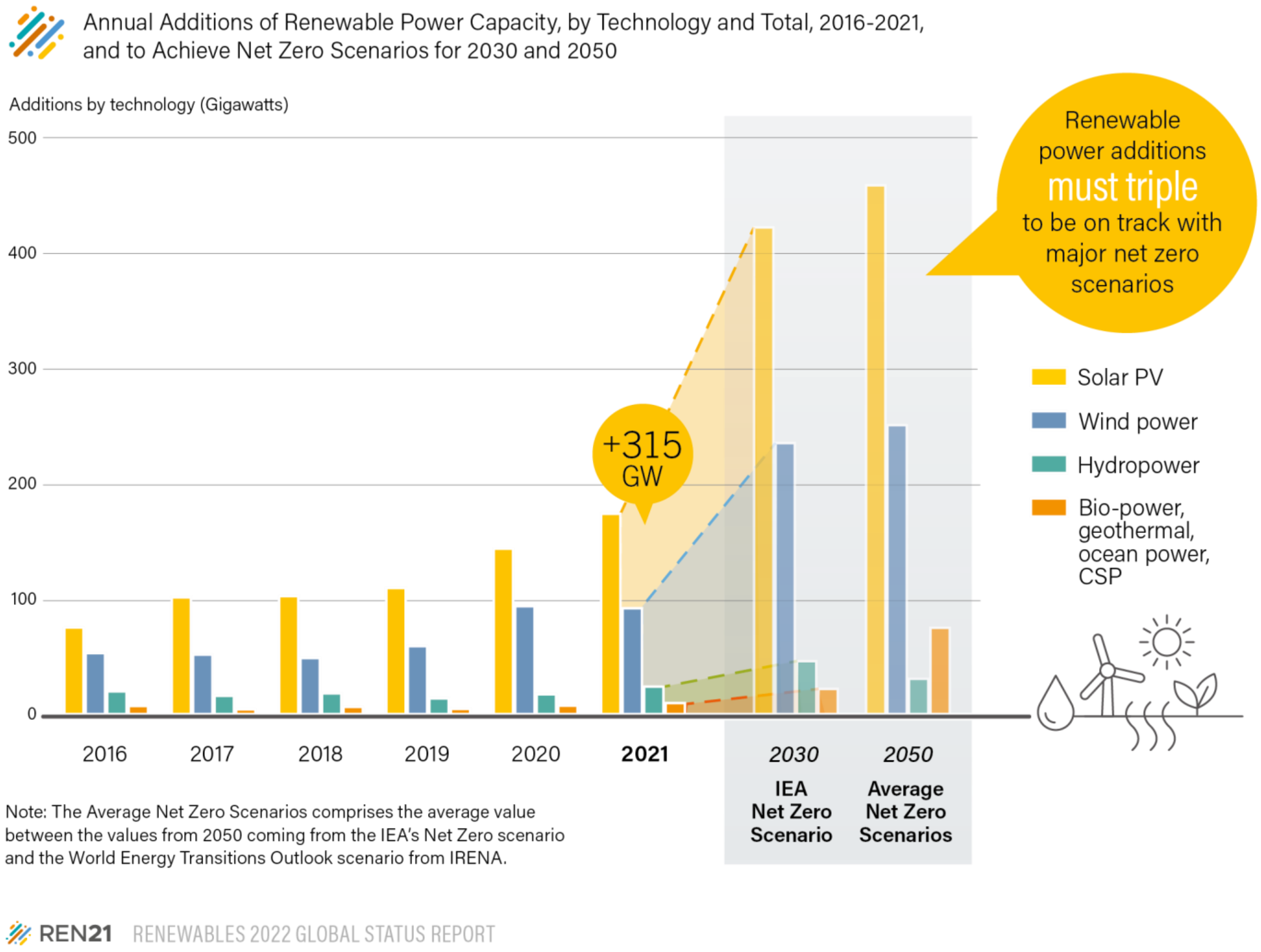
http://www.energystorage.dicp.ac.cn/

**Xianfeng Li**

**Dalian Institute of Chemical Physics, Chinese Academy of Sciences**

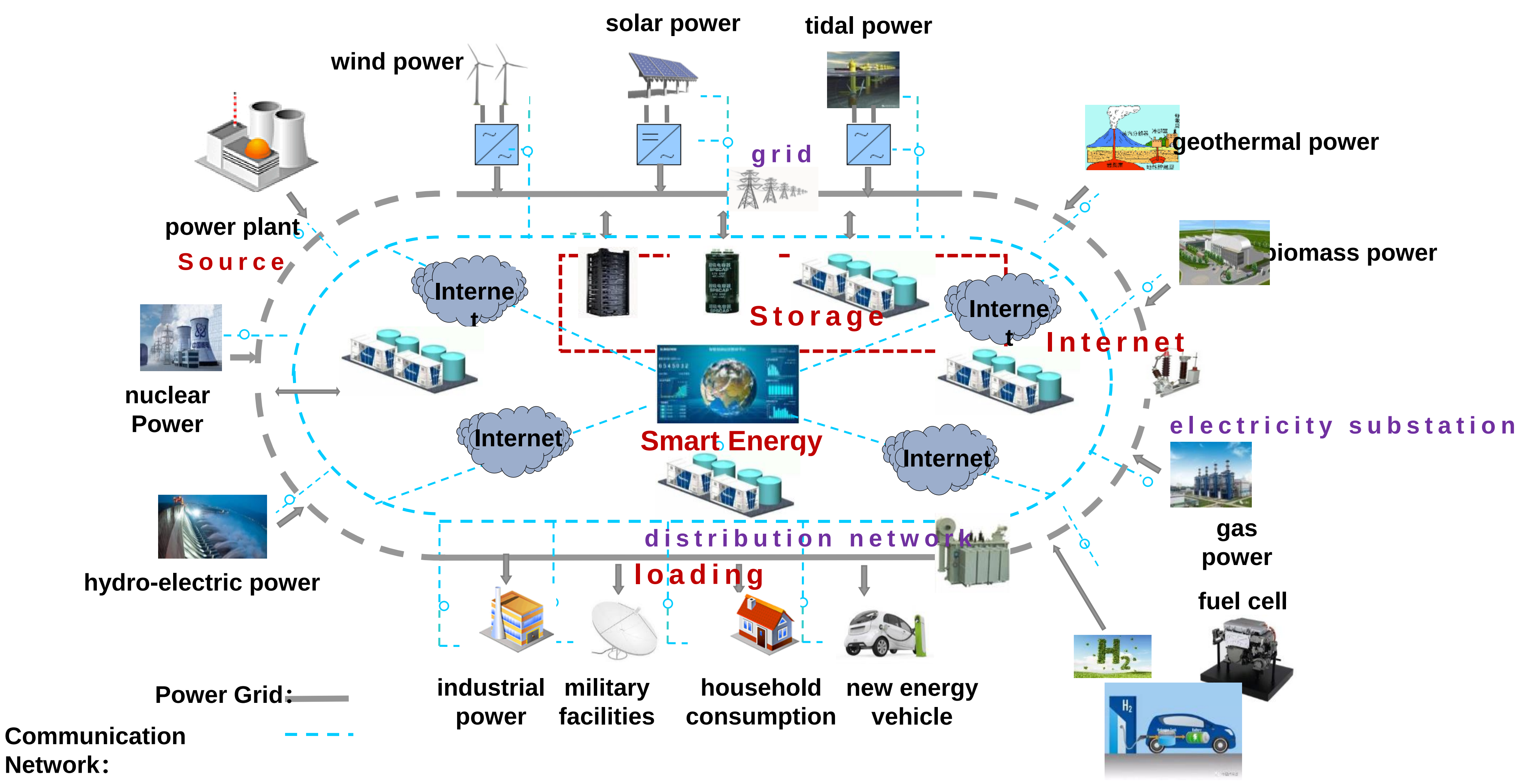
**2023-09**

# Renewable Energies become more and more important



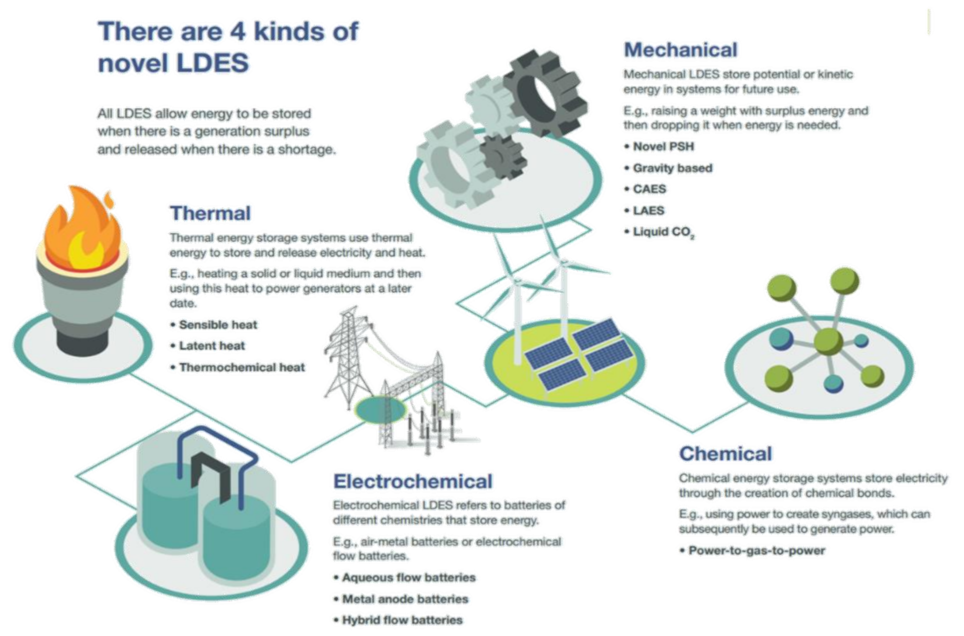

**Energy storage plays a critical role in widespread application of renewable energies!**

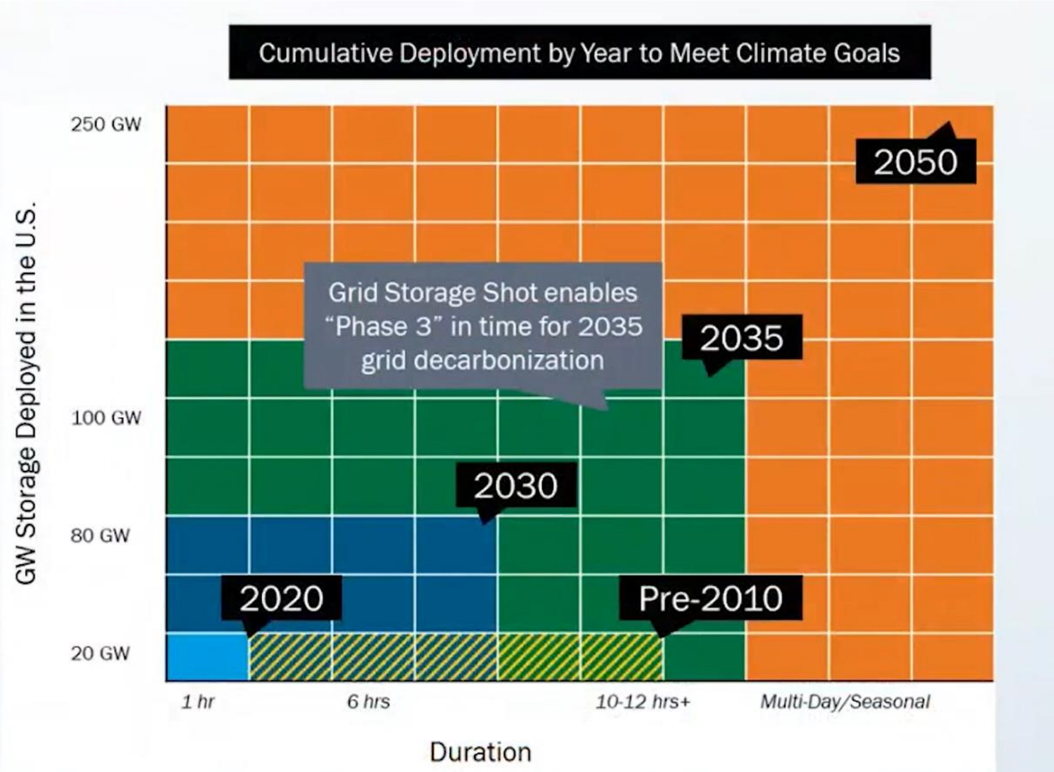
# Energy Storage Application




**Energy storage is the key technology to support the smart grid**

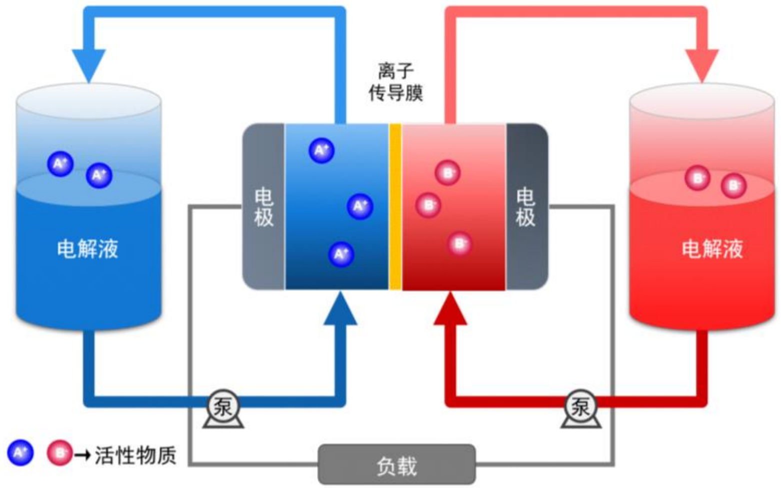
# Long Duration Energy Storage (LDES)



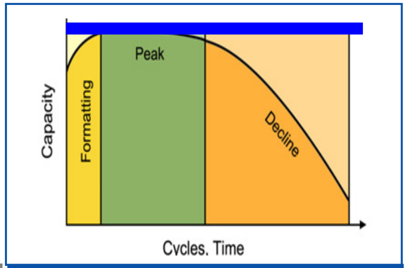




- DOE "Energy Earthshots", Long Duration Energy Storage Progam
- In next 10 years, duration >10 h, Cost reducing by 90%, to meet 100 GW renewables connecting to grid

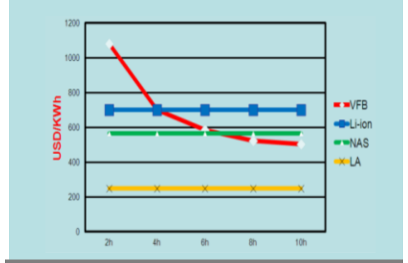
# Flow Battery



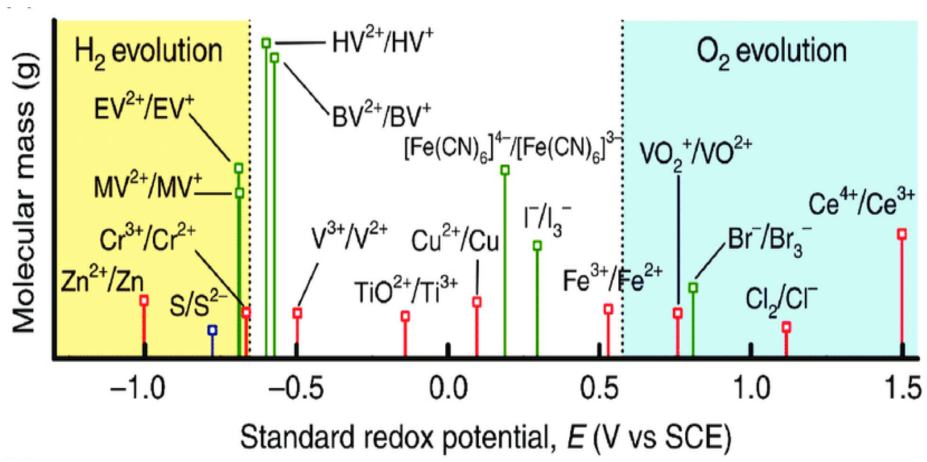

Fire accidents reported on Li-ion, Na-S, advanced Pb-acid, etc.




Capacity degrades over cycling for traditional batteries, but remains stable for FB (blue)




FB is economic competitive with long duration application (Red)




- High safety
- Independent design of power and capacity
- Long cycle life, no degradation under deep discharge
- High efficiencies, environmentally friendly
- Not suitable for power batteries due to relatively low energy density

**Flow battery is one of the preferred technologies for large-scale energy storage!**

# Vanadium Flow Battery (VFB)

## Features

- Aqueous electrolyte, high safety
- Large scale of output power and capacity

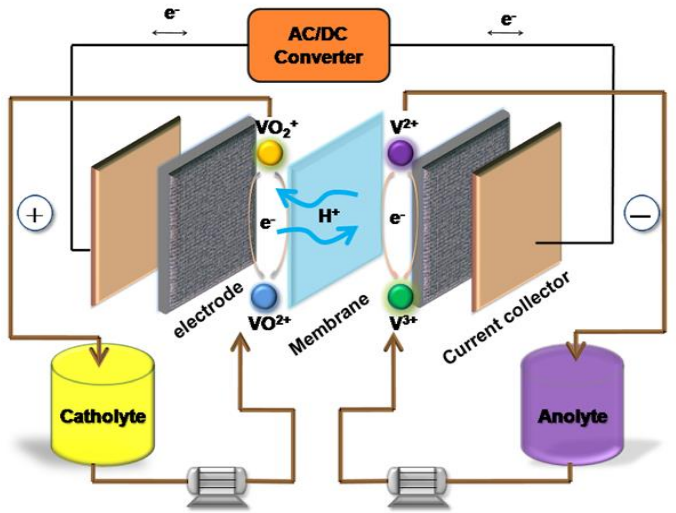
  Output power： 10 kWs-100 MWs

  Capacity： 10 kWhs-100 MWhs
- Quick response, good cycle performance
- Long lifespan, high cost performance

  Cycle numbers >16000, lifespan >15 years
- Recyclable electrolyte, environmental friendly

## Working principle

**Change of valence states of vanadium**

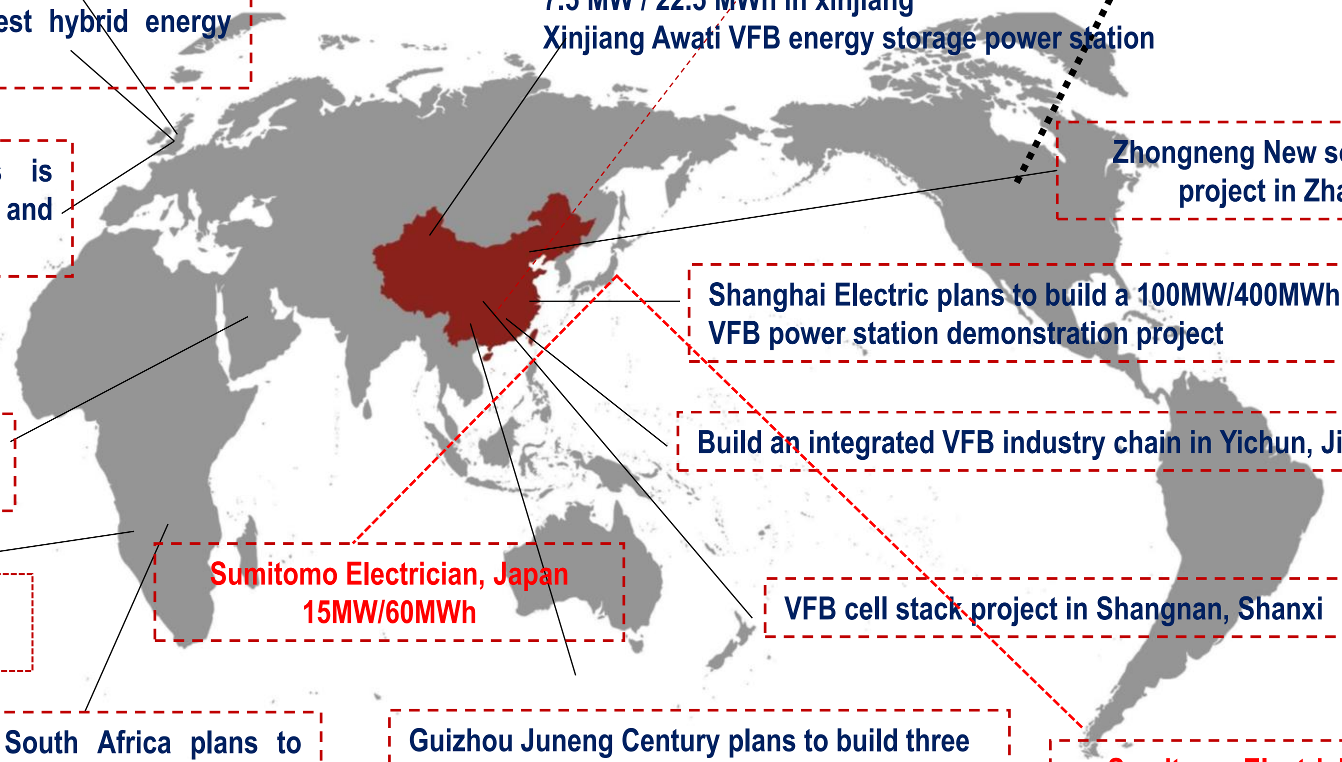



Positive : $VO^{2+} + H_2O - e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} VO_2^+ + 2H^+$

Negative : $V^{3+} + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} V^{2+}$

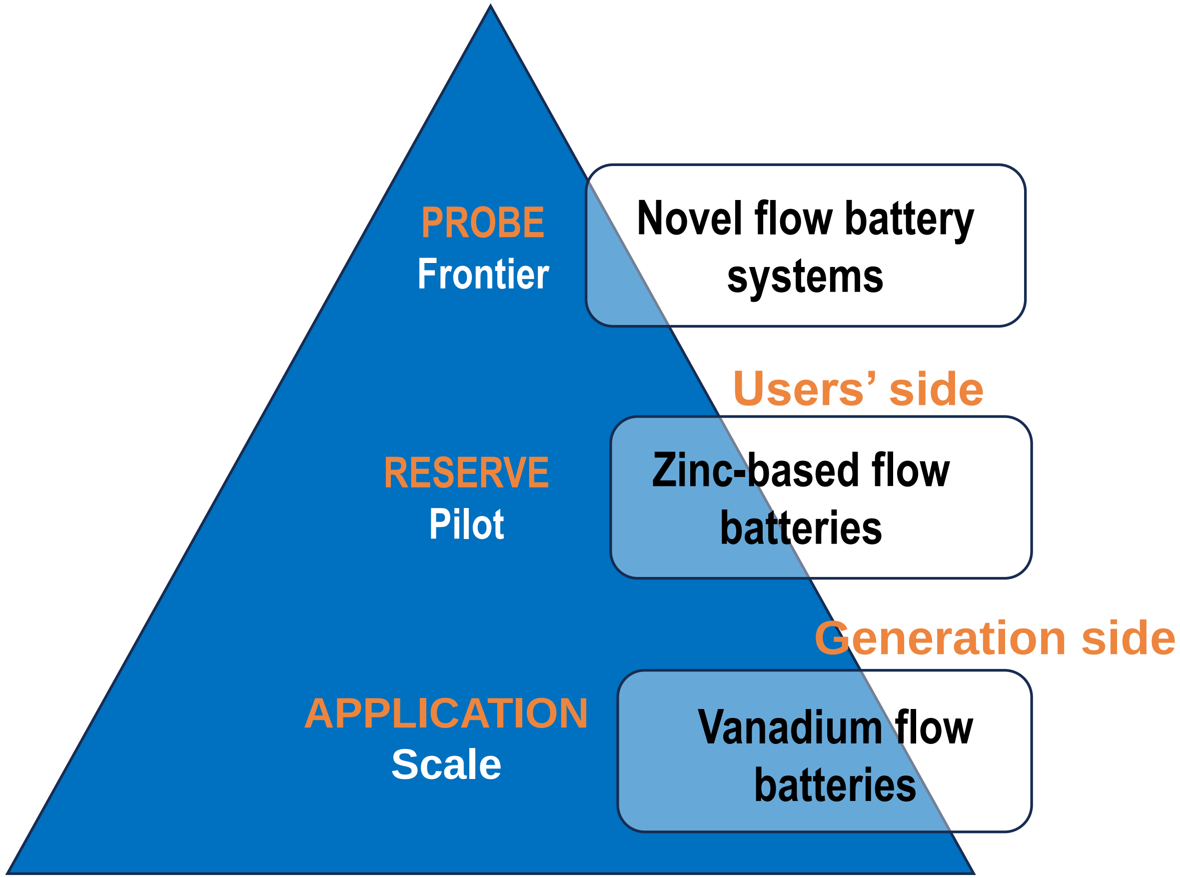
Overall : $VO^{2+} + V^{3+} + H_2O \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} V^{2+} + VO_2^+ + 2H^+$

# Global Development of VFB

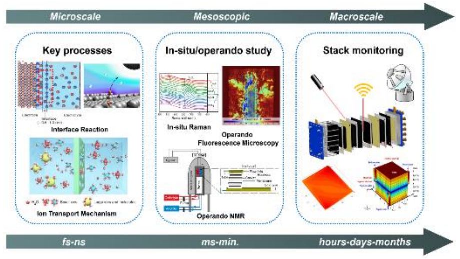



**The industrialization of VFB has recently received high attention.**

# Research and Development of Flow batteries at DICP




**Deep integration of basic, applied and translational research**

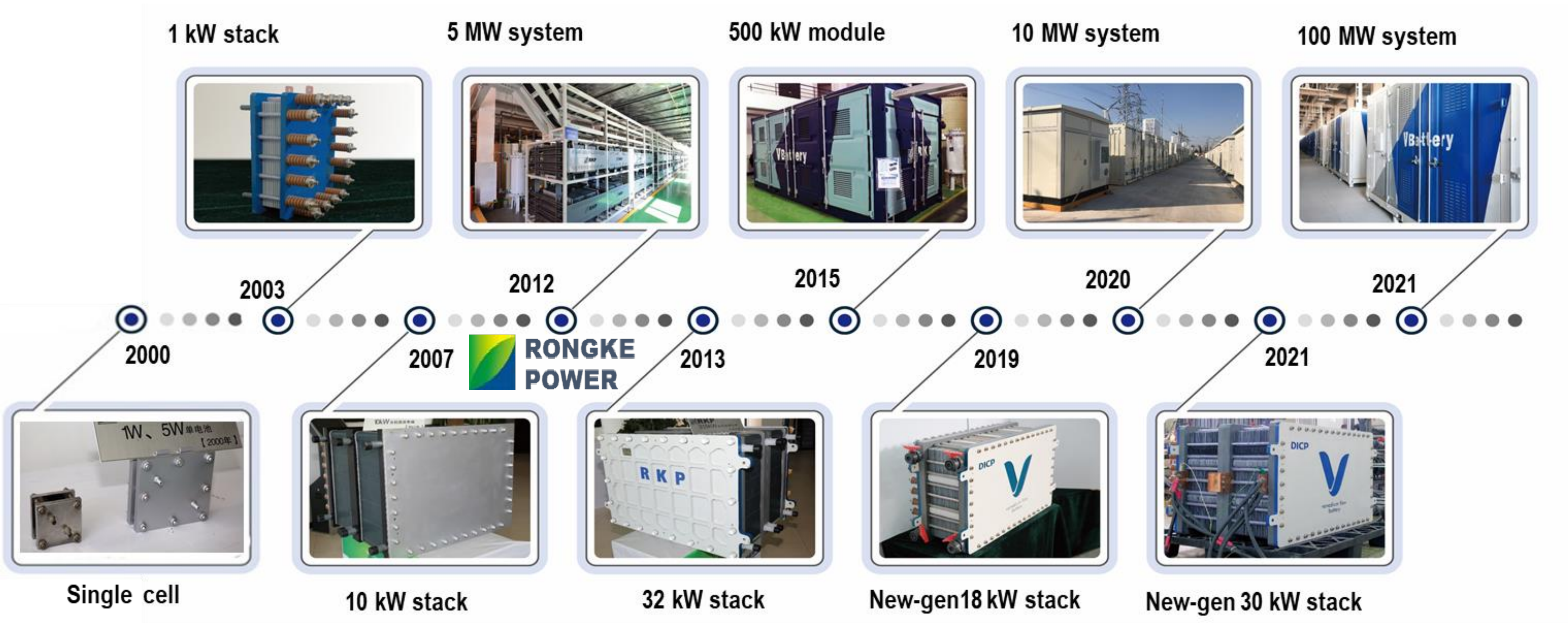



**Fundamental research**

**Pilot scale-up**

**Demonstration application**

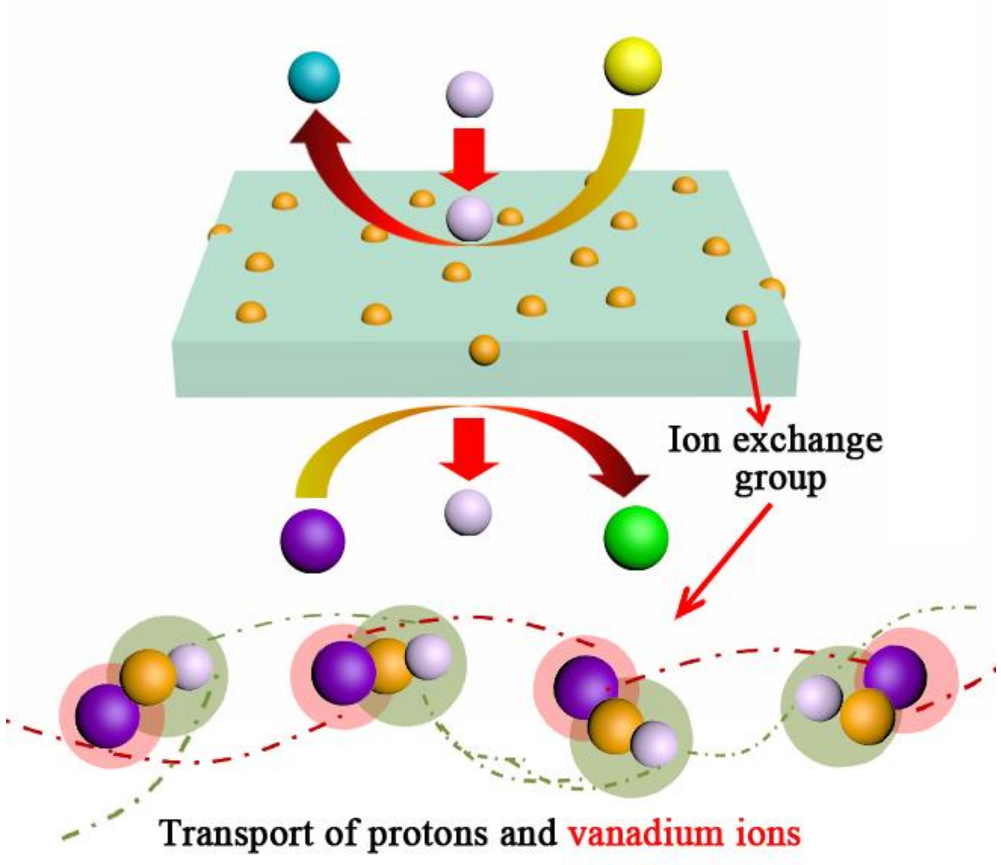
# The Research and Development of VFB in DICP




More than 300 patents were filled.

**Responsible for the formulation of domestic and international flow battery standards**

# Ion conducting membranes




**Function**

- Conducting $H^+$
- Separating V ions

**Working operation**

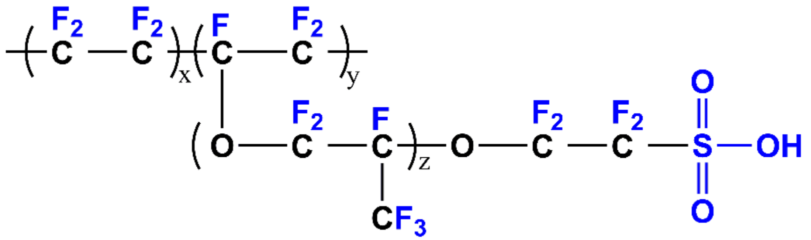
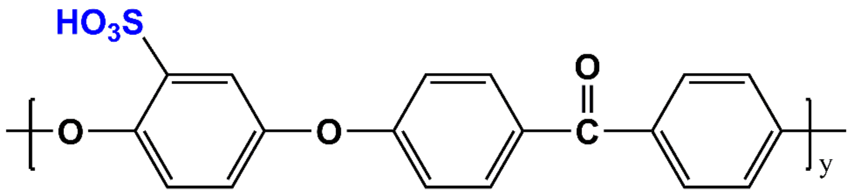
- Strongly oxidized and acidic electrolytes

**Membrane requirements**

- High ions selectivity
- High $H^+$ conductivity
- High chemical stability
- Low cost

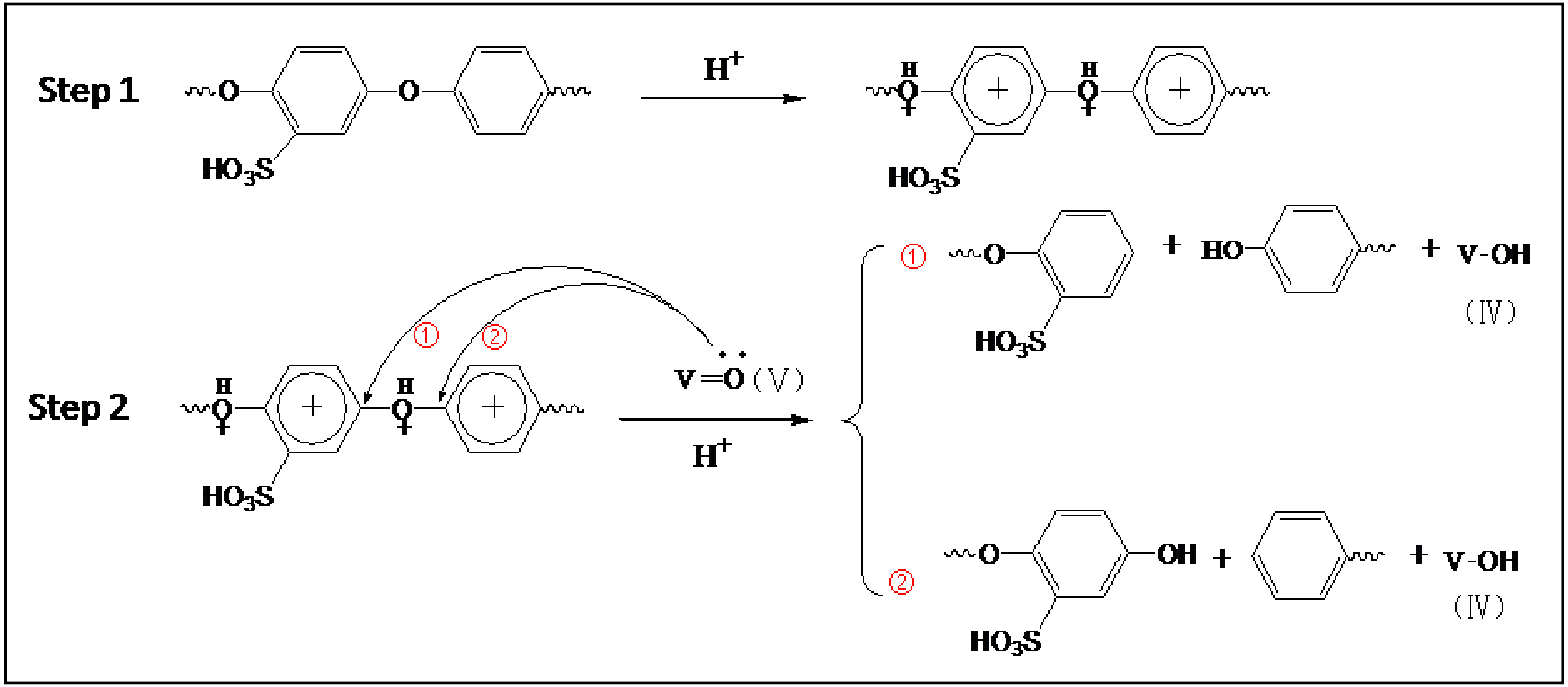
**High-performance and low-cost ion conducting membranes are the key to accelerate the industrialization of VFBs.**

# Challenges of ion conducting membranes

| Per-fluoride ion exchange membrane | Non-fluoride ion exchange membrane |
| --- | --- |
|  |  |
| ✓ High ions conductivity<br>✓ Good chemical stability<br>X High Cost<br>X Poor ions selectivity<br>(~700 $/m^2$) | ✓ Low cost<br>✓ High ions conductivity<br>✓ High ions selectivity<br>X Poor chemical stability |

**The poor chemical stability of non-fluoride ion exchange membrane restricts their large-scale application in VFBs.**

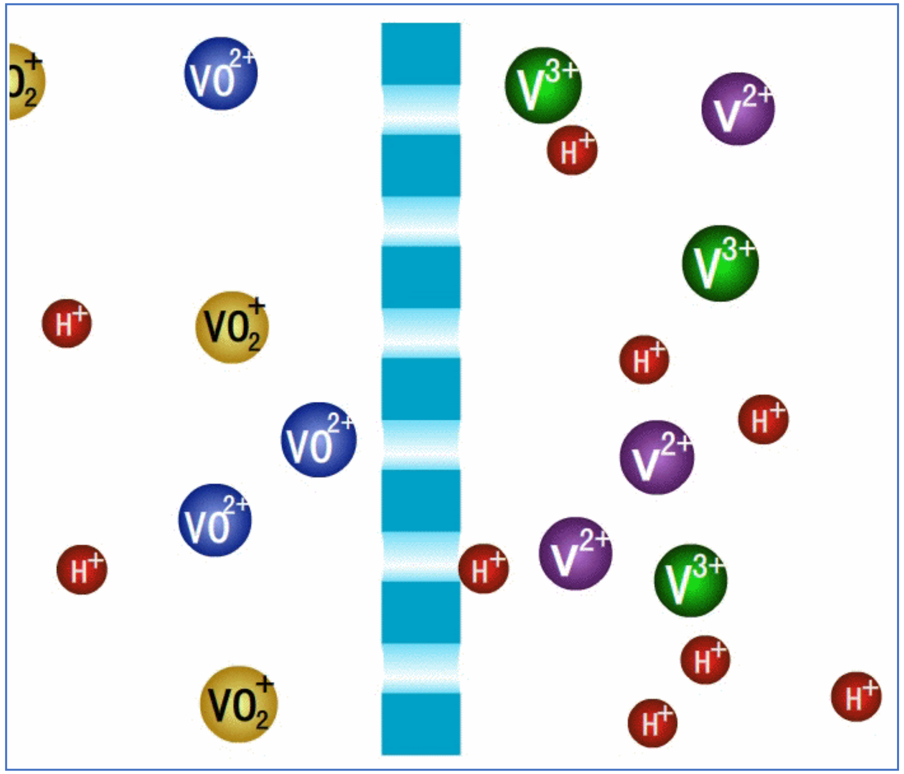
# Degradation mechanism of ion conducting membranes



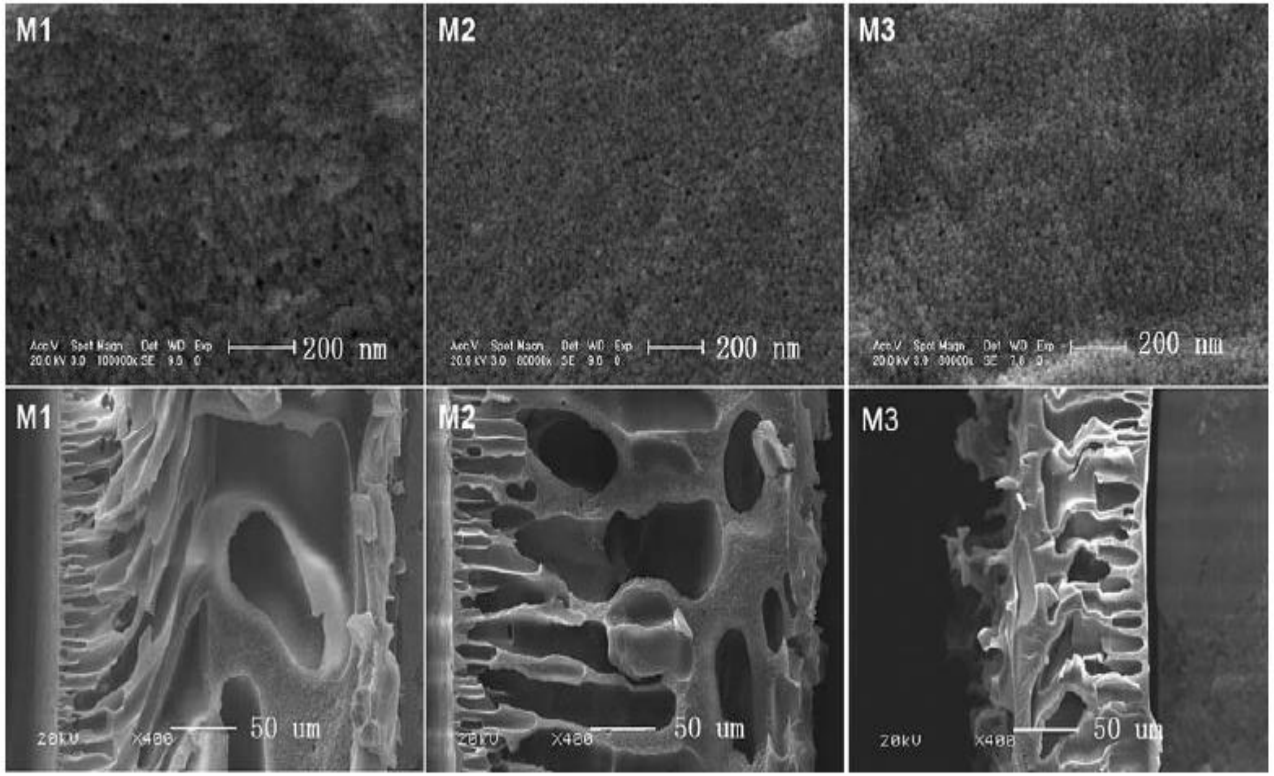

**The existence of ion exchange groups induces the poor stability of non-fluoride ion exchange membranes.**

*Phys. Chem. Chem. Phys.*, 2014, 16, 19841

# Porous Ion Conducting Membranes



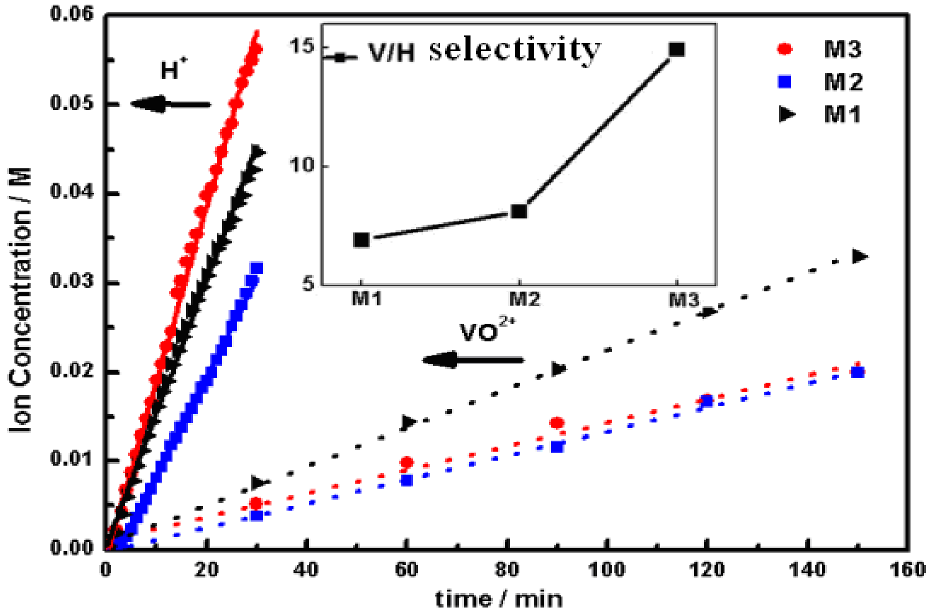
Schematic diagram of "ion screening"

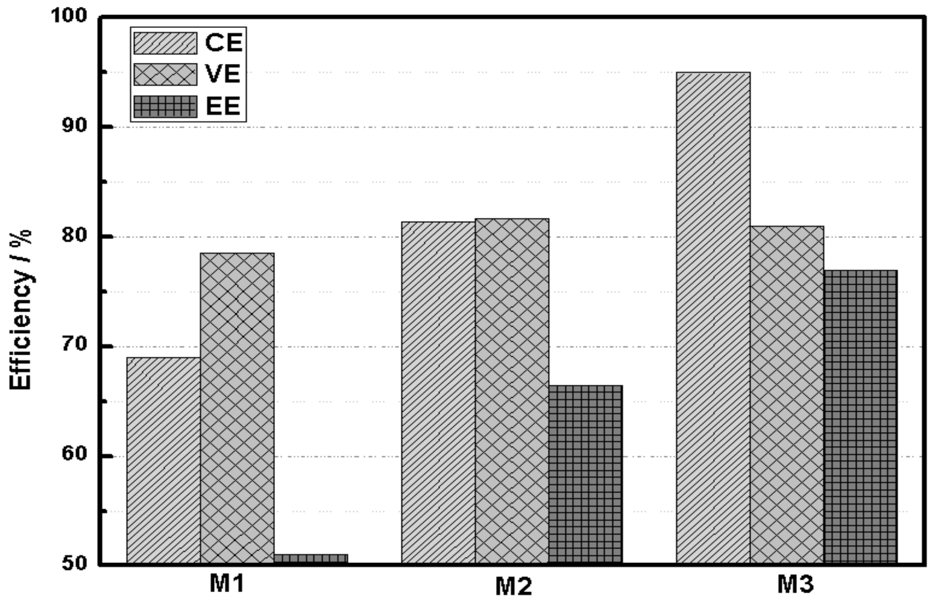


Regulating the structure of porous ion conducting membrane

***Energy Environ. Sci. 2011, 4, 1676***

# Porous Ion Conducting Membranes in Flow Battery

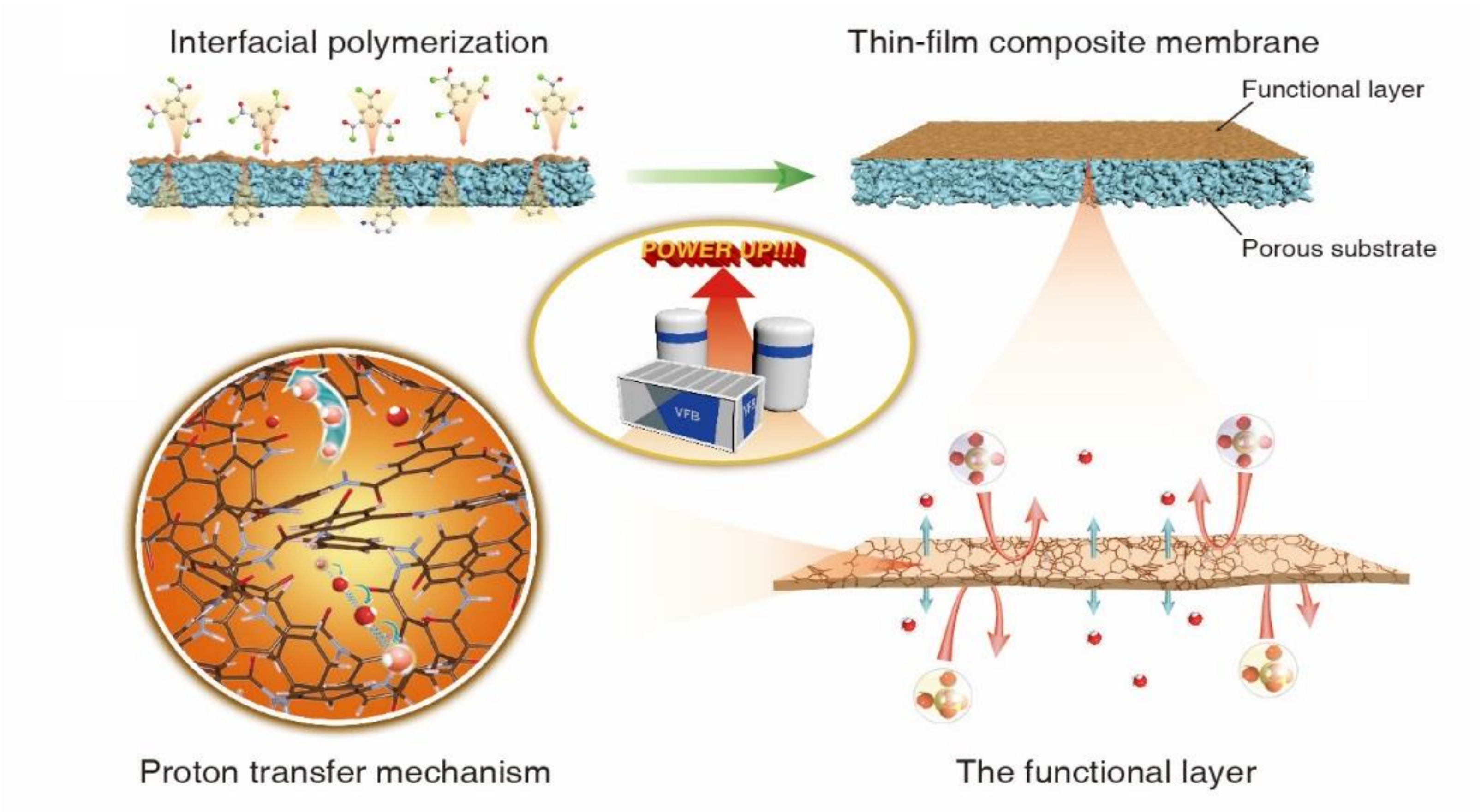



- The concept of "ion screening" without ion exchange groups was put forward.
- The screening of vanadium ions and protons on the molecular scale was realized by using the **“pore size exclusion".**

*Energy Environ. Sci.* ***2011**, 4, 1676*

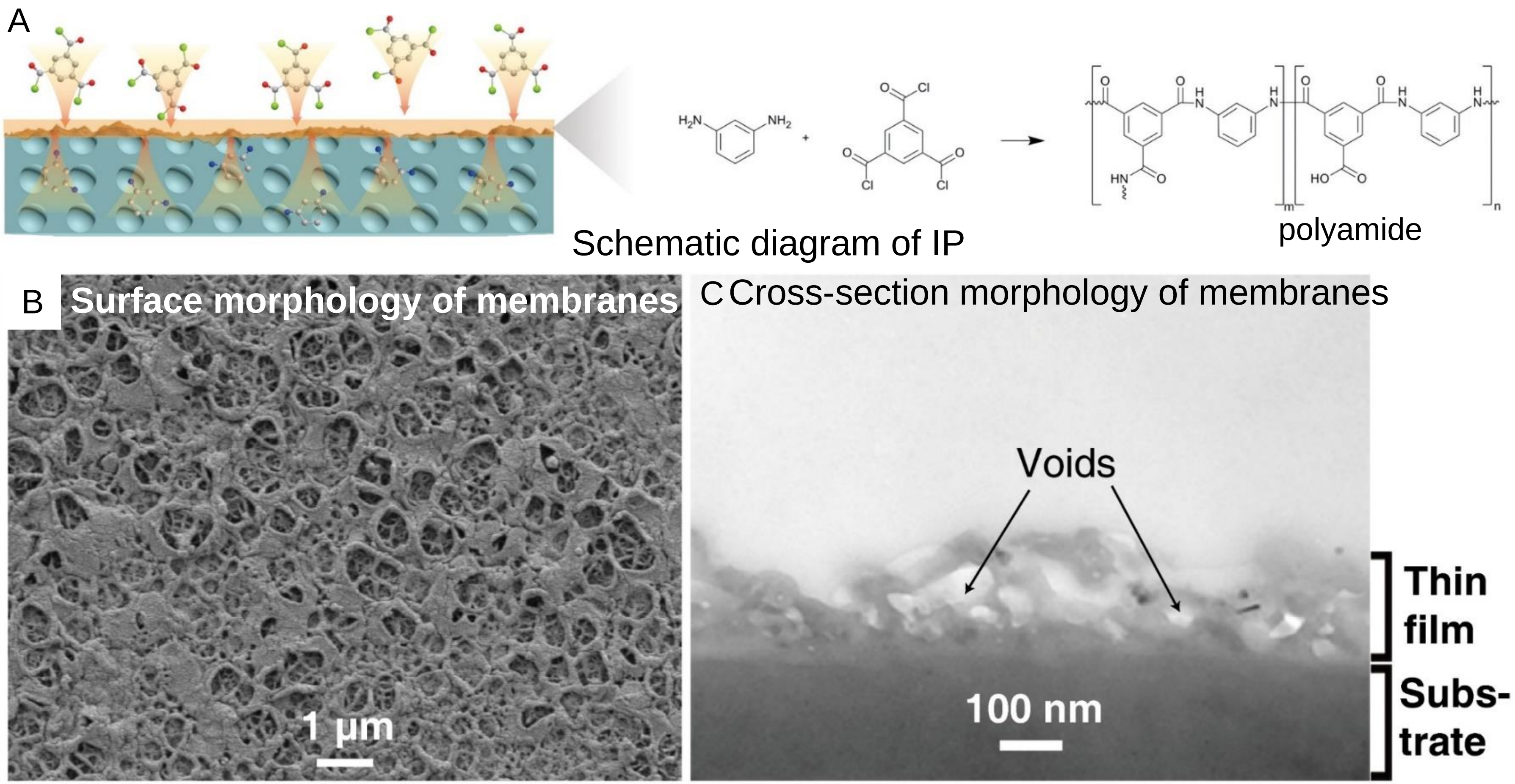
# Composite Porous Ion Conducting Membranes




Composite membranes with **ultrathin functional layers** were prepared by **interfacial polymerization.**

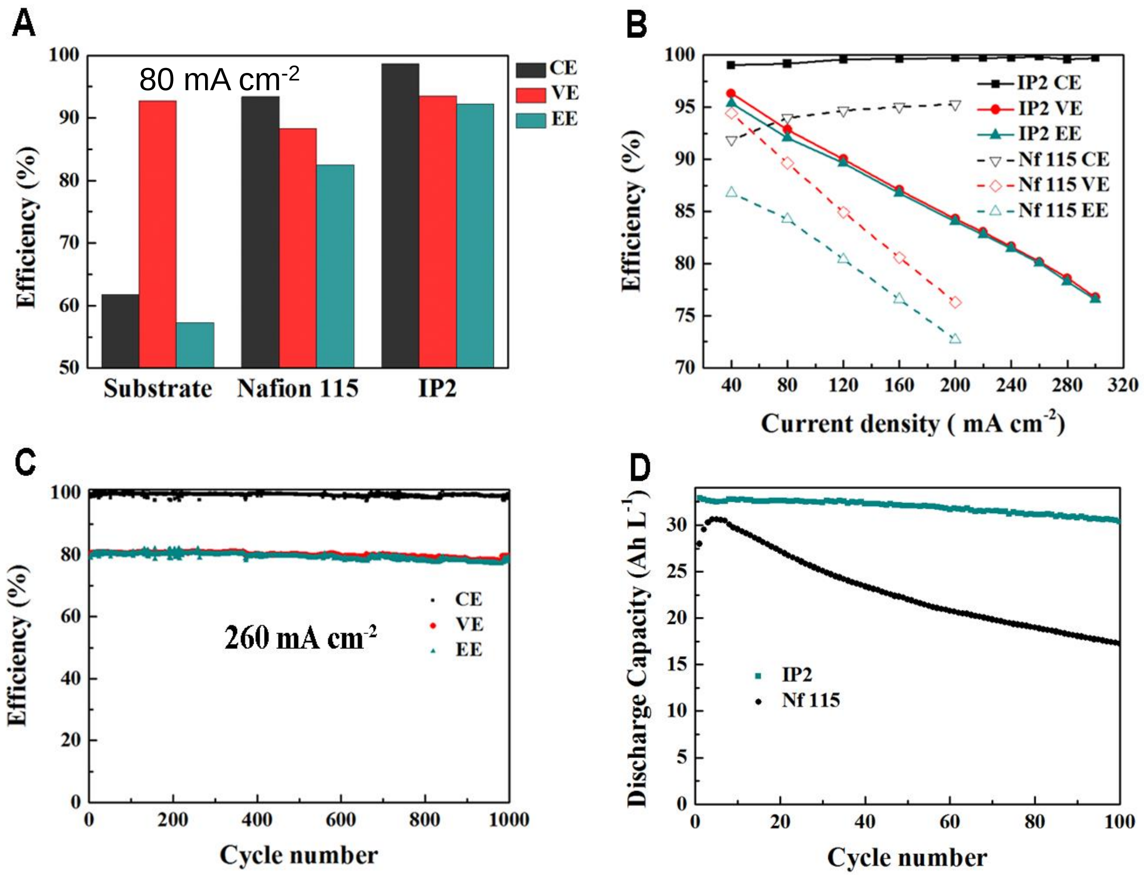
***Nat. Commun. 2020, 11, 13***

# Composite Porous Ion Conducting Membranes

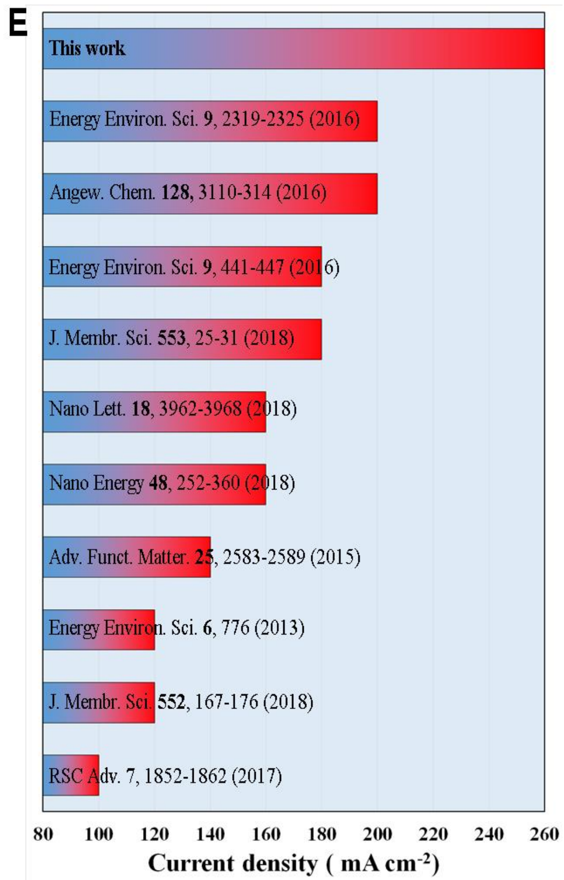



The composite membrane prepared by interfacial polymerization has typical "**ridge-and-valley**" morphology. The functional layer is about **180 nm thick**.

# Performance of the Composite Membranes



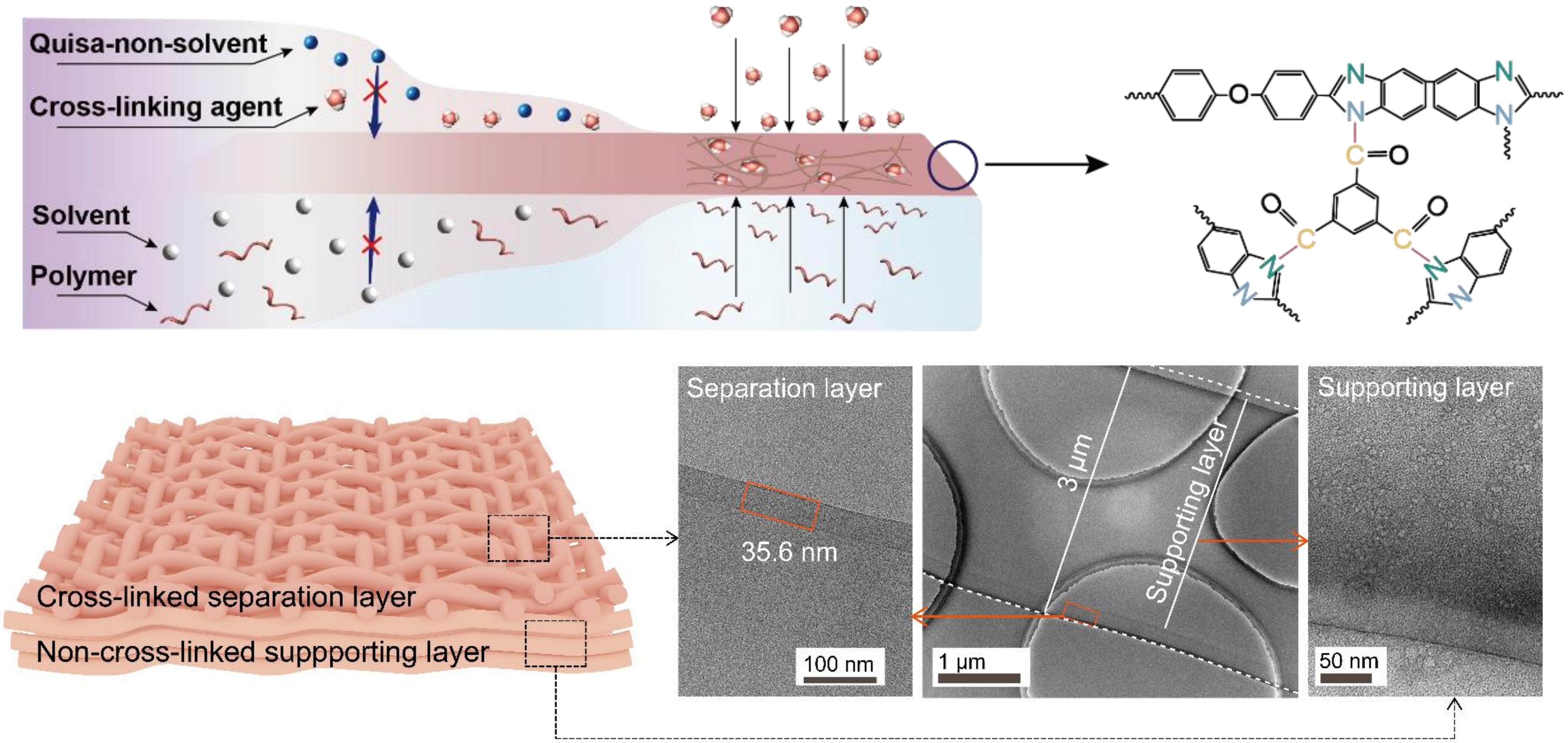

VFB performance assembled with composite membranes




Power density comparison

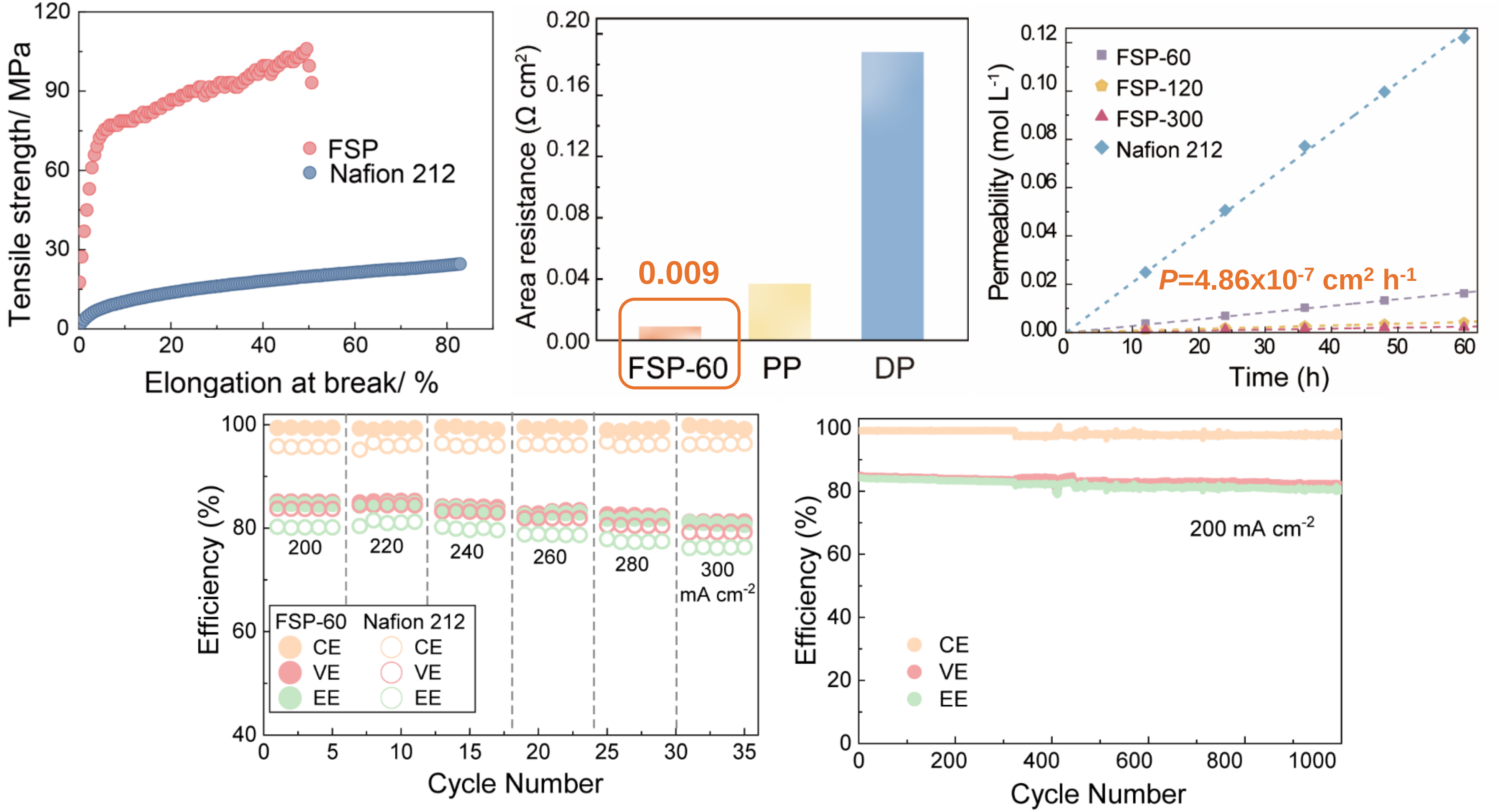
VFB with a thin-film composite membrane achieves energy efficiency **higher than 80%** at a current density of **260 mA cm$^{-2}$**, which is the highest ever reported.

# Highly mechanically stable ultrathin membranes



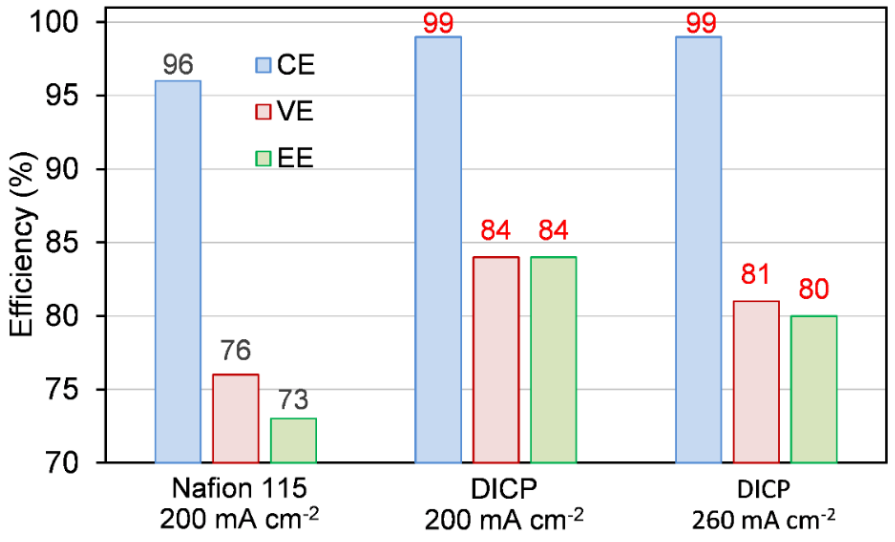

Ultrathin membranes with high selectivity, high conductivity and ultrahigh mechanical strength were fabricated by a novel **reaction-non-diffusion induced phase separation method**.

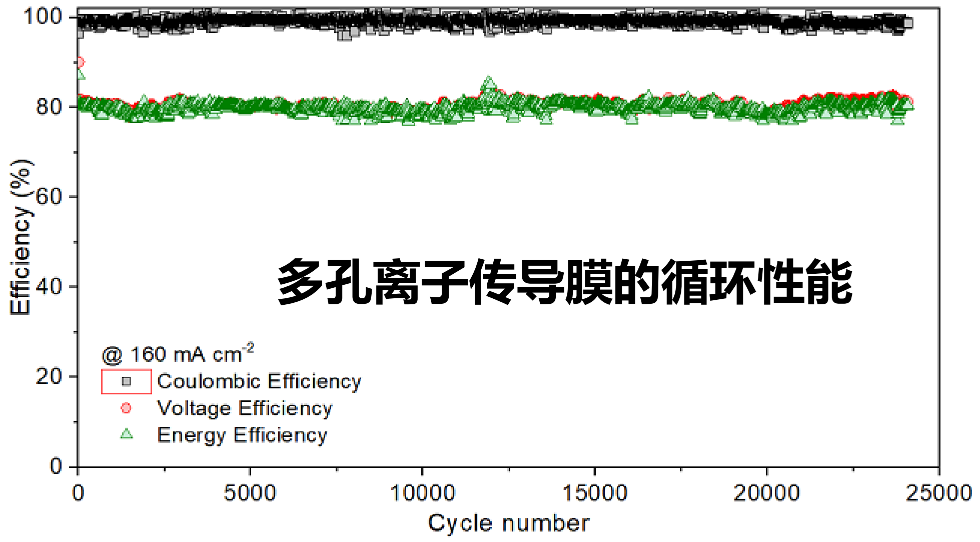
# Highly mechanically stable ultrathin membranes




The VFB assembled with the ultrathin membrane with high selectivity and high conductivity exhibited excellent performance with an energy efficiency **of >80% at 300 mA cm$^{-2}$**.

# Optimization of porous membranes for FB




*Zhang HM*, Li XF* et al, Energy Environ. Sci., 2011, 4, 1676*

*Zhang HM*, Li XF* et al, Energy Environ. Sci., 2012, 5, 6299*

*Zhang HM*, Li XF* et al, Energy Environ. Sci., 2016, 9, 441*

*Li XF* et al, Energy Environ. Sci., 2020, 13, 4353-4361*

*Li XF* et al, Energy Environ. Sci., 2022, 15, 1594-1600*

*Zhang HM*, Li XF* et al. Angew. Chem. Int. Ed., 2016, 55, 3058*

*Li XF* et al, Nat. Commun., 2020, 11, 2609*

*Li XF* et al, Nat. Commun., 2018, 9 3731*

*Zhang HM*, Li XF* et al, Energy Environ. Sci., 2016, 9, 2319*

*Hou GJ*, Li XF* et al, Adv. Energy Mater. ,2020, 10, 2001382*

- The developed non-fluoride porous membranes have **high selectivity, high conductivity and low cost**, superior to Nafion 115, and the cost is **only 10%** of that of Nafion 115.
- Over **20,000 durability test** has been completed.

**代表性专利：** *ZL201310303522.4、ZL201811118420.4、ZL201811417439.9、ZL201811451416.X、ZL201811109210.9*

# Mass production of non-fluorinated porous membrane


液流电池用质子膜采购合同

合同编号：

乙方：中国科学院大连化学物理研究所

**Realized the mass production of non-fluoride ion conducting membranes (80000 $m^2$/year).**

**Signed a sales contract for s membrane materials, and the sales volume of membrane materials exceeded 40,000 square meters.**

# High power density stack

Based on modeling and simulation , design and assemble the high power density stack

### Structure

- Design of flow channel
- Design electrode shapes
- Match compression ratio
- Regulate electrolyte flow
- Control the shunt current
- Minimize flow resistance

### Process

- Design of seal
- Design of anti-corrosion
- Machine the channel
- Design of the endplate
- Load mechanic design
- Assemble process

### Test

- Performance evaluation：
  Coulombic efficiency、
  Voltage efficiency and
  Energy efficiency。
- Operating mode
- Operating condition

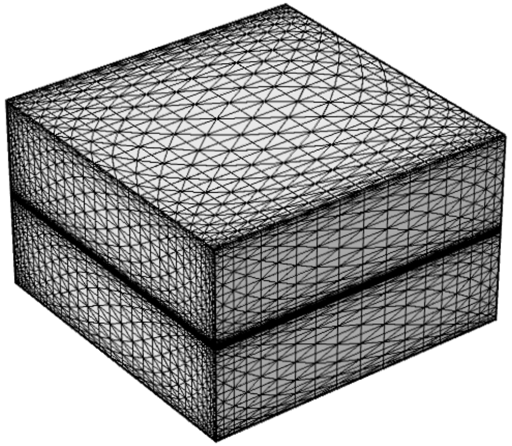
Scale up: From cell to large stack

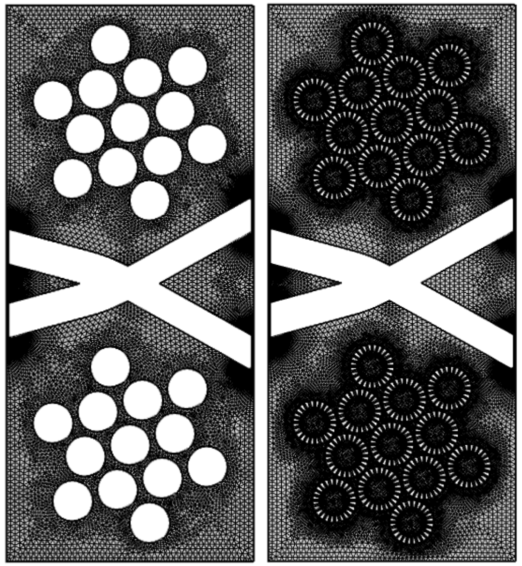
# Simulation： establish model with different material

## Geometry and equations

| | |
|---|---|
| Transient equation | $$\frac{\partial c_i^{in}}{\partial t} = \frac{v_{in}\varepsilon A_{in}}{V_{tank}}\left(\int v^{out} c_i^{out} dl - \int v^{in} c_i^{in} dl\right)$$ |
| Momentum equation | $$\vec{v} = -\frac{k}{\mu}\nabla p$$ |
| Mass equation | $$\frac{\partial(\varepsilon c_i)}{\partial t} + \nabla \cdot \vec{N_i} = -S_i$$ |
| Charge equation | $$\sum_i z_i c_i = 0 \qquad \nabla \cdot \vec{i_e} + \nabla \cdot \vec{i_s} = 0$$ |
| Electrochemical equation | $$j_1 = F k_1 (c_2)^{\alpha_{nc}} (c_3)^{\alpha_{na}} \left[\frac{c_3^s}{c_3}\exp\left(-\frac{\alpha_{nc} F \eta_1}{RT}\right) - \frac{c_2^s}{c_2}\exp\left(\frac{\alpha_{na} F \eta_1}{RT}\right)\right]$$ |
| | $$j_2 = F k_2 (c_4)^{\alpha_{pc}} (c_5)^{\alpha_{pa}} \left[\frac{c_5^s}{c_5}\exp\left(-\frac{\alpha_{pc} F \eta_2}{RT}\right) - \frac{c_4^s}{c_4}\exp\left(\frac{\alpha_{pa} F \eta_2}{RT}\right)\right]$$ |

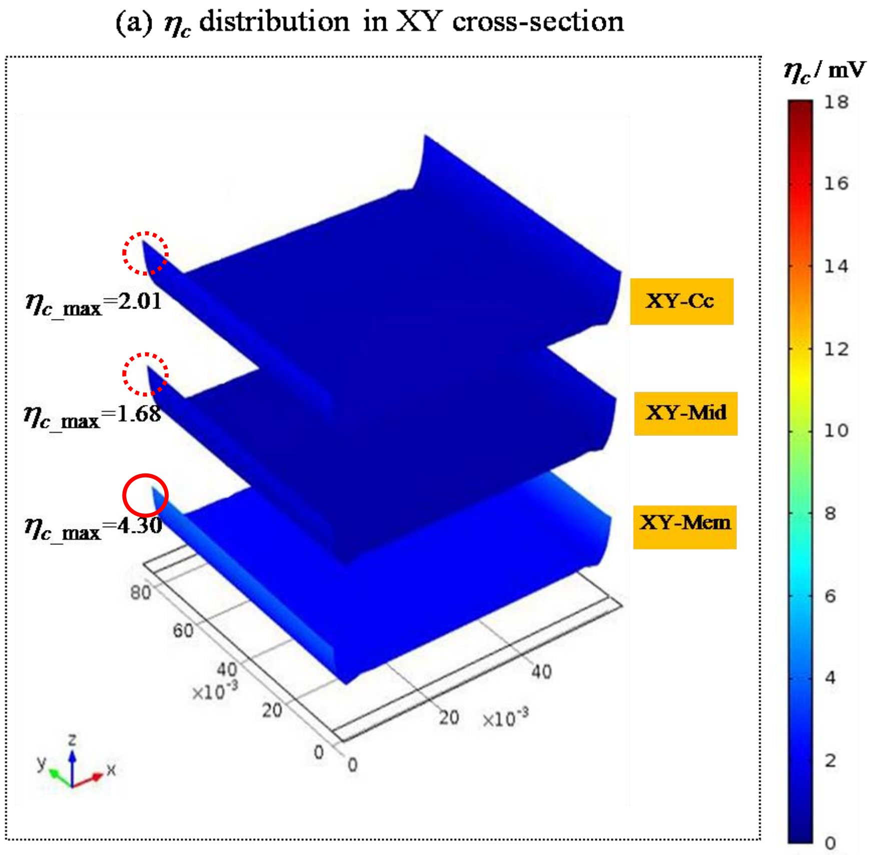
## Geometry and mesh



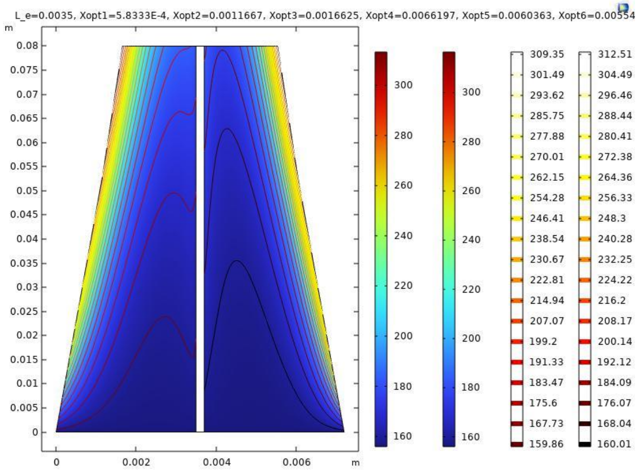


# Simulation: Polarization regulation and factor analysis

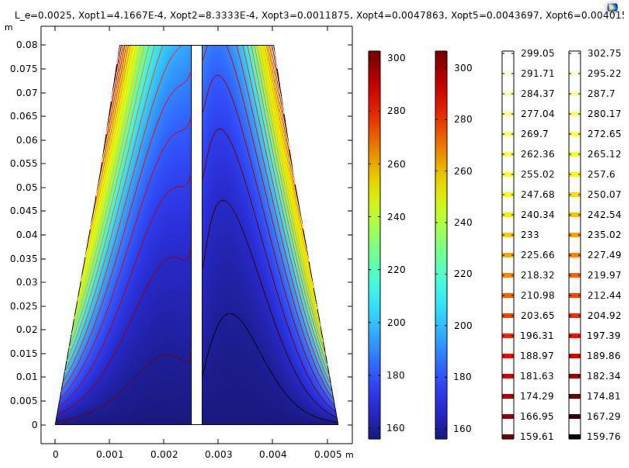
## - Effect of flow structure on concentration polarization distribution -



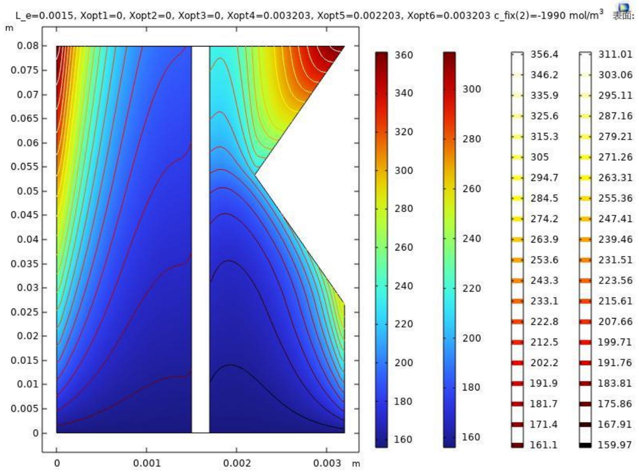

## - Effect of electrode structure on polarizaiton -



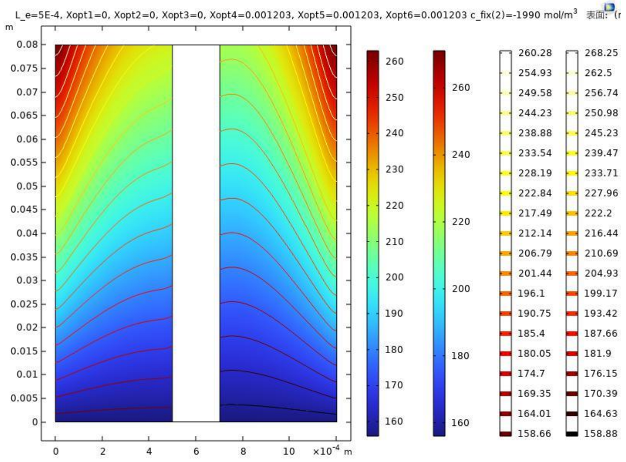
Electrode thickness: 3.5mm



Electrode thickness: 2.5mm



Electrode thickness: 1.5mm

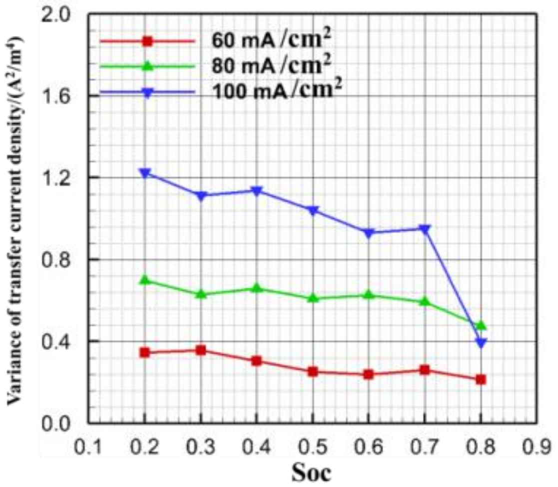


Electrode thickness: 0.5mm

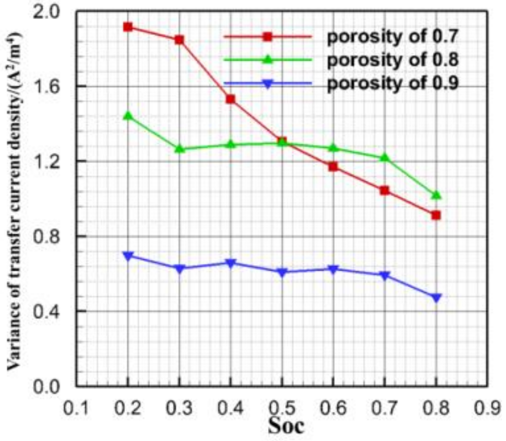
# Simulation： Current density regulation and factor analysis

**Introduce variance to quantitatively define uniformity of current density distribution**

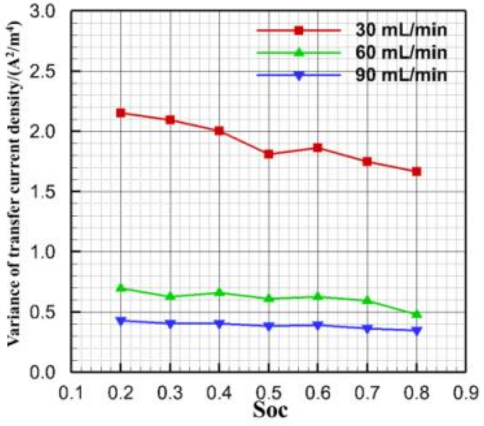
$$S^2=\frac{\sum_1^i (X_i-\bar{X})^2}{N}$$



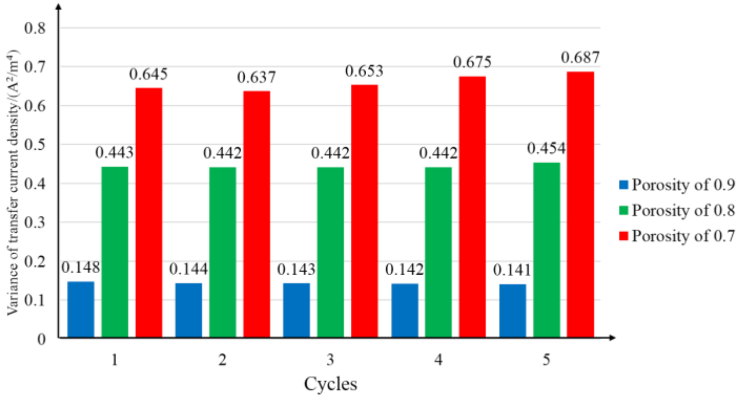

Effect of applied current on uniformity of current density distribution




Effect of porosity on uniformity of current density distribution




Effect of flow rate on uniformity of current density distribution



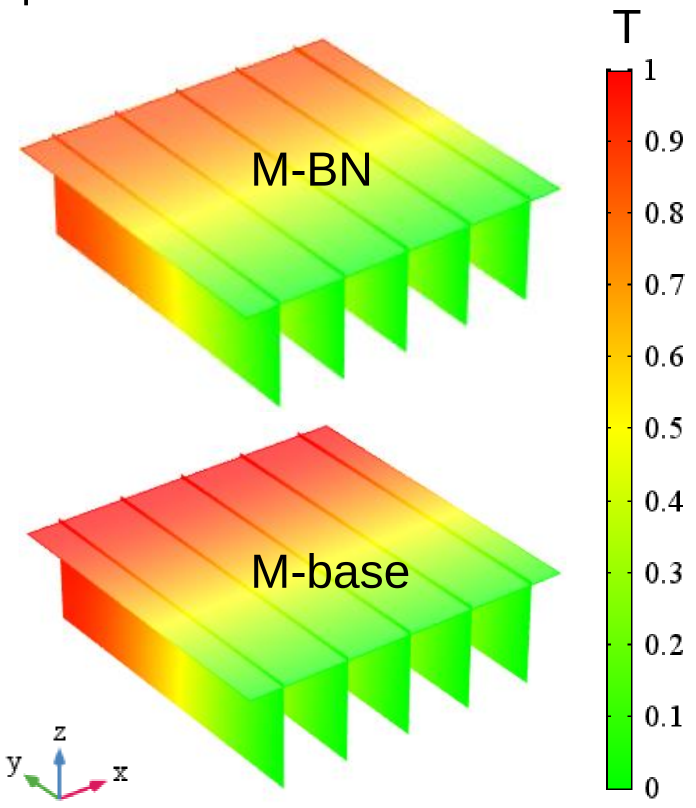

## Effect of flow rate on uniformity of current density distribution during different cycles

✓High porosity enhances uniformity of current density distribution;

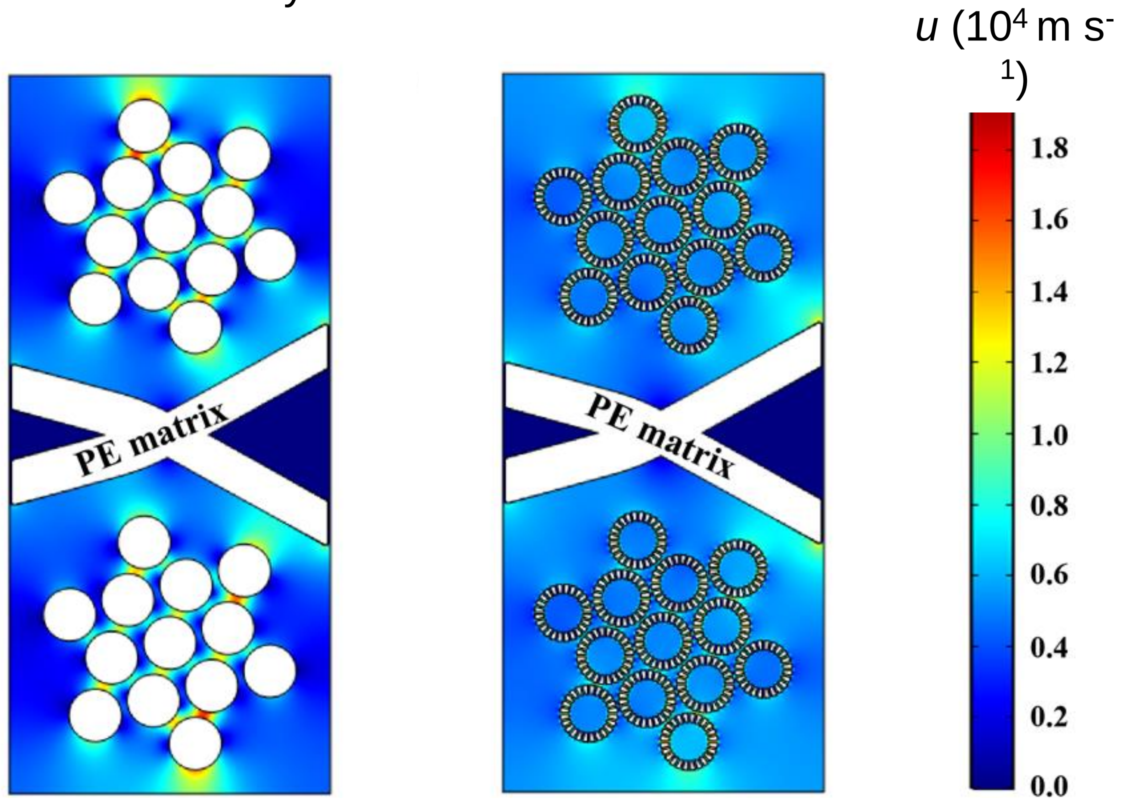
✓High porosity prevents the deterioration of uniformity of current density distribution

# Simulation:  Guide material design and optimization

Temperature distribution in the cell




Velocity distribution in the membrane




Improve the permeability and thermal conductivity of the membrane by modifying the membrane to obtain the uniformity of temperature and concentration distribution inside the battery.

# New Gen weldable high power density stack

10kW stack


30kW stack

- The energy efficiency is up to 80.6%@10kW, the current density is about 195 $mA/cm^2$.
- The energy efficiency is up to 81.8%@30kW, the cost has dropped by 40%.

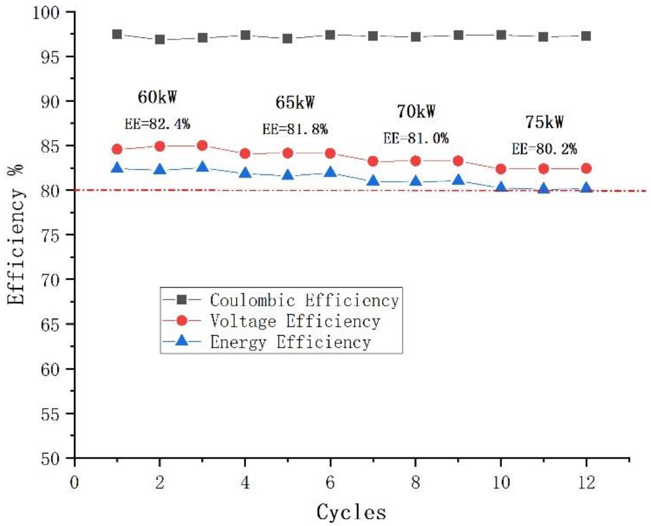
# New Gen Weldable high power density stack

## Reduce stack volume and increase stack power


Previous generation 30kW stack

Twice power with same volume


New design 70kW stack

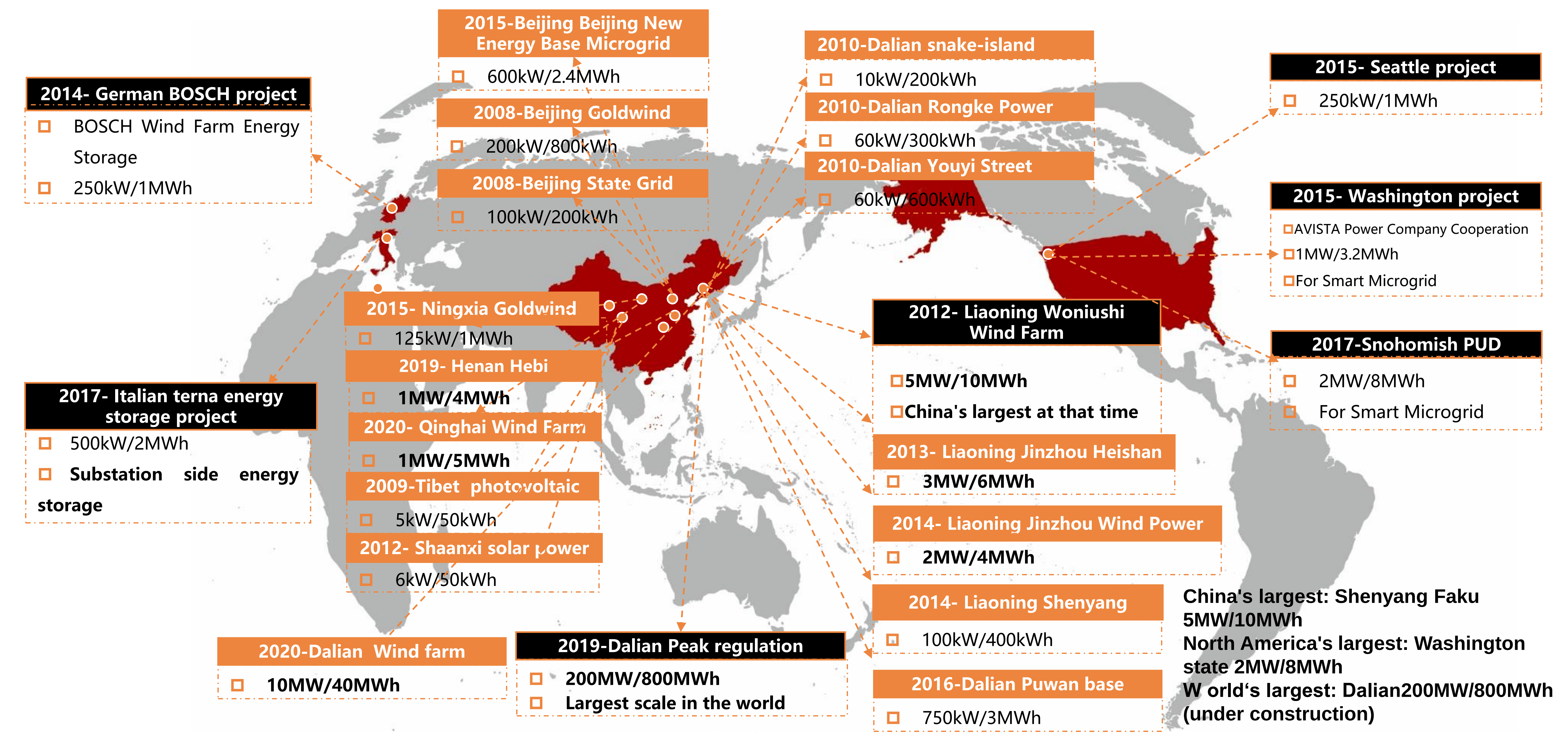



**A new 70kW stack was developed for large scale applications. The output power is more than twice than previous 30kW stack with the same volume. The current density is 160mA/cm$^2$.**

# Build a production platform with 300MW/ annual

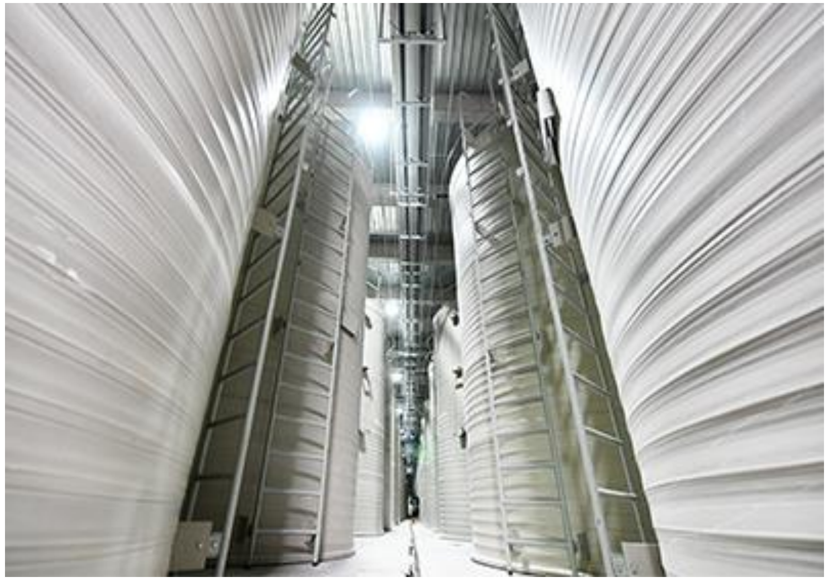
**The largest industrial equipment base for vanadium flow batteries in China has been built. （300MW/annual）**

# Demonstration projects at Dalian Institute of Chemical Physics



# Dalian 100MW VFB Demonstration Project

**The world's largest 100MW/400MWh flow battery energy storage system was connected to the grid**



**Provide technical and equipment support for energy revolution and energy structure adjustment to realize low-carbon economy.**

# License of New Gen VFB



**Kaifeng Contemporary New Energy Co. Ltd to construct 300MW/Year Stack Line**

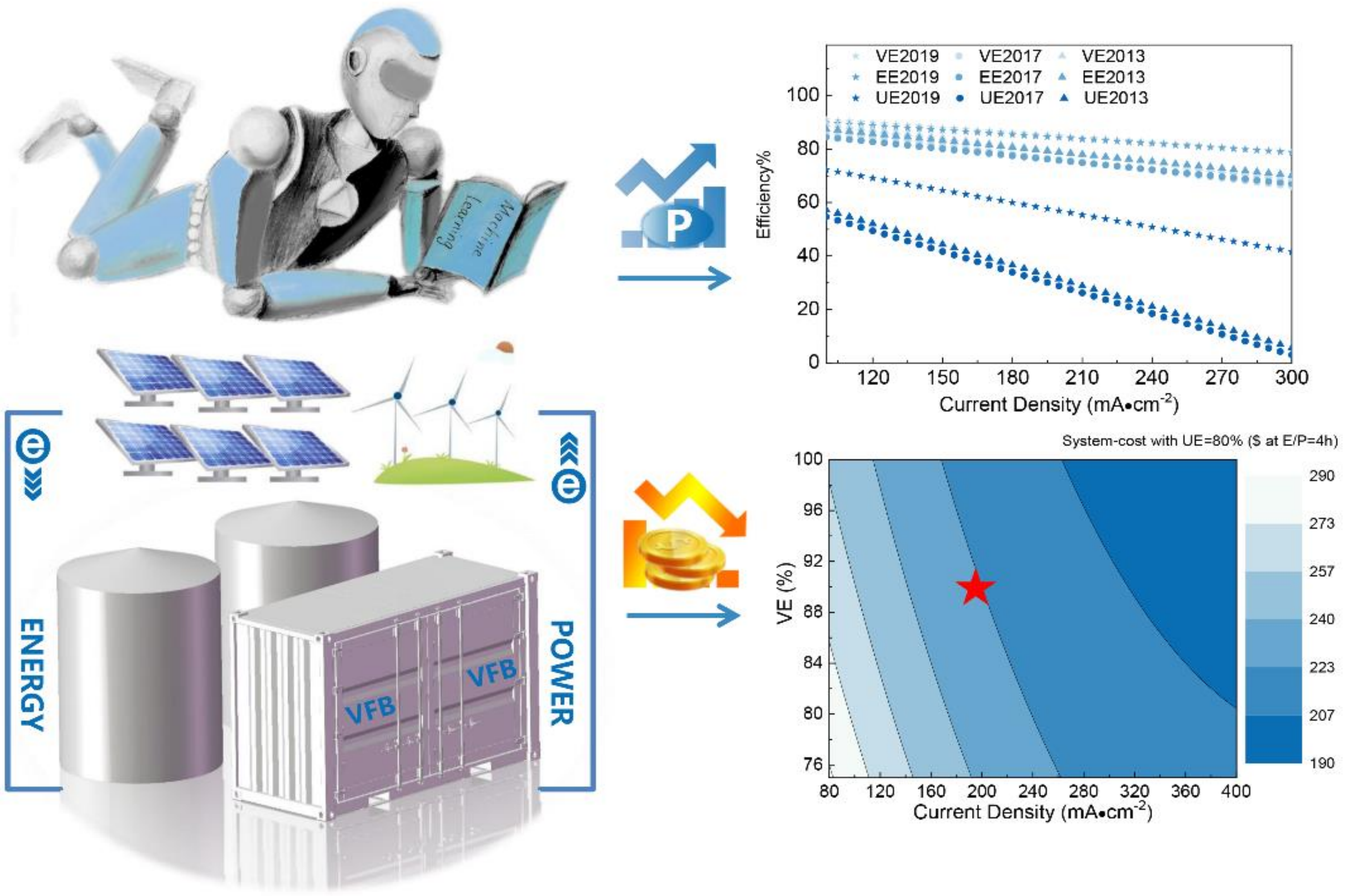
**Finished 24MW/96MWh system integration**

# License of New Gen VFB



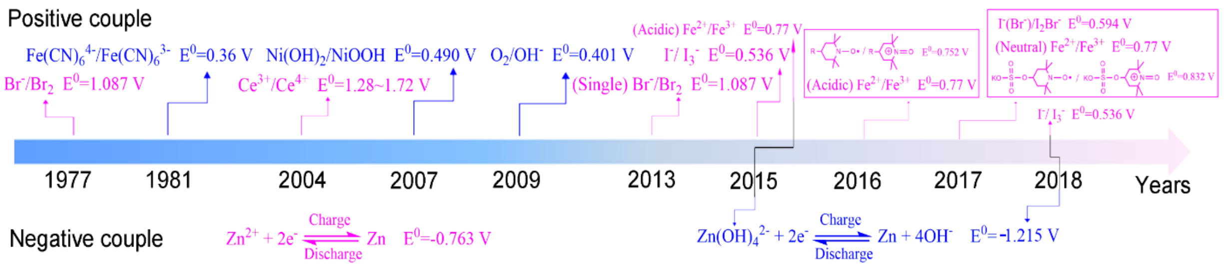
**Collaboration with EcoSourcen Belgium**

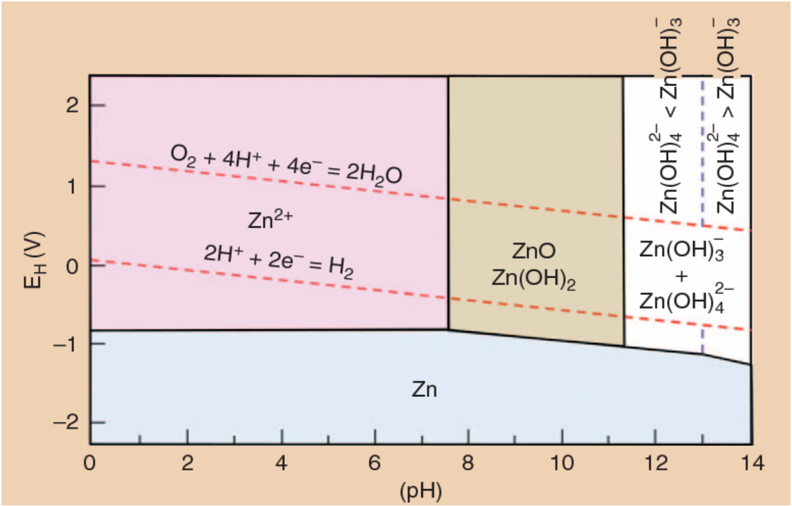
# Predicate the Cost and Development Direction of VFB by Machine Learning (ML) Methodology

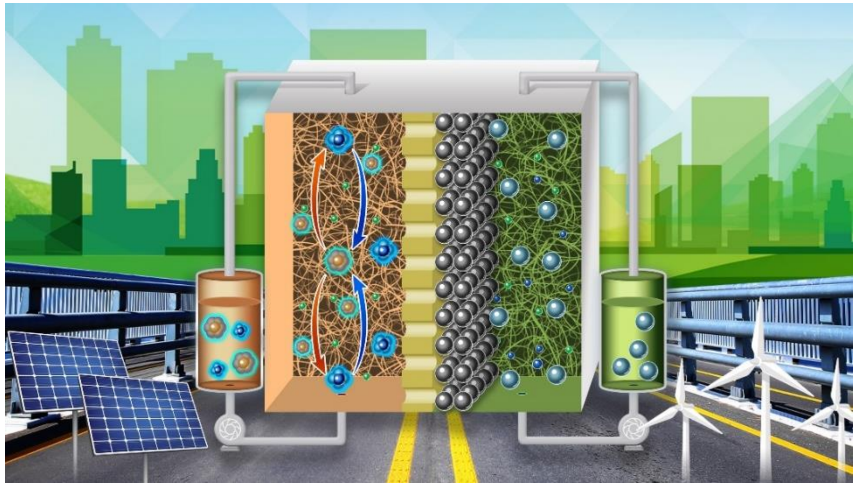


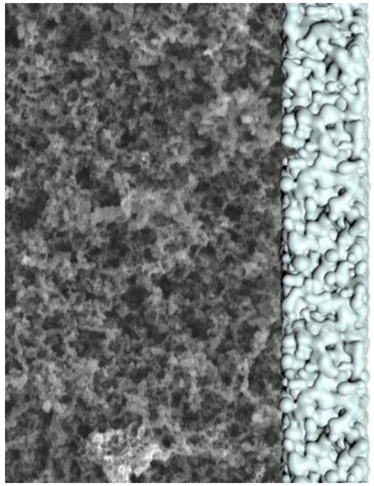

*Energy Environ. Sci. 2020, 13, 4353-4361*

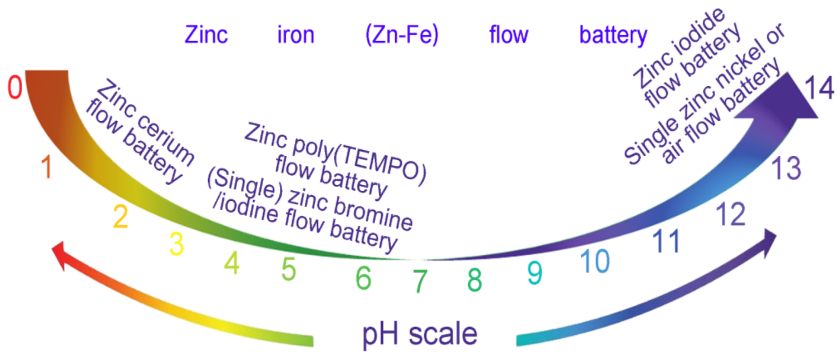
# Zinc Based Flow Battery







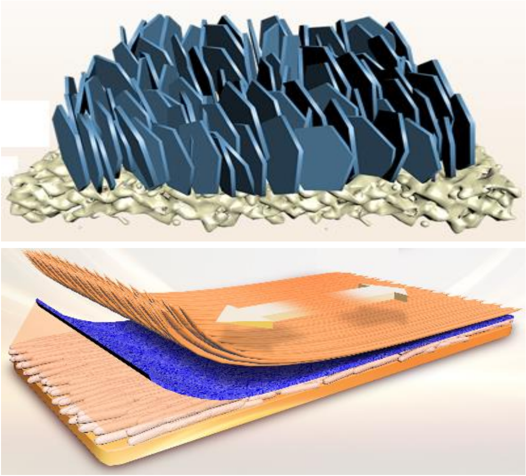

## Advantages

- Large zinc reserves and low cost
- Low potential and high energy density

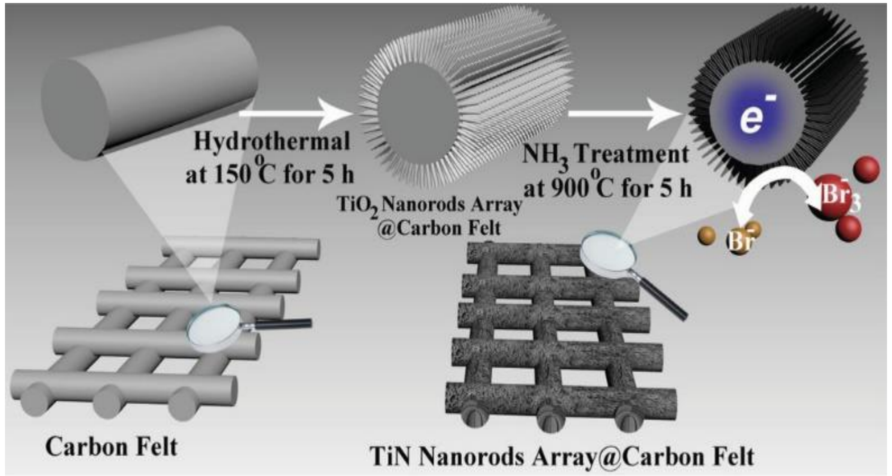
## Key scientific and technical issues

- Dendrite (short life)/low areal capacity
- Low power density, high cost of stacks

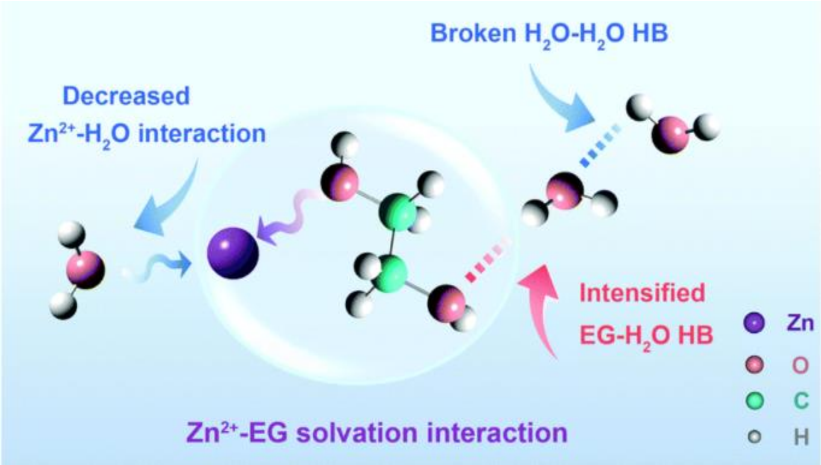
# Zinc Based Flow battery



**Membranes**




**Electrode**




**Electroltyes**

*Nat. Commun.*, 2021, 12, 3409

*Angew. Chem. Int. Ed.*, 2020, 59, 6715

*J. Am. Chem. Soc. 2021, 143, 13135*

*Adv. Mater.*, 2020, 32, 1906803

*Adv. Mater.*, 2019, 31, 1904690

*Adv. Mater.*, 2019, 31, 1902025

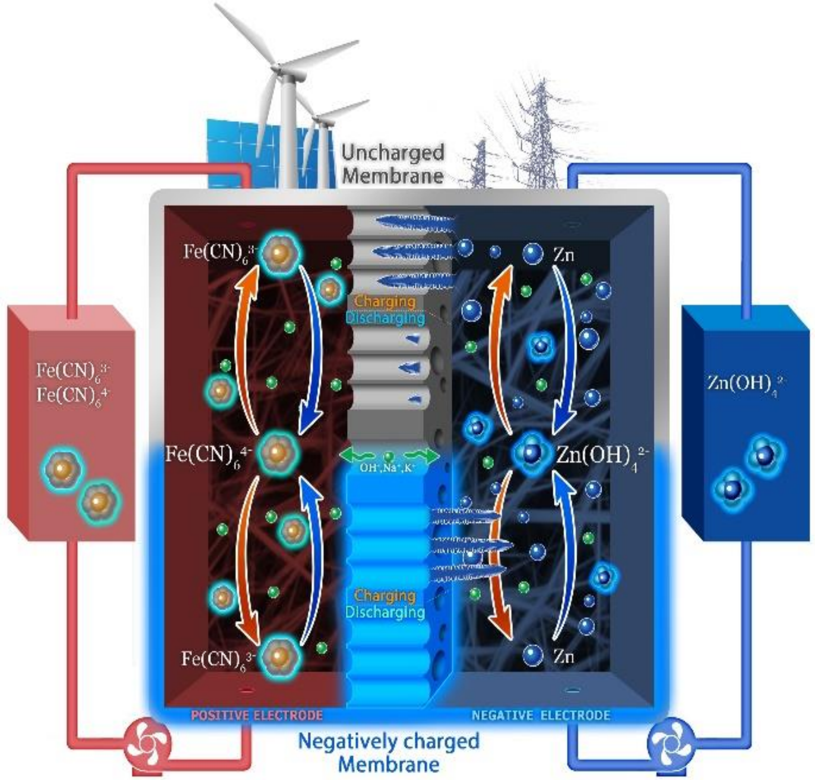
*Energy Environ. Sci.*, 2020,13, 3527

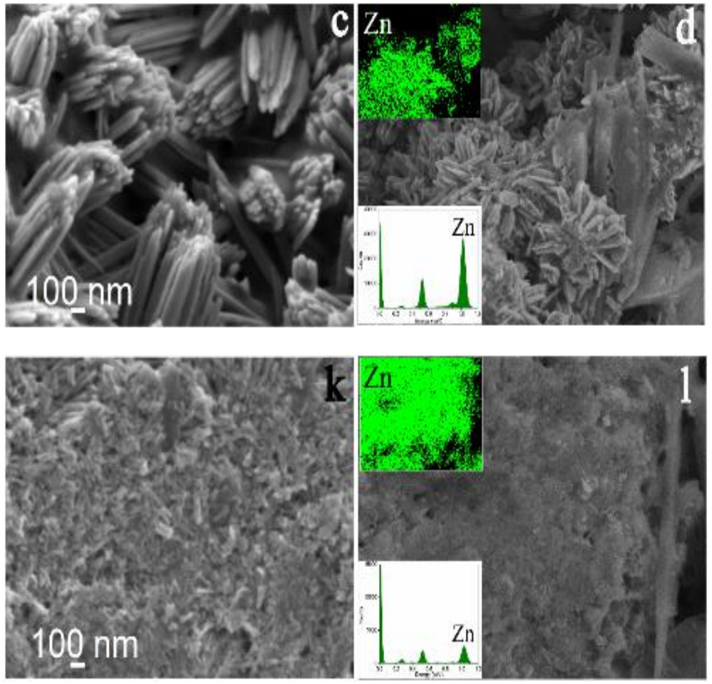
*Energy Environ. Sci.*, 2020,13, 135

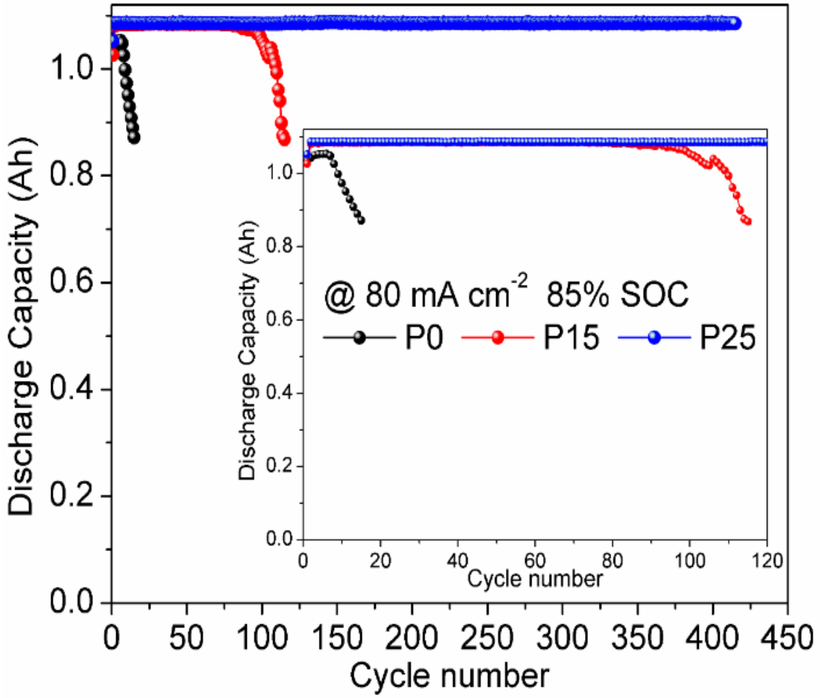
*Energy Environ. Sci.*, 2019, 12, 1834

**To solve the challenges of zinc dendrites and improve areal capacity**

# Structure design: Regulation of charge characteristics



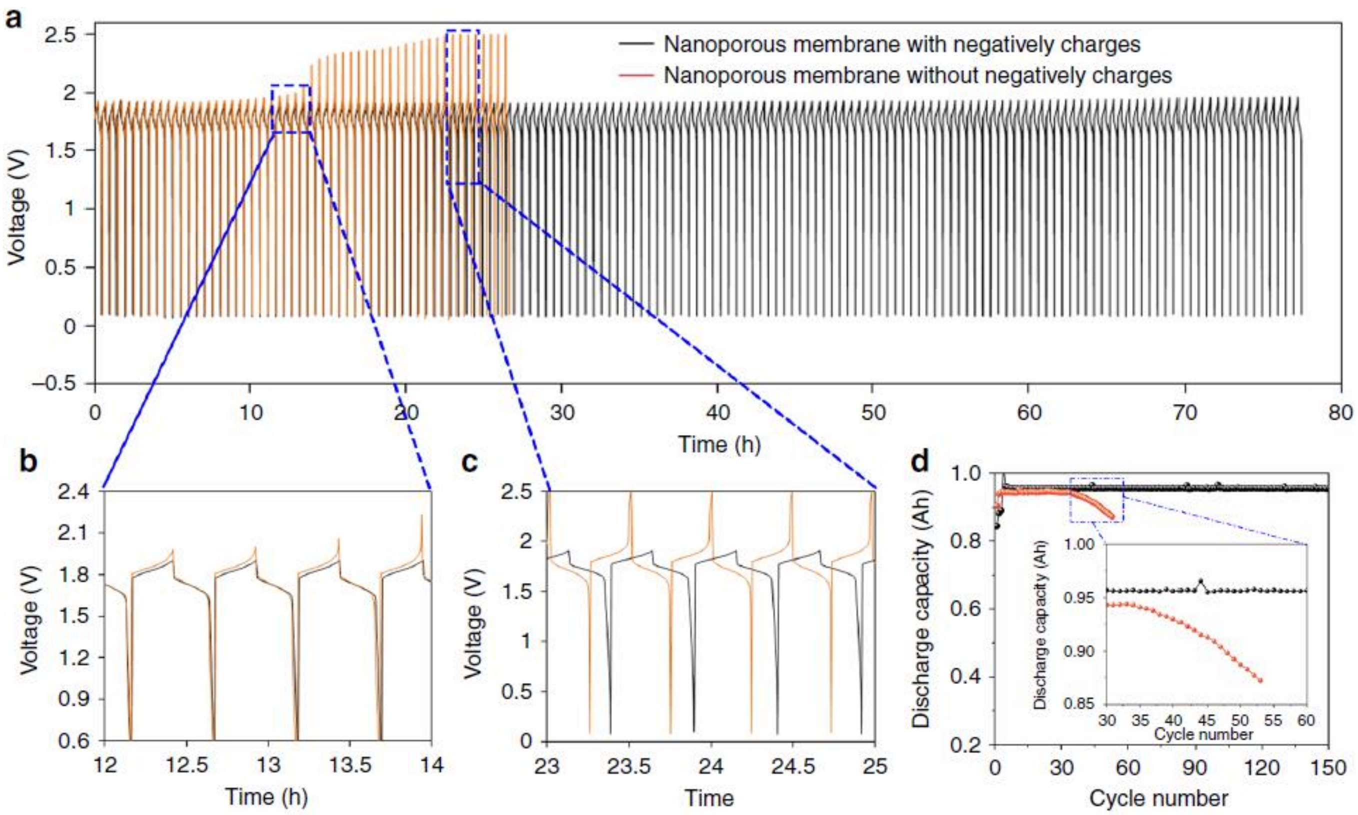



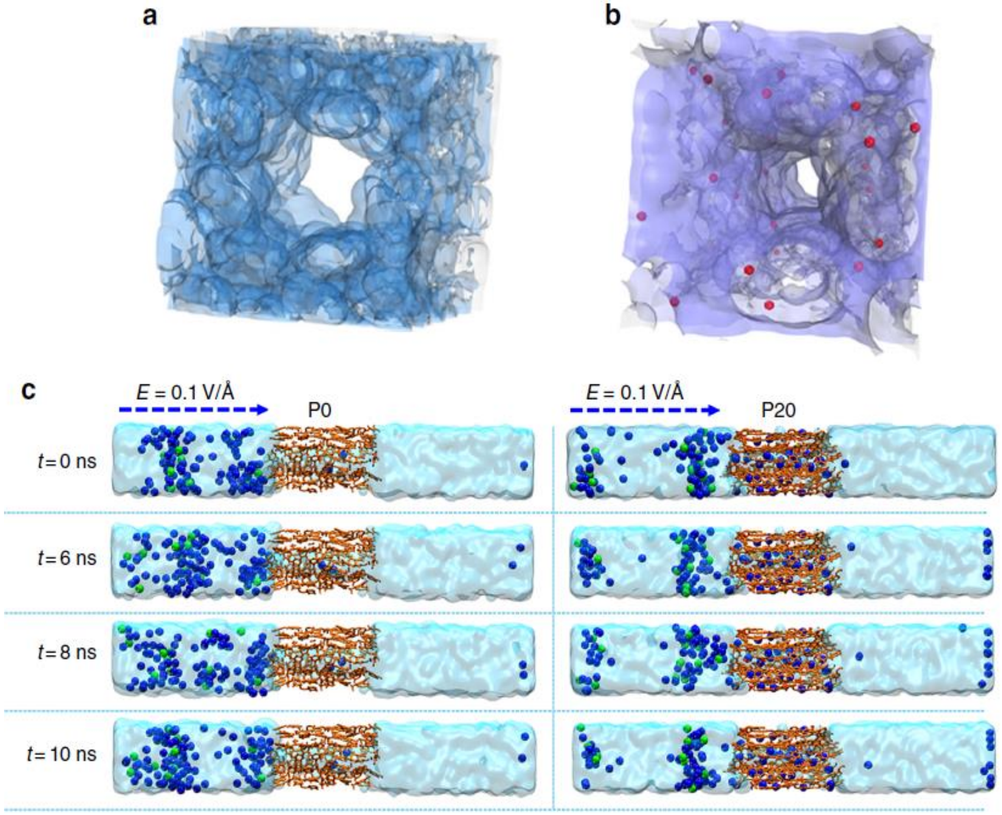




Based on the mutual repulsion between the negatively charged $Zn(OH)_4^{2-}$ and the negatively charged membrane surface, the directed zinc deposition was achieved, solving zinc dendrite/accumulation issues.

***Nat. Commun. 2018, 9, 3731***

# Structure design: Regulation of charge characteristics

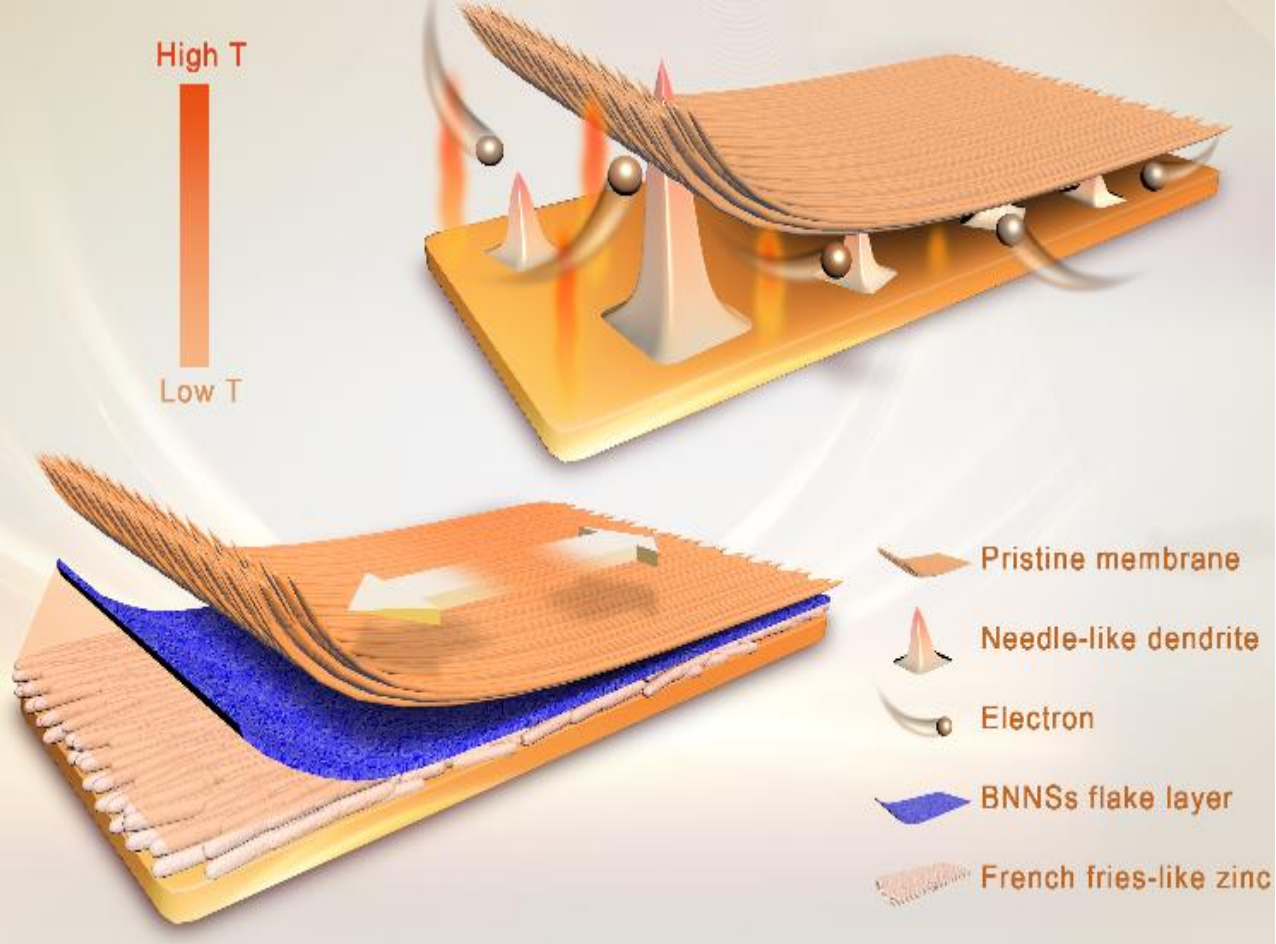


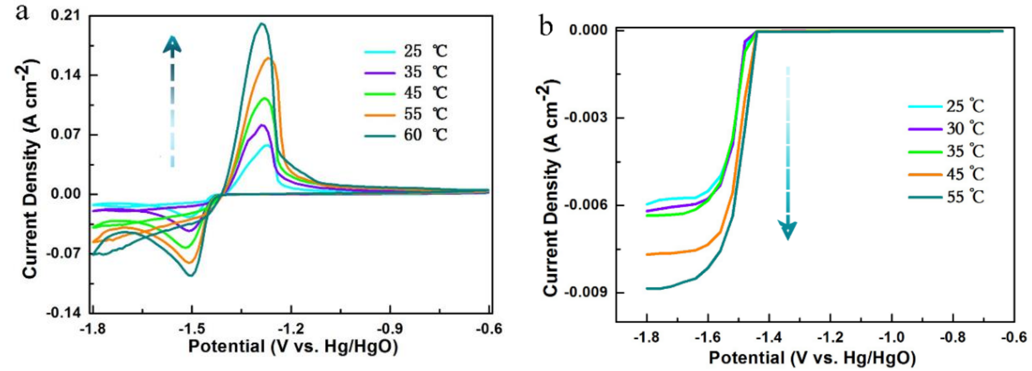



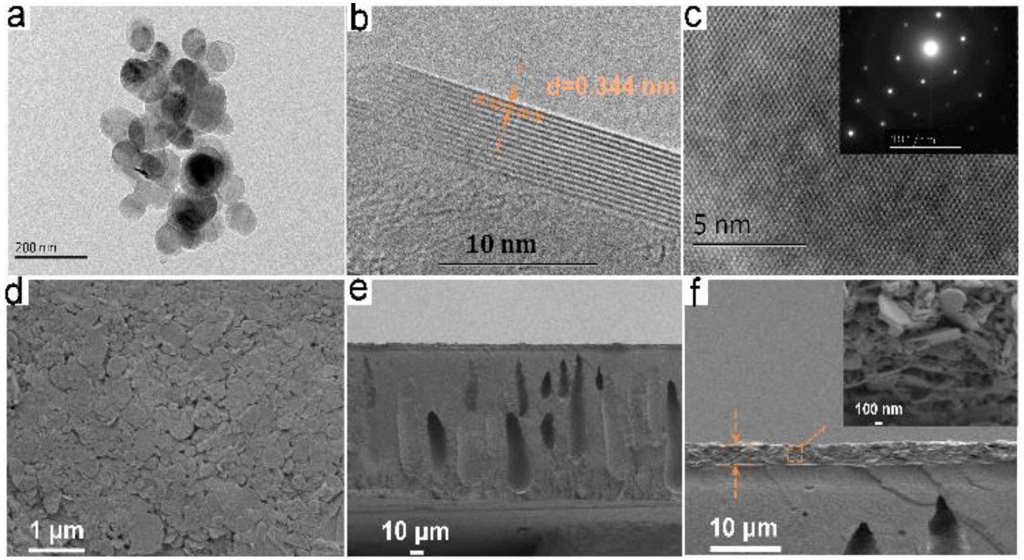

The directed zinc deposition prevented the membrane from being broken,

increasing the cycling stability dramatically of batteries.

# Structure design: BN composite membrane



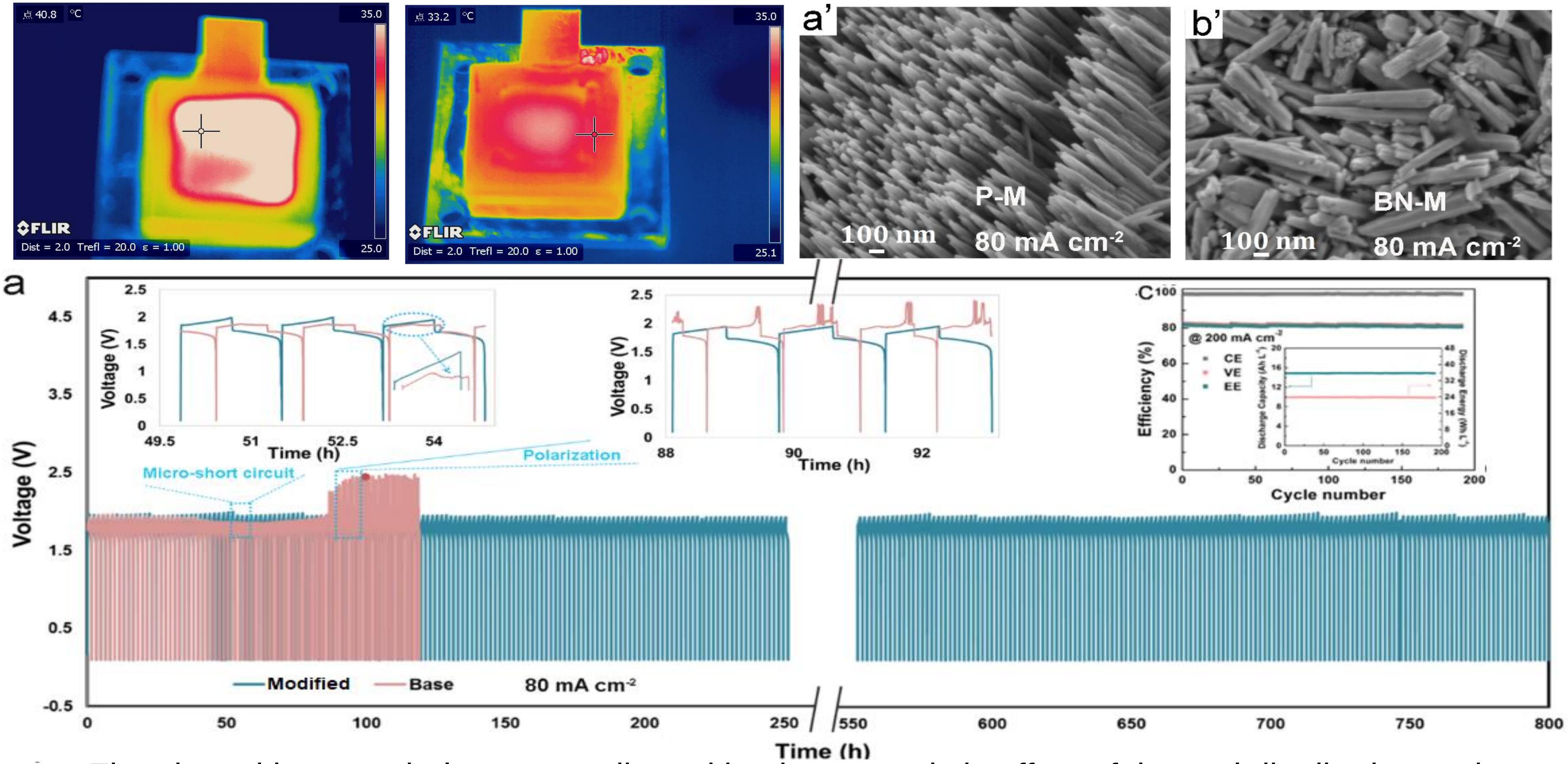




BN composite membrane —Coating thermal conductive BN layer on a porous substrate. By regulating the electrode surface temperature distribution, the uniform and dense zinc deposition was achieved.

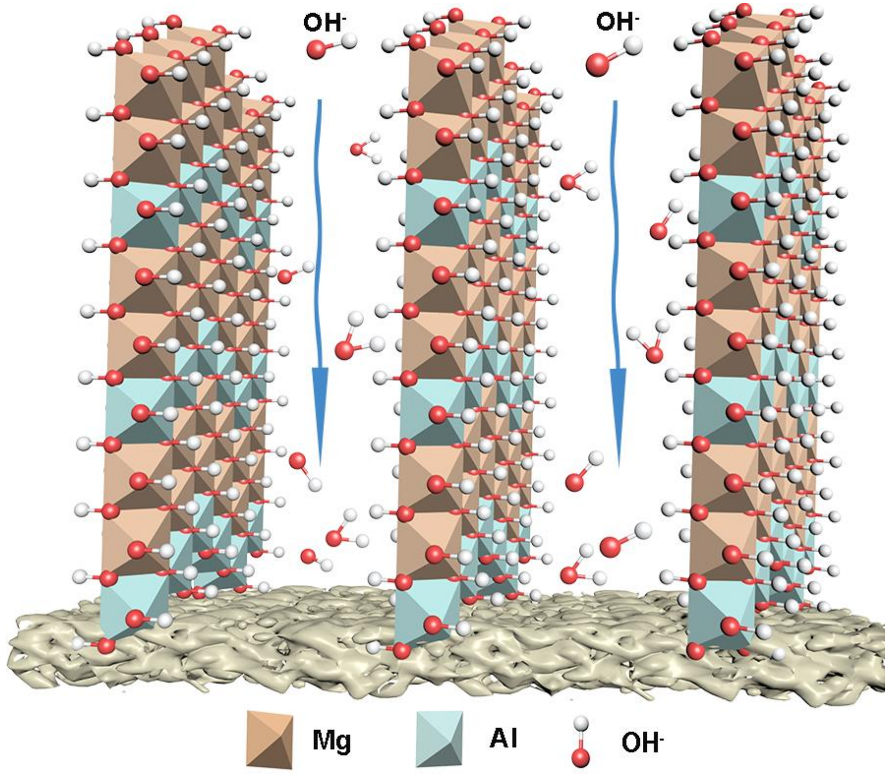
***Angew. Chem. Int. Ed. 2020, 59, 6715***

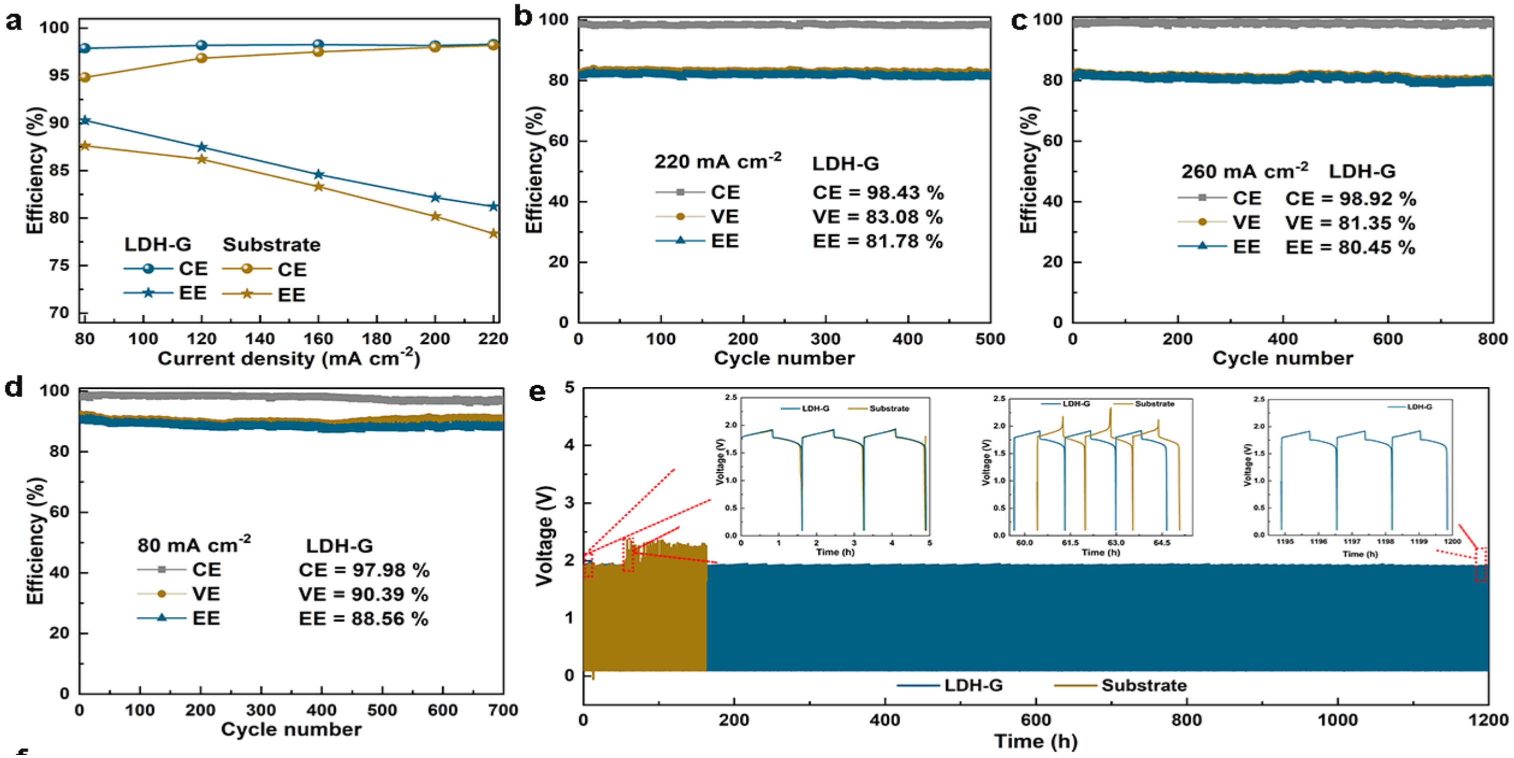
# Structure design: BN composite membrane




Zinc deposition morphology was adjusted by the synergistic effect of thermal distribution and mechanical strength, obviously increasing the lifespan and power density of batteries.

# Structure design: LDH composite membrane

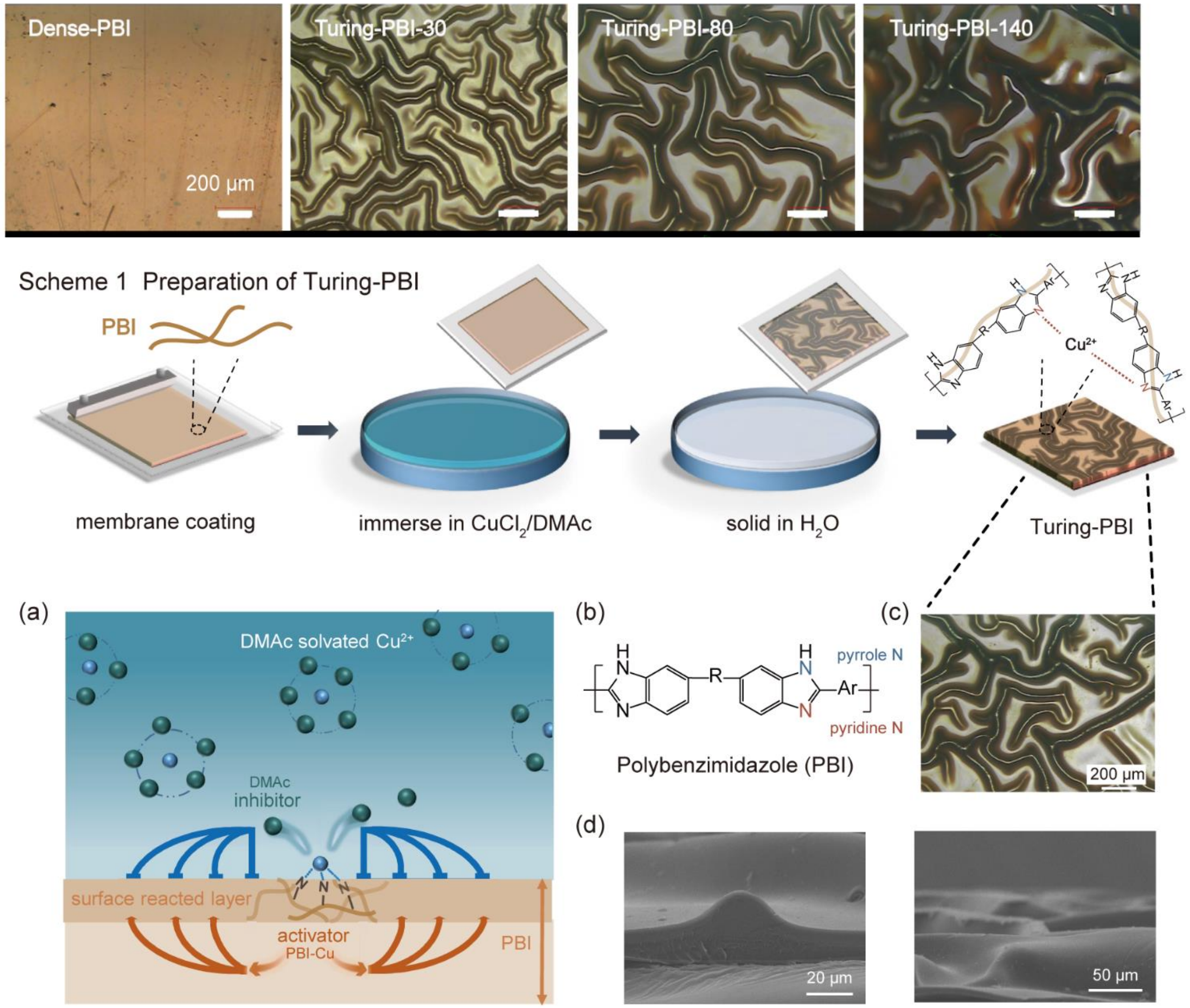


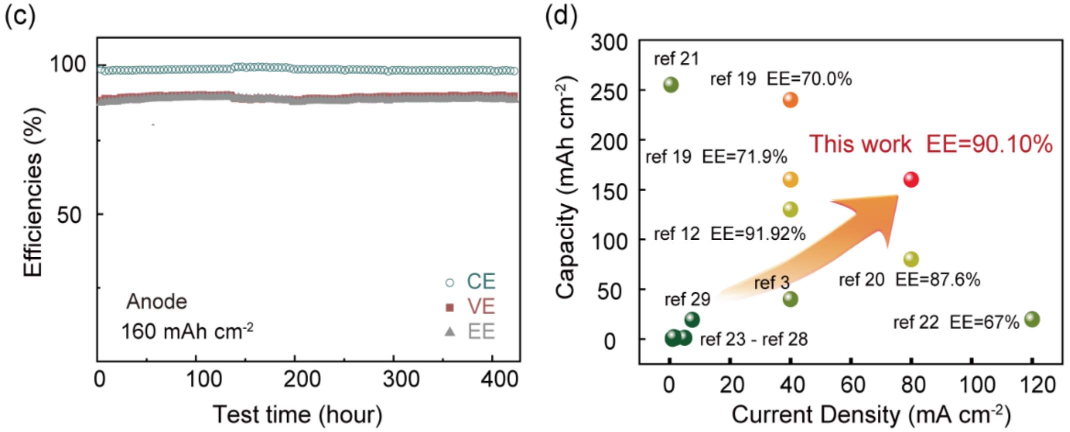



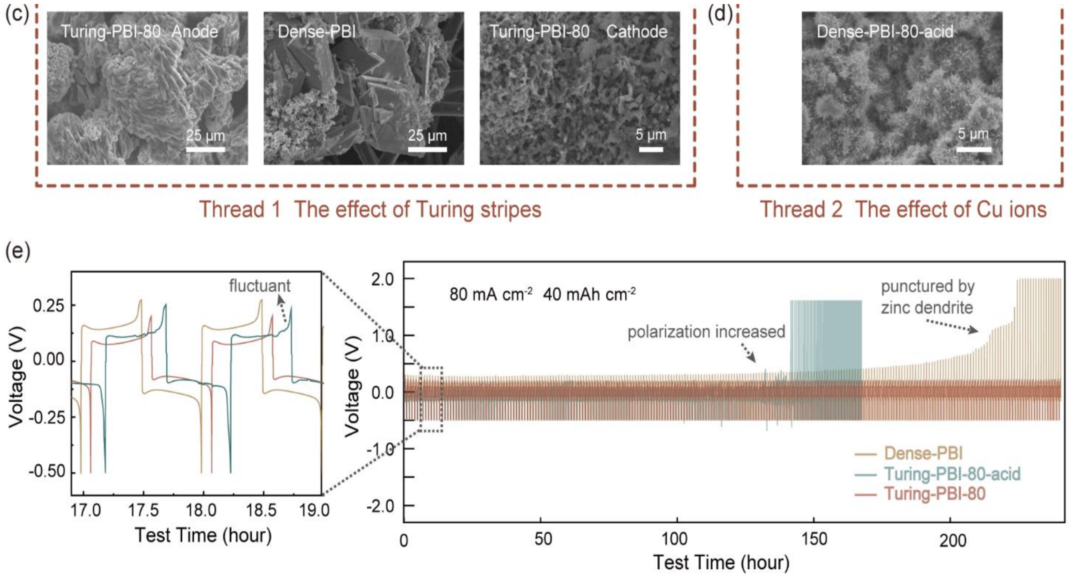

The fast hydroxide ions transport behavior in LDHs channels was attributed to the mutual effect between the hydroxyl groups, interlayer anions, and water molecules in the gallery.

***Nat. Commun.* 2021, 12, 3409**

# Structure design: Turing membrane with high specific surface area

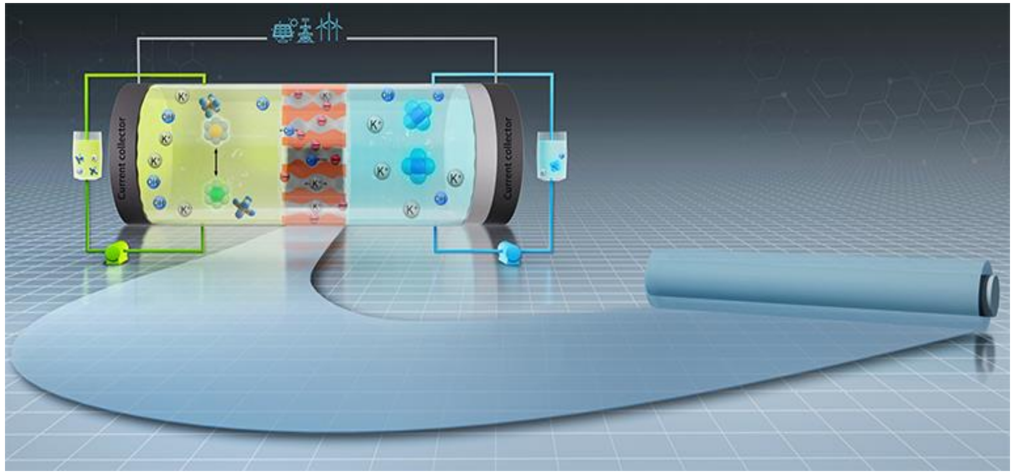


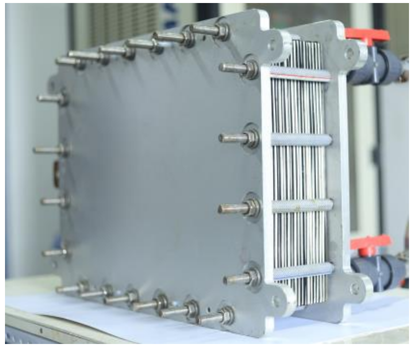

***J. Am. Chem. Soc. 2021, 143, 13135-13144, Adv. Energy Mater. 2023, 13, 2300779, Nature Communications, 2023, 14, 1149***

# Upscaling process on membranes

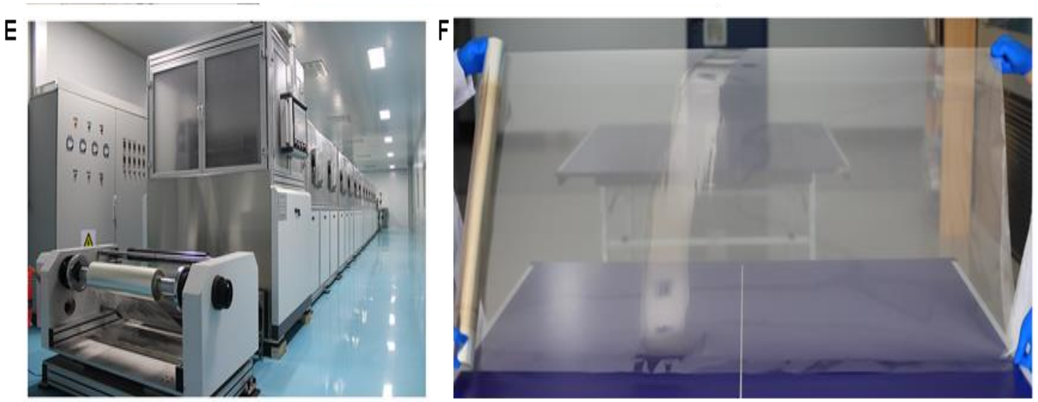


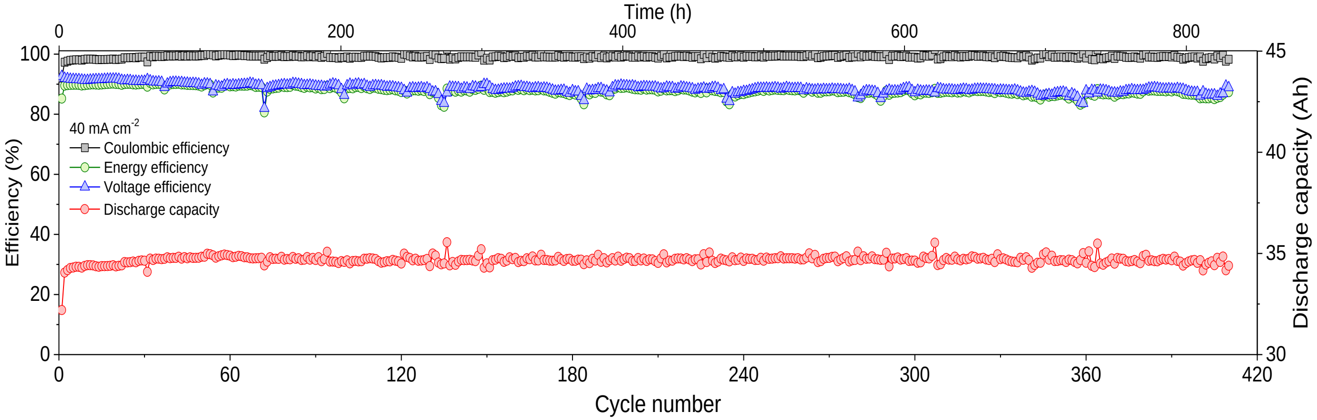

300 W


1000 W



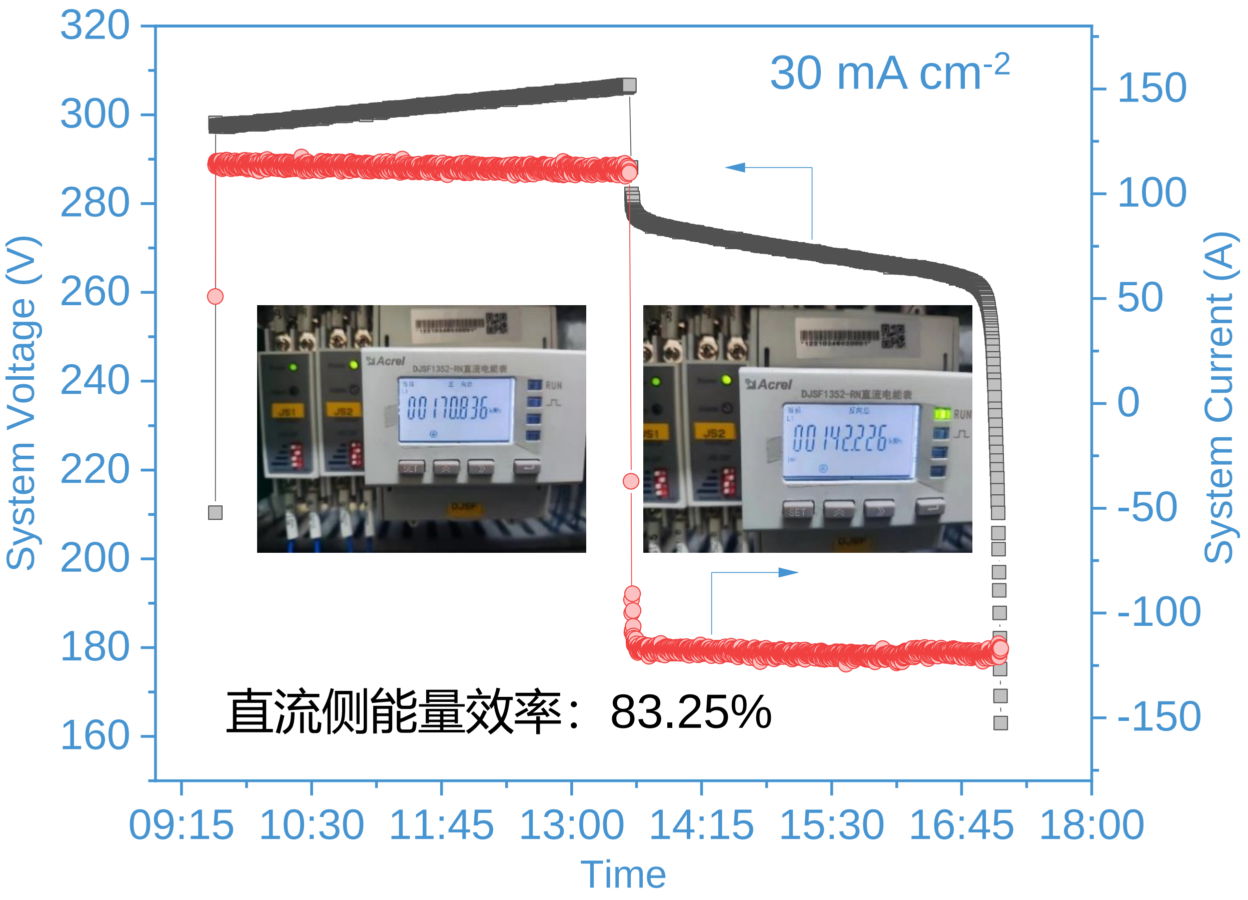
4000 W






***Joule. 2022, 4, 884-905***

# Applications of designed membranes in system


**A 100 kWh zinc-bromine flow battery system was successfully installed and operated in Yulin Branch, affording a DC-DC energy efficiency of 83.25%.**

# New flow battery system with high energy density

$$\text{Energy density} = \frac{NC_0FV}{n}$$

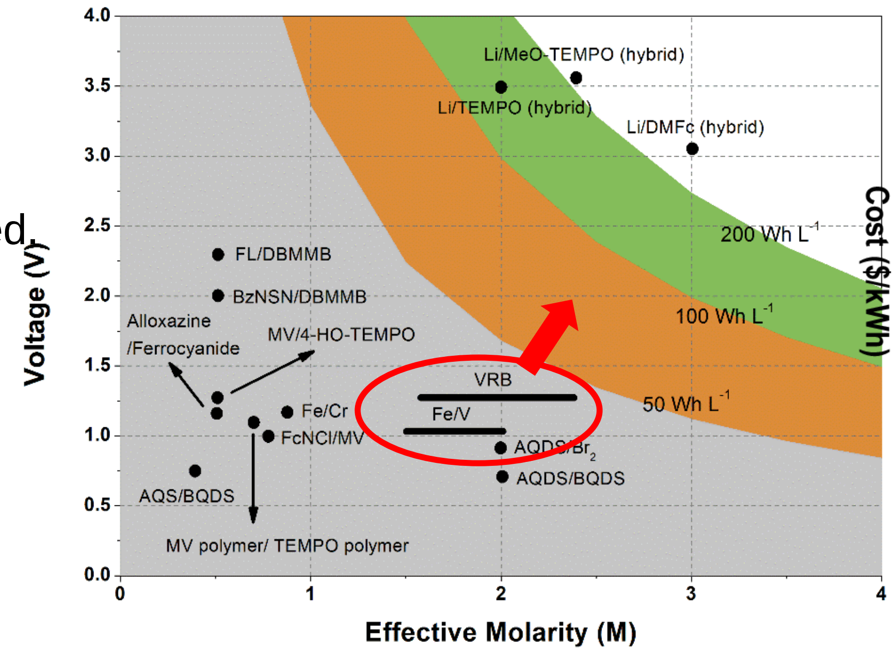
$N$ : The number of electrons transferred

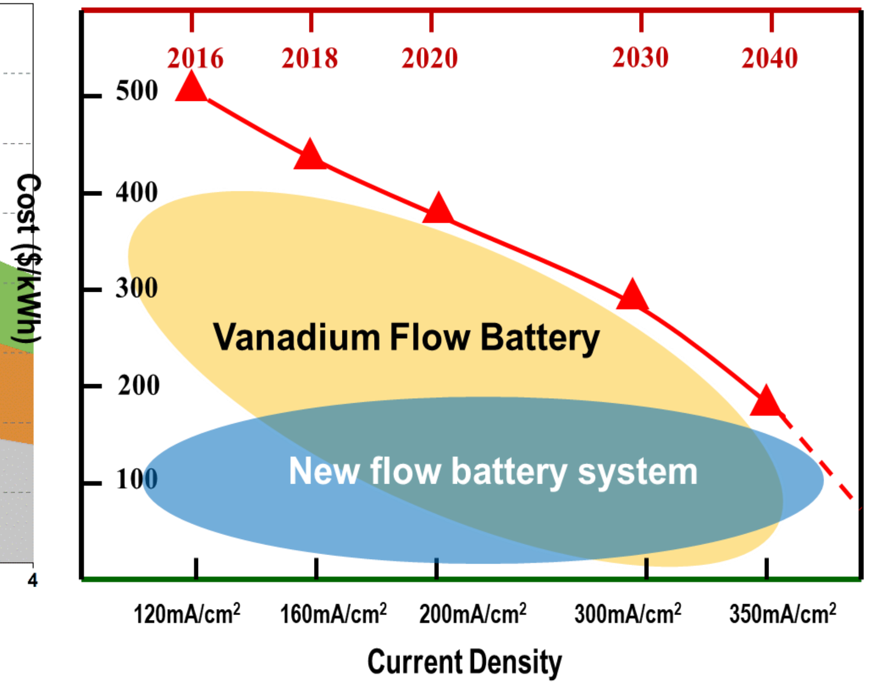
$F$ : Faraday constant (26.8 Ah mol$^{-1}$)

$C_0$ : Max concentration of redox molecules

$V$ : Voltage of the cell

$n$ : Number of electrolyte tanks



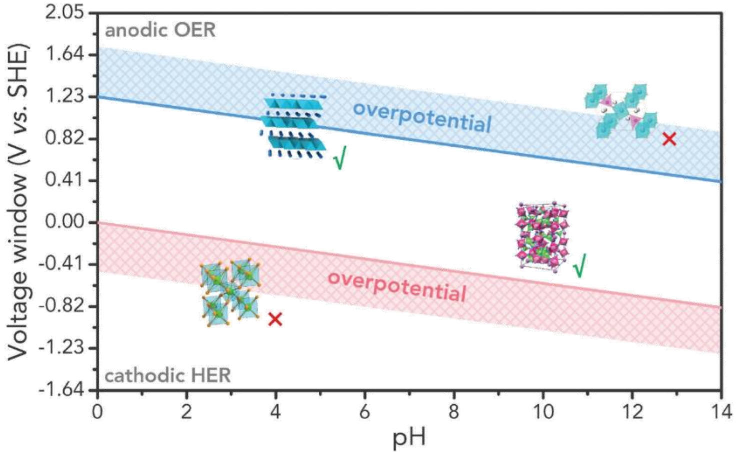




Chem. Soc. Rev. 2018, 47, 69

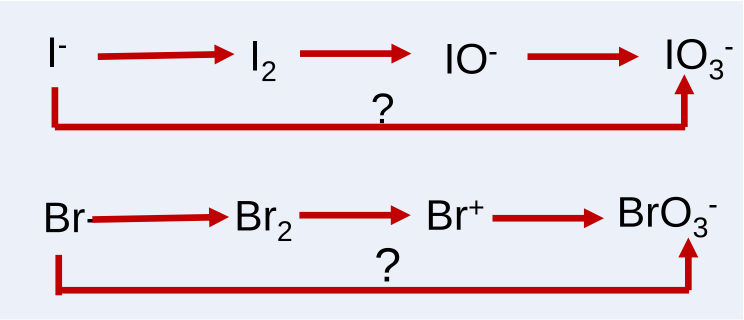
**The high-energy-density, low-cost flow batteries is of great significance to promote the sustainable development of FBs**

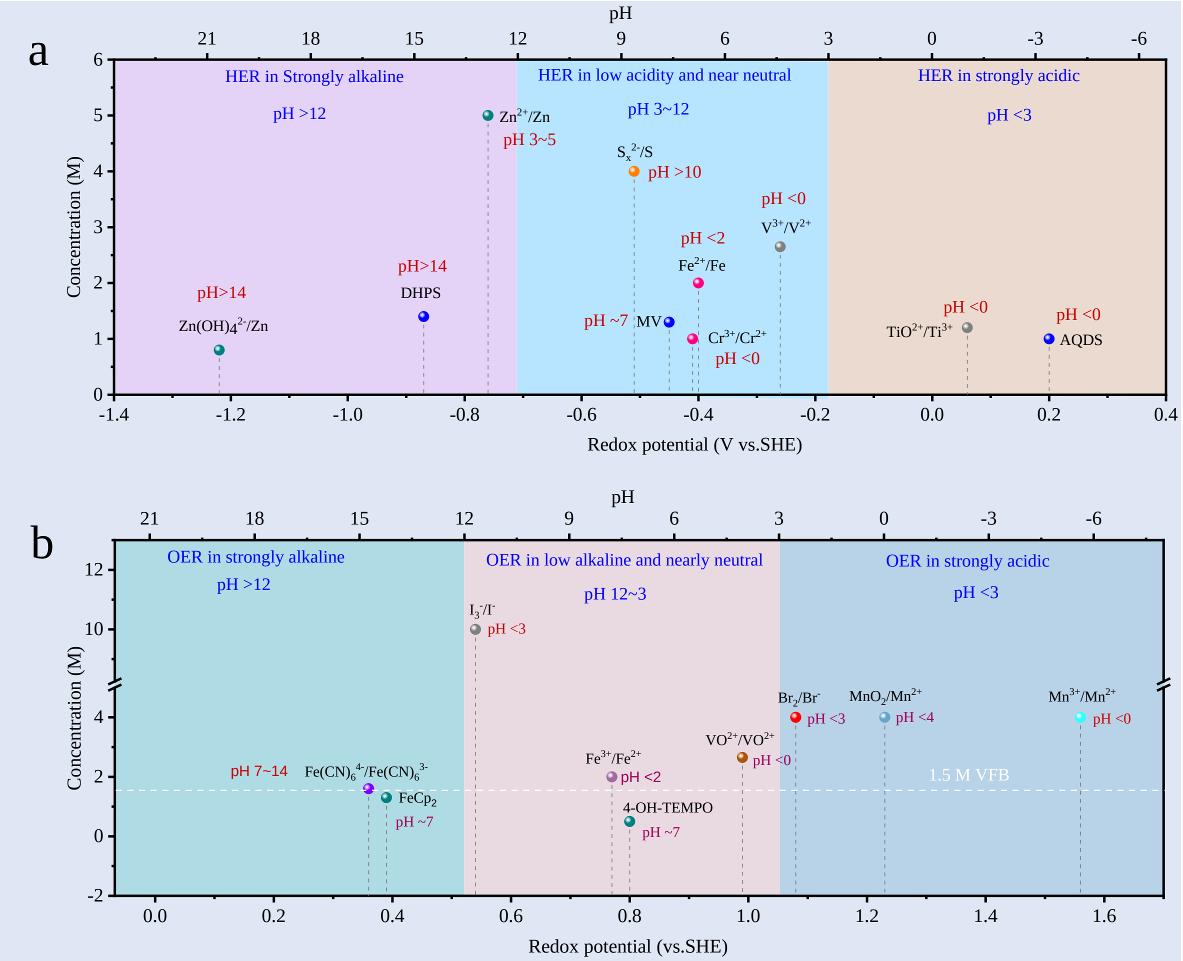
# Overall research idea: multi-electron transfer reaction

Limited potential window




Multiple electron transfer

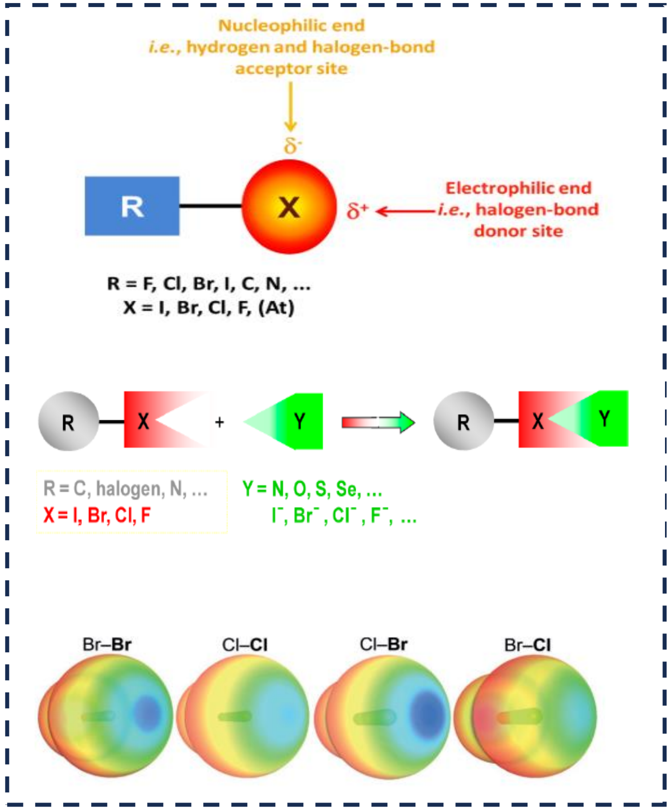


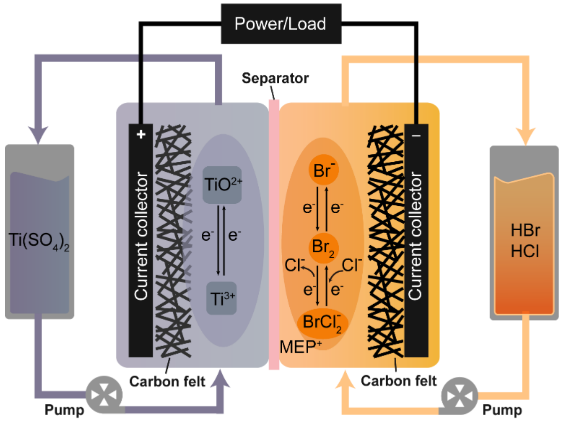



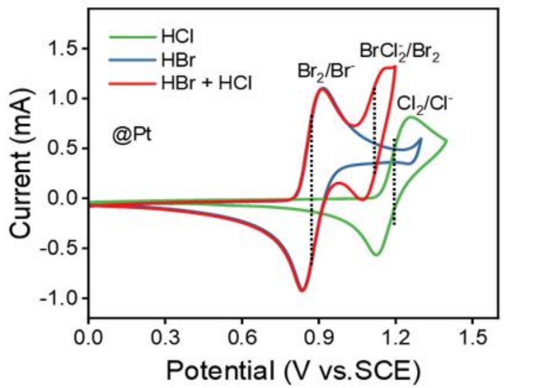

**High Energy Density Flow Batteries: Voltage, Solubility, *Electron Transfer Number***

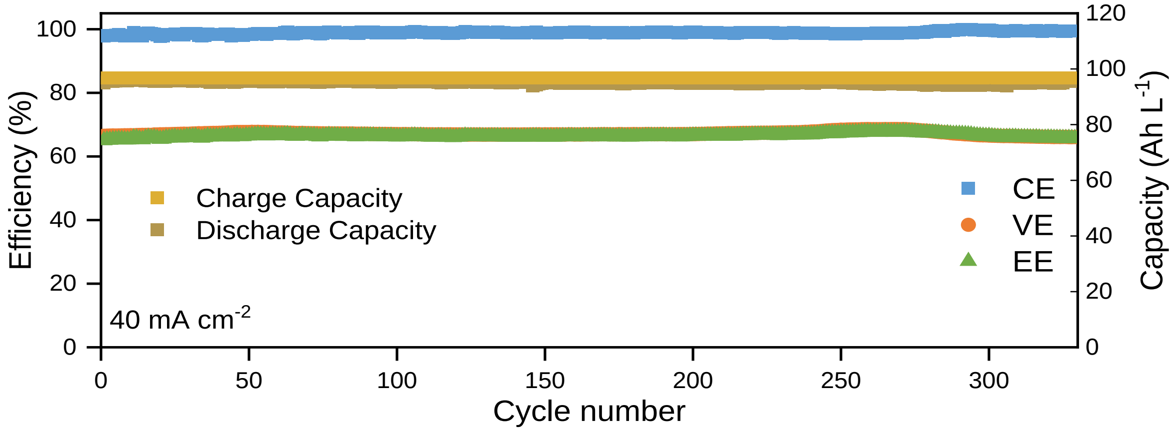
*Chemical Society Reviews*, *49*(1), 180-232

# Bromine based multi-electron transfer system



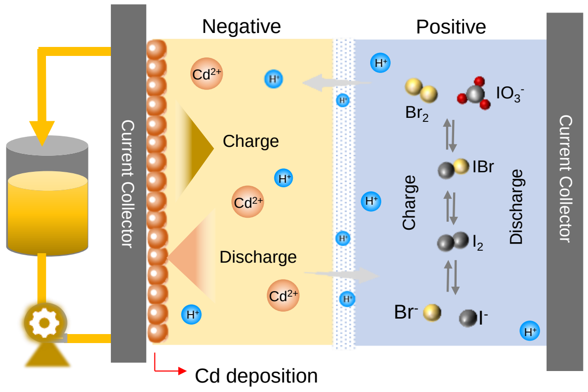



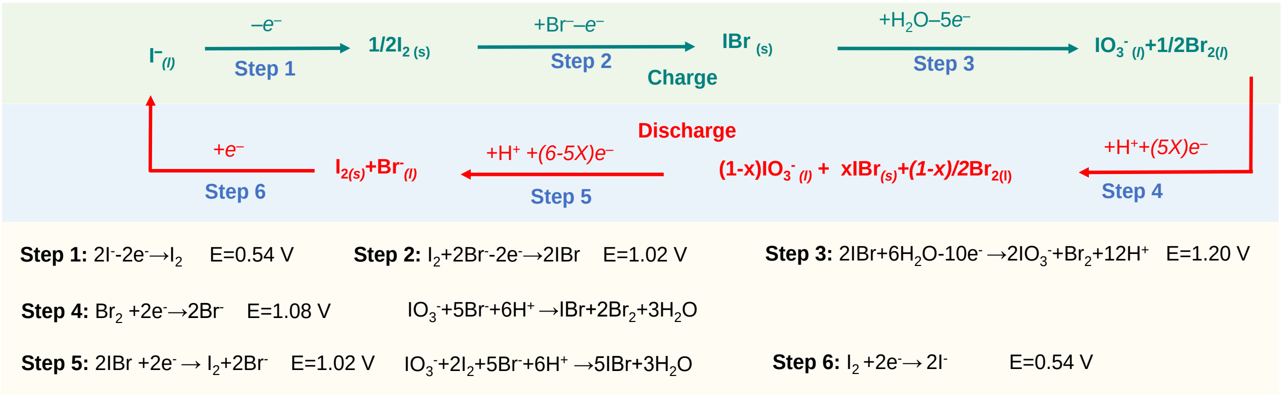

➢ There is a halogen interaction between Cl and Br to form $BrCl_2^-$, thereby realizing the two-electron transfer reaction of $Br^-/Br^+$

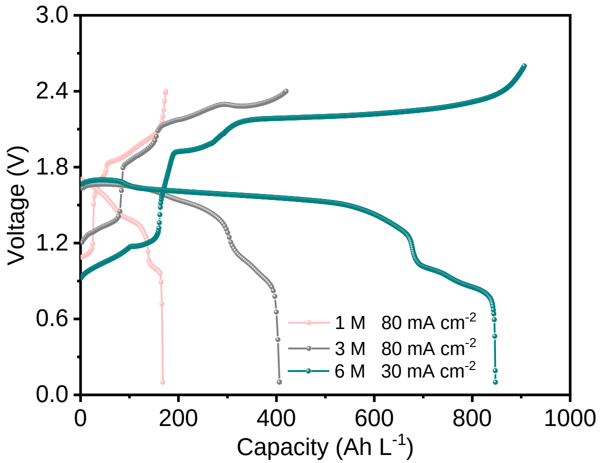
*Angew Chem, 2018, 57, 9141-9145; Angew Chem, 2020, 59, 5464-5493*

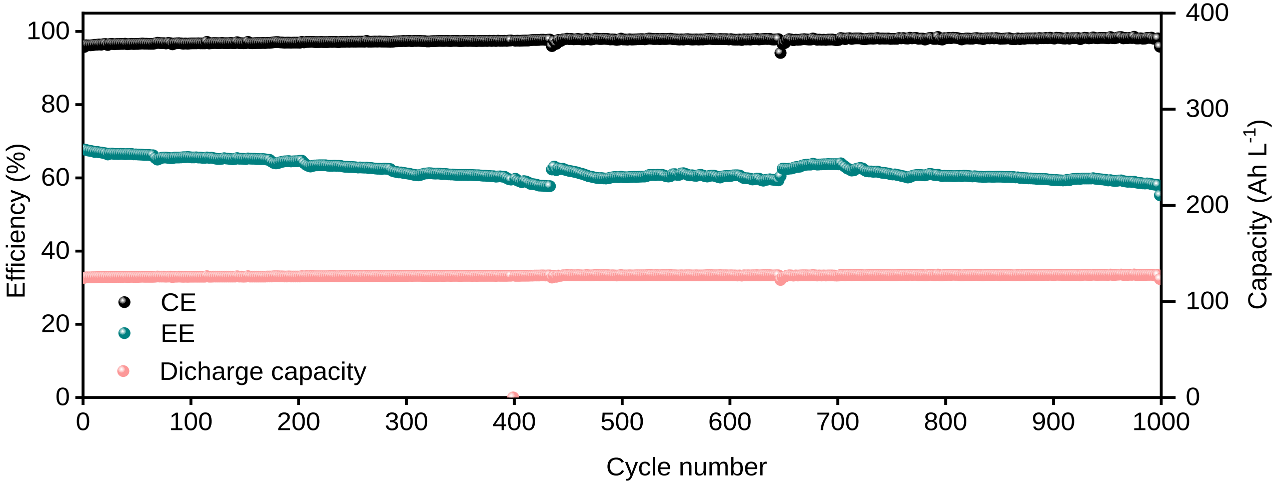
*ACS Energy Lett. 2022, 7, 1034-1039*

# Iodine based multiple electron transfer system



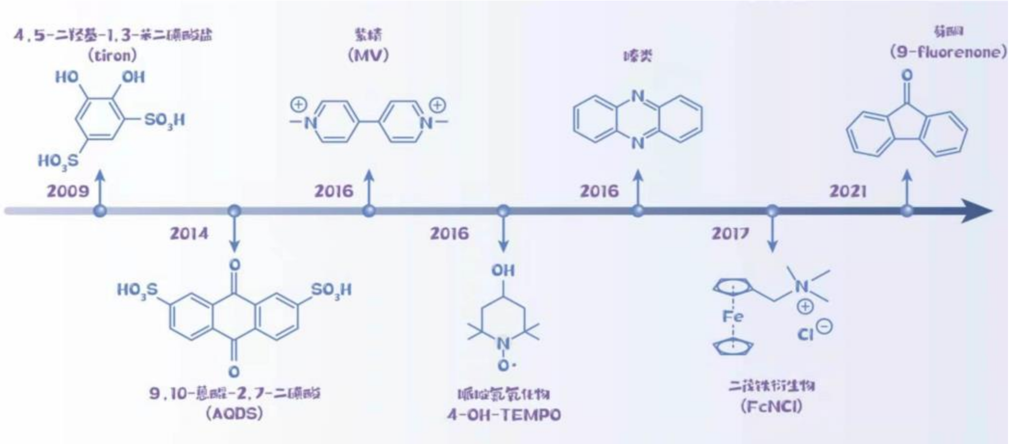



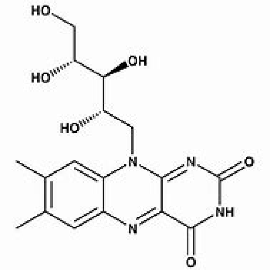




**Electron transfer number can reach 32 M. The energy density exceeds 1200 Wh L$^{-1}$.**

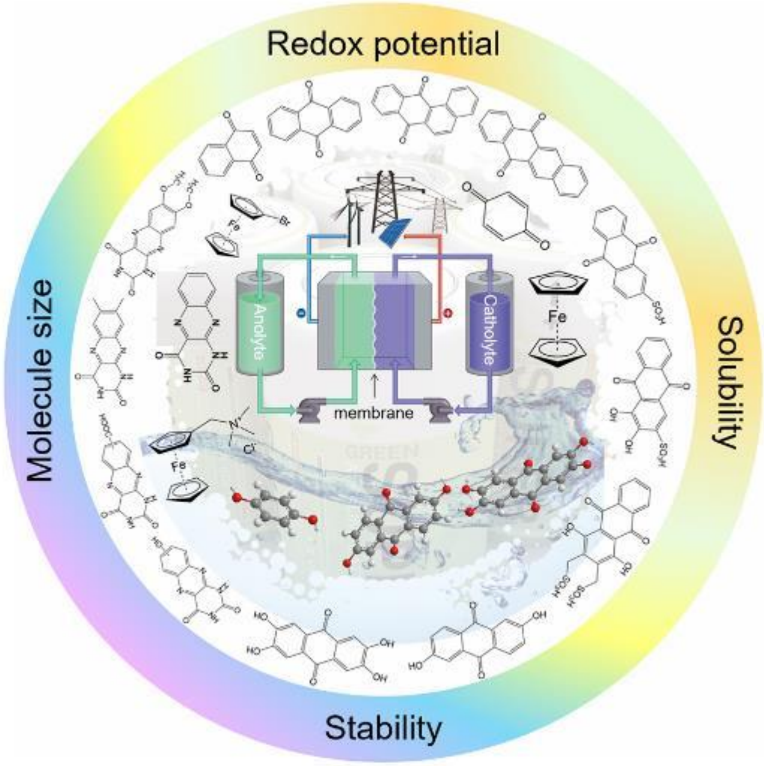
Nature Energy (In revision)

# Organic Flow batteries



*Bio-inspired materials*




**Advantages:**

Scalability, efficient biodegradability

Minimal environmental footprint

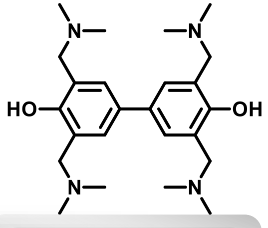
Highly tailorable chemical and physical properties by molecular engineering methods

Science, 2021, *372,* 836. Science, 2015, 349, 1529. Chem. Soc. Rev., 2018, 47, 69

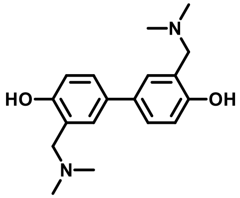
# High voltage-Biphenyl based Catholyte

## Biphenols based derivatives

TABP

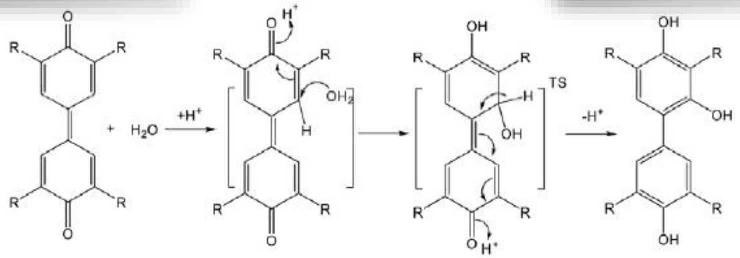


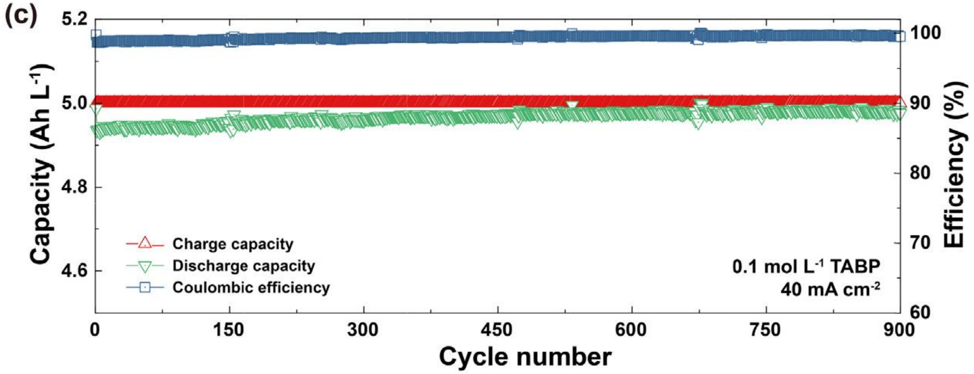

DABP




stable

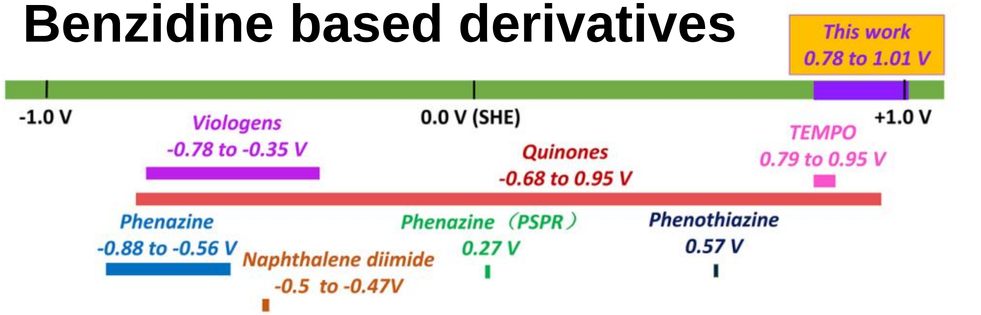
unstable



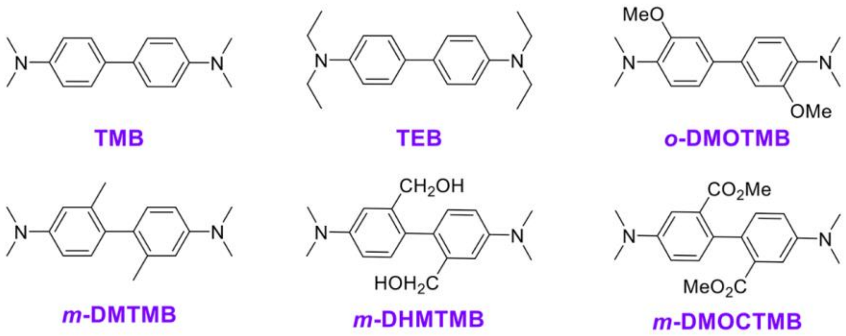



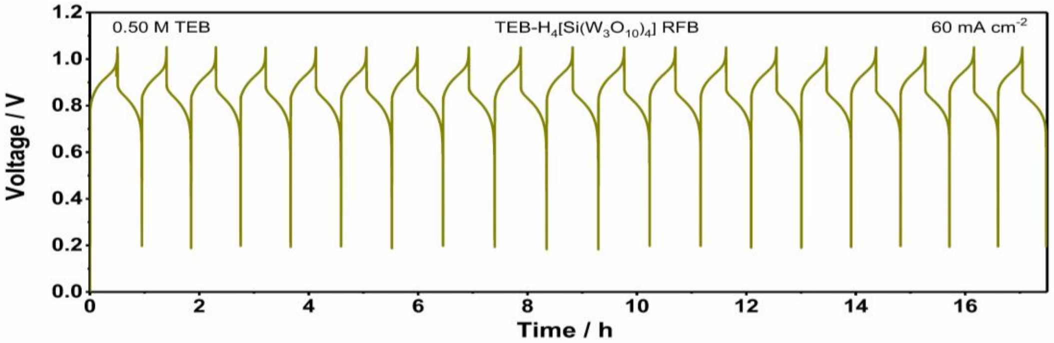

W. Liu, Z. Zhao, T. Li, S. Li, H. Zhang, X. Li, *Science Bulletin* 2021, 66, 457

## Benzidine based derivatives




This work

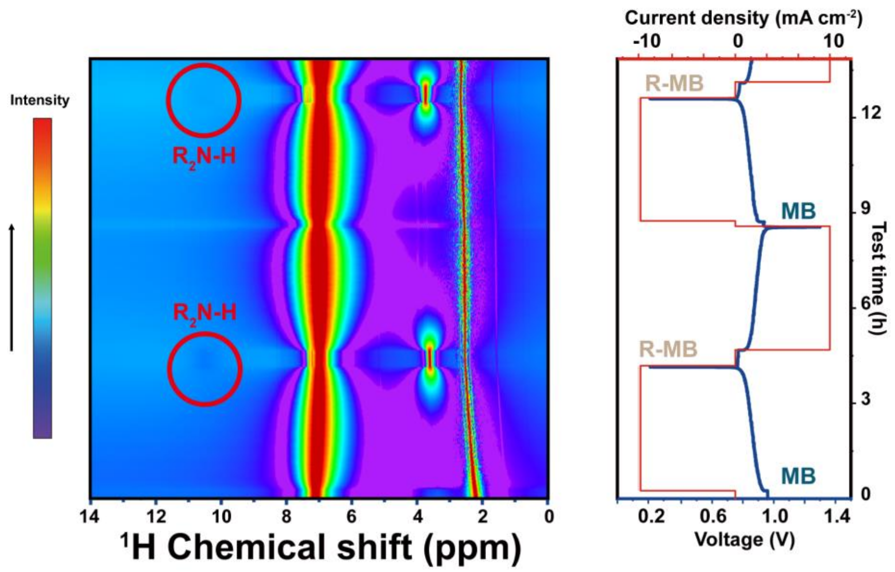


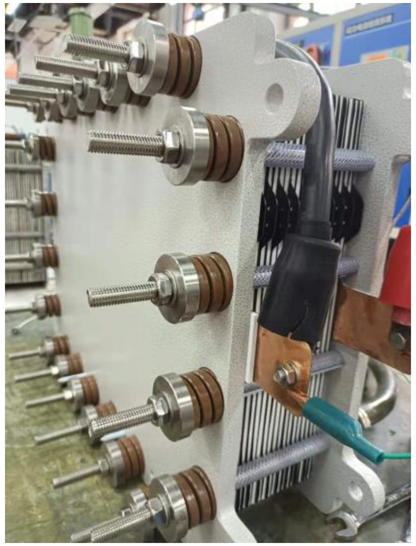

**Average discharge capacity 24.47 Ah L$^{-1}$ Energy efficiency 84.69%**

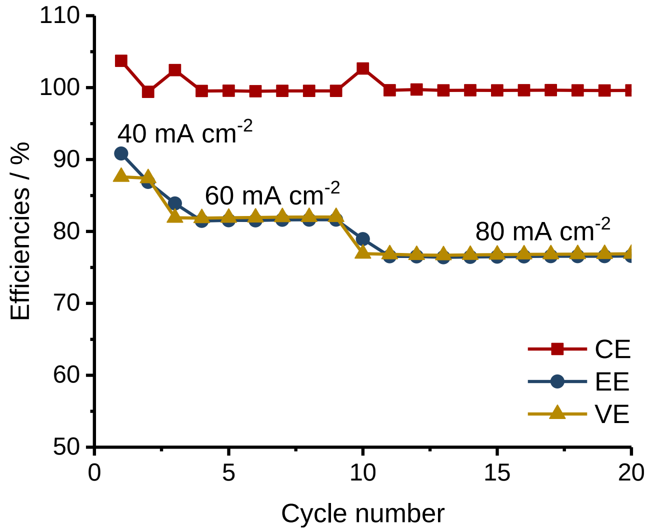
Angew. Chem. Int. Ed. 2023, DOI: 10.1002/ange.202307796

# Develop stable kilowatt-scale AOFBs

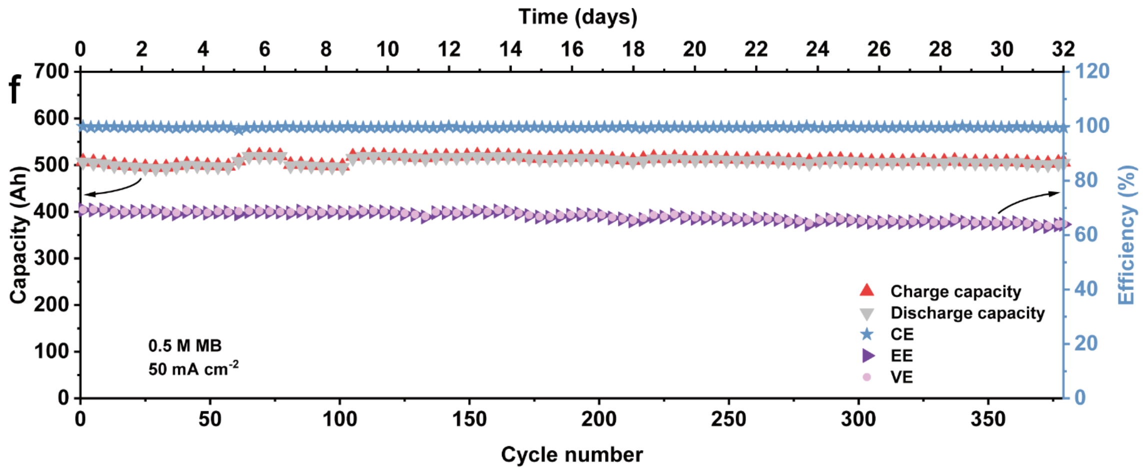



In-stiu NMR






V-MB stack 1000 cm$^2$ 10 cells




- MB is reversible during charge-discharge process
- The stack achieved a stable long-life cycle performance at 0.5 M MB electrolyte with the capacity of ~ 510 Ah

*Energy Environ. Sci. 2023, 16, 231-240*

# Summary

- Vanadium flow battery needs to further increase power density and optimize operation mode.
- Zinc-based flow batteries exhibit application prospects for distributed energy storage, which have been in the stage of pilot scale-up and need to further improve their reliability.
- Improving the stability, reliability, and energy density of organic aqueous flow batteries and developing multi-electron transfer aqueous batteries have good application prospects.

# Acknowledgement


The ministry of Science and Technology of PRC (MOST)

National Natural Science Foundation of China (NSF)

Chinese Academy of Science (CAS)

Dalian Institute of Chemical Physics (DICP)



Dalian Rongke Energy Storage

Kaifeng Times New Energy

Belgian Cord Group

Shaanxi Huayin

Shaanxi Huaqin Energy Storage

Yantai Jinsun New Energy

Liaoyang Xinde New Material

Israel Chemical Group

Our cause, the future of energy

# Thanks!

Contact us

Tel: +86-0411-84379669

E-mail: lixianfeng@dicp.ac.cn

Website: www.energystorage.dicp.ac.cn