Development and Challenge of Vanadium flow Battery Technology

Prof. Huamin Zhang

Dalian Institute of Chemical Physics (DICP)
VP. and CTO. Rongke Power Co., Ltd. (KRP)

Sep. 27th, 2013 Beijing
Energy storage division

Dalian National Lab for Clean energy

Division of Energy storage
Division Head: Prof. Huamin Zhang

Around 30 staffs
20 graduate students

PEMFC & flow battery testing, evaluation

High energy density Li battery

Materials and technologies
For flow batteries

Li-Air
Li-S

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

- Materials
- Stacks
- System integration

- Materials
- Components
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 m² 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
Why energy storage?

Non-controllable
Too “random” to be connected to the grid for widely use.

Solar energy
Wind energy
Tide energy

Smart grid

Energy Storage

Grid

Solutions: to combine renewable energies with energy storage technologies

Affected by weather
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

<table>
<thead>
<tr>
<th>Installation Capability</th>
<th>Wind</th>
<th>Solar</th>
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<tbody>
<tr>
<td>2009 yr (GW)</td>
<td>20</td>
<td>0.75</td>
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<tr>
<td>2010 yr (GW)</td>
<td>30</td>
<td>1</td>
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<tr>
<td>2020 yr (GW)</td>
<td>150</td>
<td>20</td>
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</table>
Characteristics of Different Energy Storage Techniques

- **UPS (Power Quality)**
  - Load shifting
- **Grid Support**
  - Bridging Power
- **Energy Management**
  - Bulk Power Mgt

**Flow Batteries**
- Metal-Air Batteries
- NaS Batteries
- Advanced Lead Acid battery
- Compressed Air Energy Storage
- Pumped Hydro

**System Power Ratings**

- **Discharge Time at Rated Power**
  - Hours
  - Minutes
  - Seconds

- **UPS**
  - Power Quality

- **Grid Support**
  - Load shifting

- **Energy Management**
  - Bulk Power Mgt

**System Power Ratings**
- 1 kW
- 10 kW
- 100 kW
- 1 MW
- 10 MW
- 100 MW
- 1 GW

**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.
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.
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: $Zn^{2+} + 2e^- \rightarrow Zn^{0}$  
Pos. electrode side: $2Br^- \rightarrow Br_2 \text{ (aq)} + 2e^-$  
(Zn plated on neg. electrode)  
(Br, complexed into a thick, oily sludge, is stored in a separate location inside container)

At Discharge:
Neg. electrode side: $Zn^{0} \rightarrow Zn^{2+} + 2e^-$  
Pos. electrode side: $Br_2 \text{ (aq)} + 2e^- \rightarrow 2Br^-$  
(Zn ions dissolved in both electrolytes)  
(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:**

\[
\text{VO}^{2+} + \text{H}_2\text{O} - e^- \leftrightarrow \text{VO}^{2+} + 2\text{H}^+
\]

**Cathode:**

\[
\text{V}^{3+} + e^- \leftrightarrow \text{V}^{2+}
\]

**Total reaction:**

\[
\text{VO}^{2+} + \text{V}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{VO}^{2+} + \text{V}^{2+} + 2\text{H}^+
\]
Electrolytes of Vanadium Flow Battery

Positive Electrolyte

\[ \text{V}^{5+} \quad \text{V}^{4+} \quad \text{V}^{3+} \quad \text{V}^{2+} \]

\[ \text{V}^{3+} + \text{V}^{5+} \rightarrow 2\text{V}^{4+} \quad \text{V}^{2+} + \text{V}^{4+} \rightarrow 2\text{V}^{3+} \]

Membrane

Negative Electrolyte
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
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
  - Stability
  - Solubility

- Ion membrane
  - Stability
  - Durability
  - Selectivity
  - Cost

- Electrode/Bipolar plate
  - 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

- Stack: 35%
- Electrolyte: 35%
- BoP & BMS: 20%
- Others: 10%

Cost Target: 3000 RMB/kWh

- High performance, 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

Challenges

Lower power density, high material cost!
Polarization analysis of VFB

- Electrochemical polarization: 5%
- Electrode structure: 21%
- Electrode material: 74%
- Contact resistance: 74%
- Ohmic polarization: 74%
- Electrode resistance: 74%
- Electrode structure: 74%
- Electrocatalytic activity of electrode material: 74%
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 ($600-800 \$ /m^2 \rightarrow 100 \$ /m^2$)
- Low ion selectivity (Vanadium crossover)
Morphology of Perfluorosulfonic acid membranes

\[
\begin{align*}
[CF_2 - CF_2]_x [\text{CF} - CF_2]_y \\
[OCF_2 CF]_z O(CF_2)_{2}SO_3H \\
CF_3
\end{align*}
\]

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.

Adjust the side chain.
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.

Non-Fluoride IEMs Developed by DICP

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.

<table>
<thead>
<tr>
<th></th>
<th>Nafion-115</th>
<th>DICP</th>
</tr>
</thead>
<tbody>
<tr>
<td>CE (%)</td>
<td>95</td>
<td>97.6</td>
</tr>
<tr>
<td>EE (%)</td>
<td>80</td>
<td>84%</td>
</tr>
<tr>
<td>Life (cycles)</td>
<td>&gt;13000</td>
<td>&gt;10000</td>
</tr>
<tr>
<td>Cost ($/m²)</td>
<td>650</td>
<td>100</td>
</tr>
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</table>
Porous membranes as VFB separators

Larger molecules unable to pass

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.

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

<table>
<thead>
<tr>
<th>Property</th>
<th>Specification</th>
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<tbody>
<tr>
<td>Bulk resistance</td>
<td>&lt; 0.17 Ω.cm</td>
</tr>
<tr>
<td>Bending strength</td>
<td>&gt;28 MPa</td>
</tr>
<tr>
<td>Corrosion resistance</td>
<td>&lt;0.7 uA.cm⁻²</td>
</tr>
<tr>
<td>Thickness</td>
<td>1 mm</td>
</tr>
<tr>
<td>Cost</td>
<td>&lt;100 RMB/m²</td>
</tr>
<tr>
<td>Yield</td>
<td>10,000 m²/year</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Energy efficiency (EE) of stacks</th>
<th>&gt;80%</th>
</tr>
</thead>
<tbody>
<tr>
<td>352 kW subsystem (EE)</td>
<td>&gt;75%</td>
</tr>
<tr>
<td>90% Charge ↔ 90% discharge conversion time</td>
<td>&lt;90ms</td>
</tr>
</tbody>
</table>
A wind/solar/VFB joint power supply system for intelligent residence (2009)

3.5kW PV

3.5kW Wind Turbine

5kW/50kWh VFB
energy storage Delegation of US DOE visit my home
A “BIPV-VFB” Demonstration in Rongke Power Co. Ltd. (Dec. 2009)

PV: 60 kW

VFB: 60 kW / 300 kWh
Solar-VFB-Diesel Engine Power Supply System for An Isolated Island
(Sep. 2011)

Solar Cell 20kW
VFB 10kW/200kWh
Charger
Diesel Engine

PV controller
Inventor
Island load

Snake Island
Distributed Energy Storage
Micro-grid Power Supply System

200kW/800kWh VFB for a micro grid

PV1              PV2            PV3
2.5MW wind turbine 200kW*4h Li battery 200kW*10s super capacitor

Load1         load2           load3         load4
EV Charging station 200kW*10s Fly wheel

Energy controlling system
# 200kW/800kWh VFB for Micro grid

<table>
<thead>
<tr>
<th>Items</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rated Power</td>
<td>200 kW</td>
</tr>
<tr>
<td>Capacity</td>
<td>800 kWh</td>
</tr>
<tr>
<td>DC Voltage</td>
<td>250-390 V</td>
</tr>
<tr>
<td>Rated Current</td>
<td>DC 640A</td>
</tr>
<tr>
<td>Stack</td>
<td>20kW * 10 5 serials, 2 parallel</td>
</tr>
<tr>
<td>Temp.</td>
<td>-20°C – 40°C</td>
</tr>
<tr>
<td>Size</td>
<td>12.5m × 7.2m × 2.5m</td>
</tr>
</tbody>
</table>
5MW/10MWh VFB for a 50MW Wind Farm
(Since Oct. 2012)

Wind farm 35kV line

110/220kV grid

Wind farm transformer

15 sets basic systems

352kW VFB subsystem

Inventor DC400-620V

Inventor DC400-620V
Demonstration project of the world’s largest scale VFB system of 5MW/10MWh in the 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.
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

#### Table: Efficiency under Different Current Densities

<table>
<thead>
<tr>
<th>Current density (mA/cm²)</th>
<th>CE (%)</th>
<th>VE (%)</th>
<th>EE (%)</th>
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<tbody>
<tr>
<td>80</td>
<td>93.8</td>
<td>92.5</td>
<td>86.7</td>
</tr>
<tr>
<td>120</td>
<td>94.7</td>
<td>89.7</td>
<td>85.0</td>
</tr>
<tr>
<td>160</td>
<td>95.7</td>
<td>86.6</td>
<td>82.9</td>
</tr>
<tr>
<td>200</td>
<td>97.1</td>
<td>84.2</td>
<td>81.8</td>
</tr>
</tbody>
</table>

#### Graph:
- Efficiency (%)
- Cycle

**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/cm².**
Development of High Power Density VFB Stacks

Materials and structural optimization

The operating current density increased from 80 to 160 mA/cm²

<table>
<thead>
<tr>
<th>Current density (mA/cm²)</th>
<th>CE (%)</th>
<th>VE (%)</th>
<th>EE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>97.4</td>
<td>90.1</td>
<td>87.8</td>
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<tr>
<td>100</td>
<td>98.2</td>
<td>88.0</td>
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<td>120</td>
<td>98.5</td>
<td>85.9</td>
<td>84.6</td>
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<tr>
<td>140</td>
<td>98.7</td>
<td>83.9</td>
<td>82.8</td>
</tr>
<tr>
<td>160</td>
<td>98.9</td>
<td>81.9</td>
<td>81.0</td>
</tr>
</tbody>
</table>

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

<table>
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<th>标准名称</th>
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<td>全钒液流电池 术语</td>
<td>国标</td>
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<td>全钒液流电池通用技术条件</td>
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<td>行标</td>
<td>NB/T 42007−2013</td>
<td>颁布实施</td>
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行业标准：2件 已颁布实施
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工作组的牵头单位。

<table>
<thead>
<tr>
<th>WG ( # of Members)</th>
<th>WHO</th>
<th>COORDINATOR</th>
<th>WHEN</th>
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<tr>
<td>WG1 (5)</td>
<td>HORNE Craig/Enervault</td>
<td>HORNE Craig/Enervault</td>
<td>Week of January 23rd</td>
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<tr>
<td></td>
<td>FERRAIRA Summer/SNL</td>
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<td></td>
<td>N.N/Cellstrom</td>
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<td></td>
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<td></td>
<td>CUTHBERT Sean/LR</td>
<td></td>
<td></td>
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<td>ZHANG Huamin /DICP</td>
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<tr>
<td>WG2 (5)</td>
<td>GARCIA LORENS Vicent/IronFlow</td>
<td>GARCIA LORENS Vicent/IronFlow</td>
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<td>VISWANATHAN Vilayanur/PNNL</td>
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<td>HORNE Craig/Enervault</td>
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<td>GARCIA Alberto/Tecnalia</td>
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<td>WG3 (10)</td>
<td>ZHANG Huamin /DICP</td>
<td>SCHREIBER Martha/Cellstrom</td>
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<td>MENICTAS Chris /NSIP</td>
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<td>WG4 (3)</td>
<td>WANG Xiaoli/Rongke</td>
<td>WANG Xiaoli/Rongke</td>
<td></td>
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<tr>
<td></td>
<td>ADAMS Bret/Enervault</td>
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<td></td>
<td>ZHOU Hantao (Hunter)/Linyang</td>
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<td>OTHERS TO BE ADVISED</td>
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<tr>
<td>WG5 (5)</td>
<td>欧洲液流电池标准化各工作组成员名单</td>
<td></td>
<td></td>
</tr>
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</table>
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）
- 作为组织者推进设立IEC液流电池标准分技术委员会。
- 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

Study on the Development of International Standards in the Field of Flow Battery Systems
Acknowledgments

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Thank you for your attention.