

The Vanadium Redox Flow Battery: Science and Materials

Maria Skyllas-Kazacos



School of Chemical Engineering
University of NSW, AUSTRALIA



The UNSW Vanadium Redox Battery



- **FIRST PROPOSED BY SKYLLAS-KAZACOS & CO-WORKERS AT UNSW IN 1983**
- **ENERGY STORED IN TANKS, SEPARATE FROM CELL STACK:**
 - Capacity increased simply by adding more solution.
 - Instant recharge possible by exchanging solutions
 - Cost per kWh decreases as storage capacity increases.
- **SAME SOLUTION IN BOTH HALF-CELLS so:**
 - Cross-mixing of electrolytes across membrane does not lead to contamination of electrolytes.
 - Solutions have indefinite life so replacement costs are low (only battery stacks need replacement at end of life).

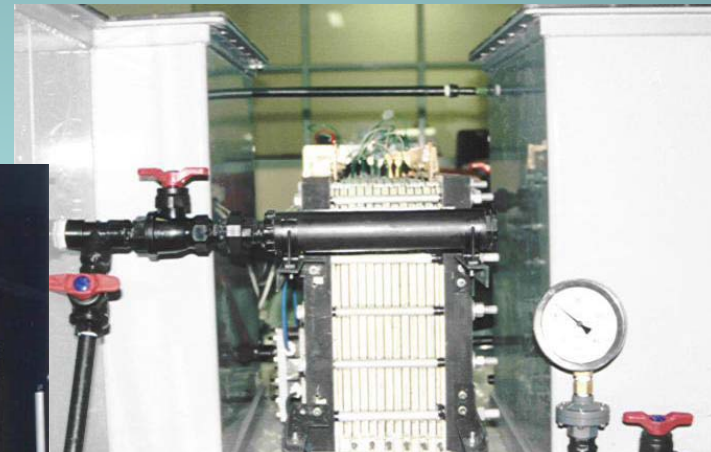


All-Vanadium Redox Battery Development at University of New South Wales

1984-2002

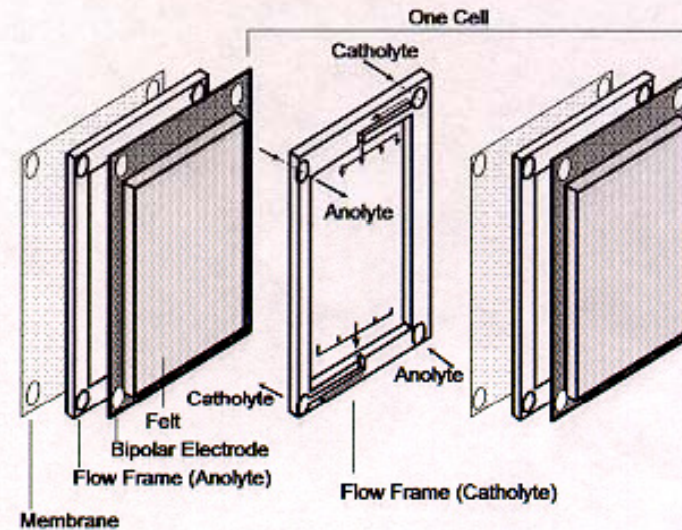


UNSW Cell and Stack Early Designs: 1986 to 1995





Stack Components

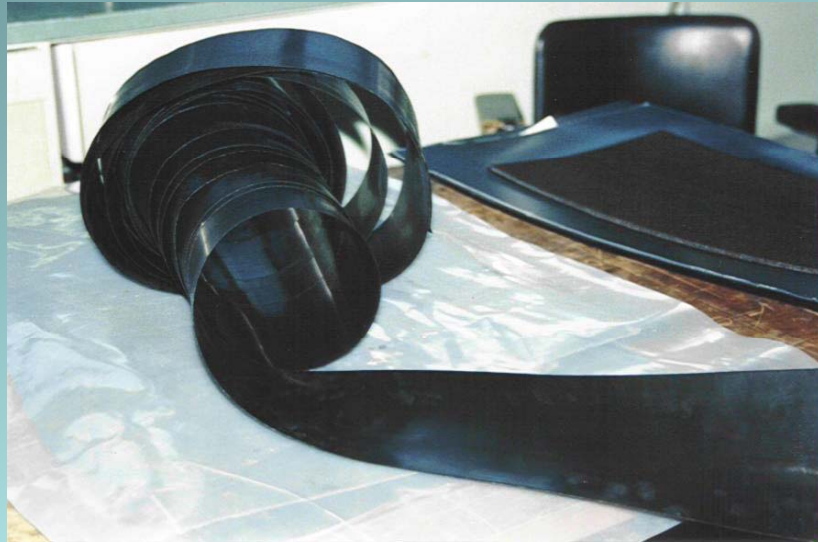


Main stack components are:

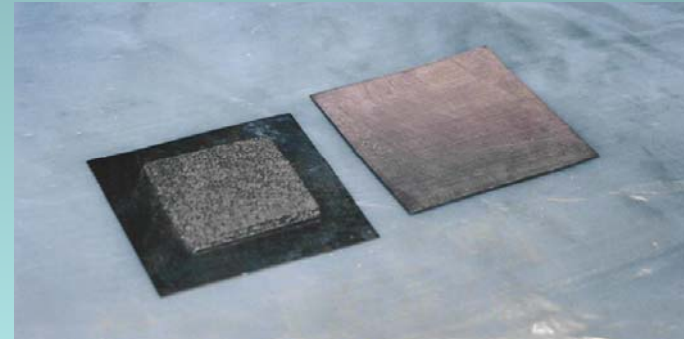
- bipolar electrodes (usually graphite felt on conducting plastic substrate)
- flow-frames
- ion-exchange membrane to prevent mixing of solutions
- detailed investigations on each component of cell stack and vanadium electrolytes at UNSW between 1985 and 2002



Bipolar Electrode Development



Conducting plastic substrate-
carbon filled PE/PP/rubber blends



End electrodes



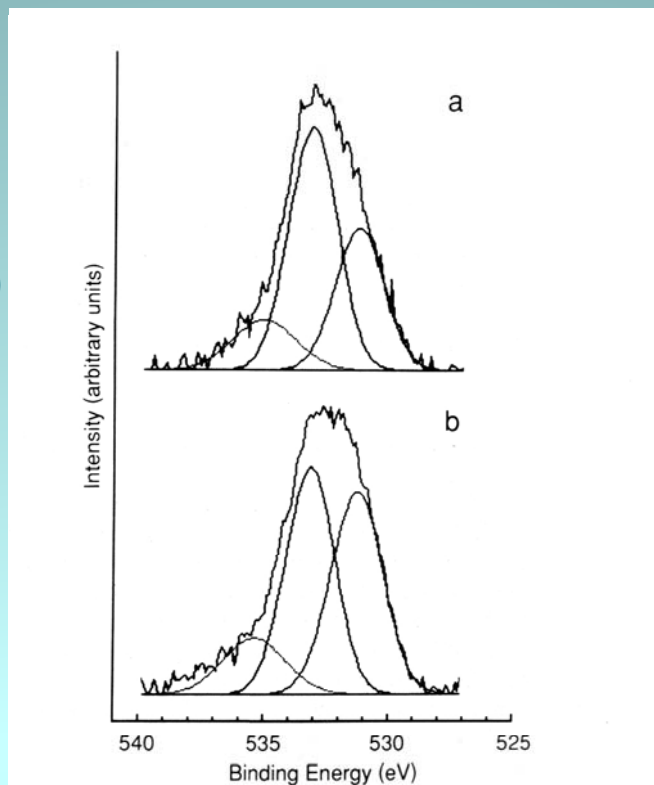
Bipolar electrode

From : S.Zhong, 1992
V. Haddadi-Asl, 1995

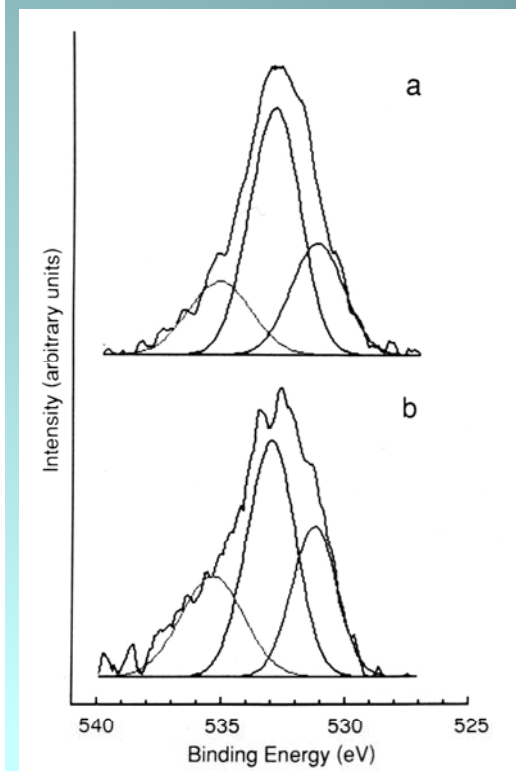
Graphite / carbon felt evaluation

To understand different electrochemical response of carbon/graphite felt materials, detailed study conducted on two graphite felts, based on rayon or polyacrylonitrile (PAN) precursors:

- Electrical conductivity of PAN-based felt superior to that of rayon-based felt.
- XPS analysis shows rayon-based felt reacts more easily with oxygen and forms C=O carbon-oxygen groups, while PAN based felt is more resistance to oxidation and preferentially forms C-O groups.



XPS Spectra for Rayon-based Carbon Felt
(a) After 30 h at 400°C in N₂ and
(b) After 30 h at 400°C in air



XPS Spectra for PAN-based carbon felt
(a) After 30 h at 400°C in N₂ and
(b) After 30 h at 400°C in air

From Zhong, Padeste, Kazacos & Skyllas-Kazacos J. Power Sources, 45 (1992) 29-41



Graphite Felt Activation Studies

Investigation of thermal, chemical and electrochemical activation processes for graphite felt electrodes. Used to generate active sites on carbon surface

– Activity measured by decrease in cell resistance for different treatment conditions

- XPS analysis showed that $-C-O-H$ functional groups behave as active sites for vanadium redox reactions

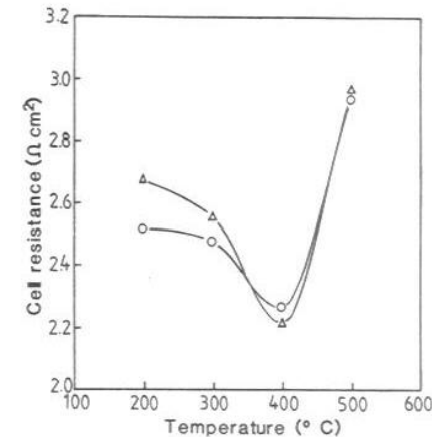


Fig. 2. Effect of treatment temperature on the cell resistance for activated graphite felt, (○) charge and (△) discharge.

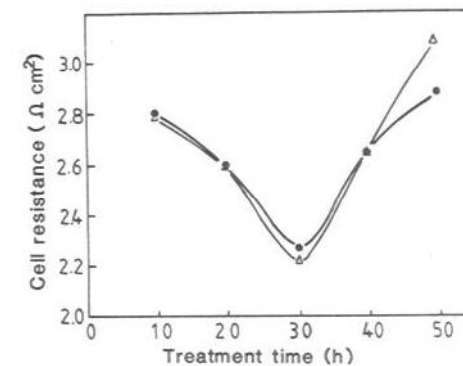


Fig. 3. Effect of activation time on the cell resistance at a constant temperature of 400°C for graphite felt, (○) charge and (△) discharge.



Membrane Screening and Modification Studies

Wide range of commercial membranes screened for:

- electrical conductivity
- permeability
- chemical stability
- water transfer behaviour

Novel low cost composite membrane based on “Daramic” separator.

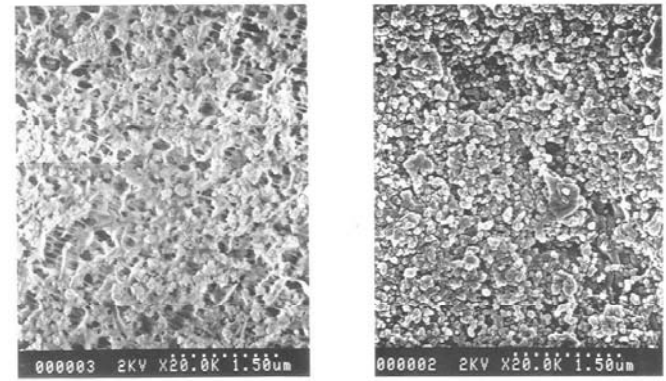


Fig. 1. FESEM micrograph of Daramic (surface).

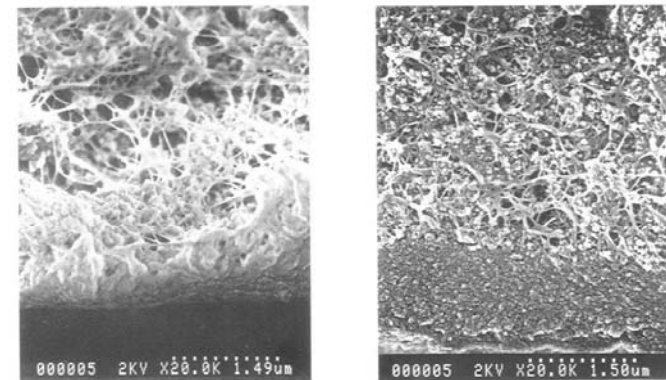
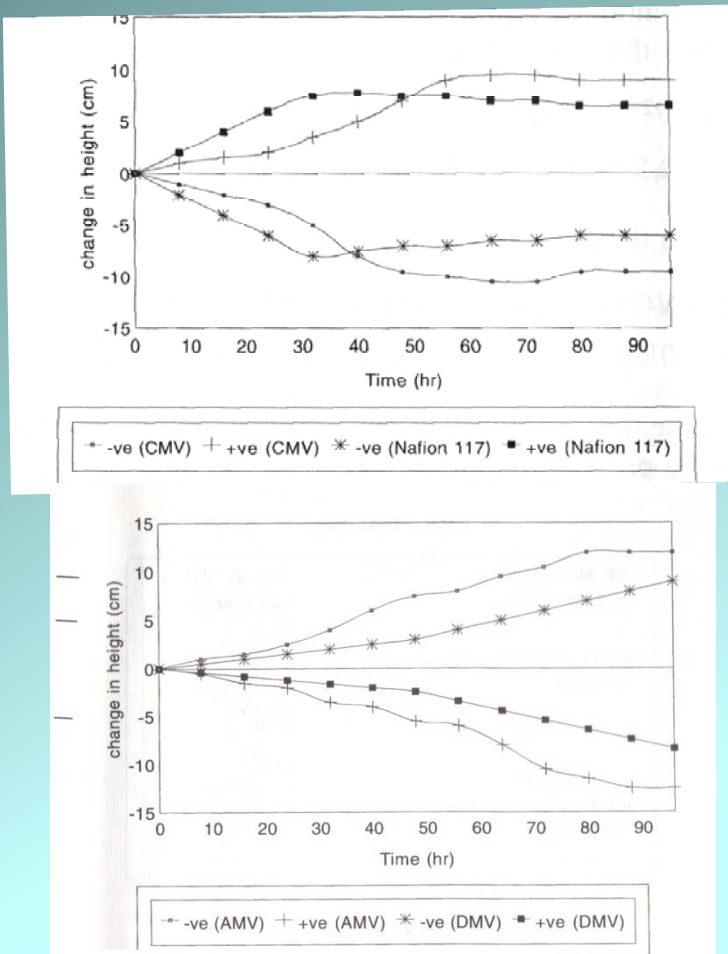


Fig. 4. FESEM micrograph of composite membrane (cross section).

From T. Mohammadi, 1995

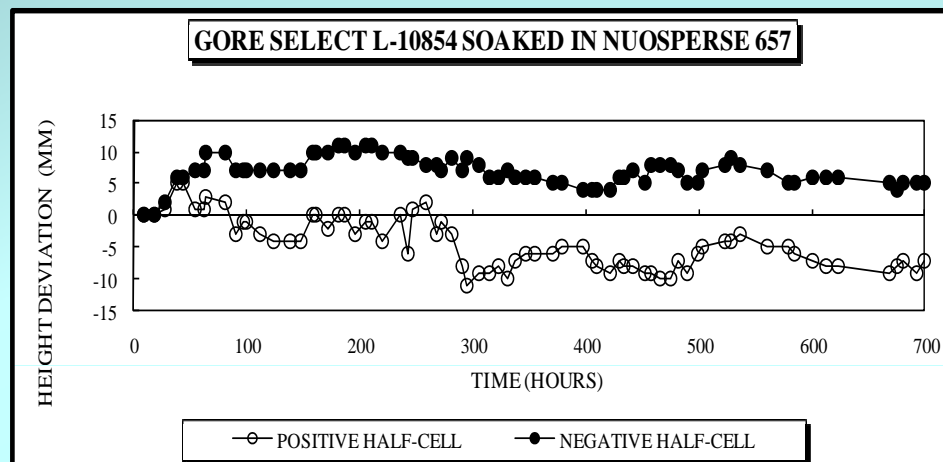
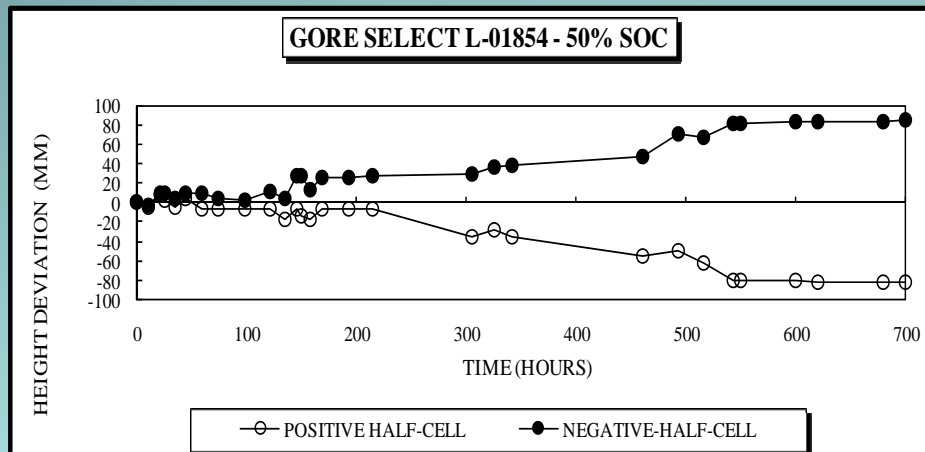
Water transport behaviour of ion exchange membranes in VRB



- Direction of net volumetric transfer during cycling dependent upon nature of ion selective membrane.
- Direction changes with SOC
- For cell employing anion exchange membrane net volumetric transfer is toward the negative half-cell
- For cation exchange membranes net volumetric transfer is toward the positive half-cell.
- Can be modified by chemical treatment

Volumetric transfer for cation (CMV and Nafion) and anion (AMV and DMV) exchange membranes with 50% SOC vanadium solutions.

Membrane modification to reduce water transport



- Various polyelectrolytes and membrane treatments evaluated to improve selectivity and water transport behaviour of different membranes in vanadium redox cell solutions.

- Both anionic and cationic polyelectrolytes evaluated improved the water transfer properties of the membranes by modifying ion exchange capacity

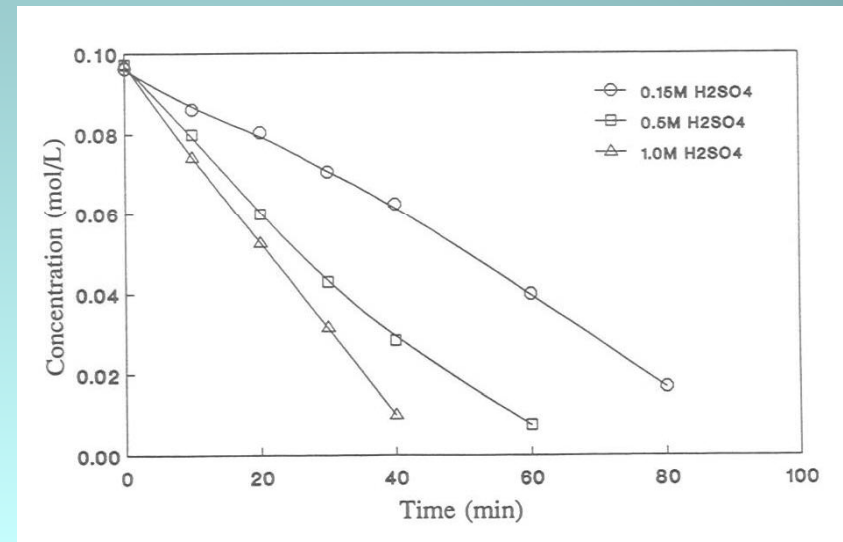
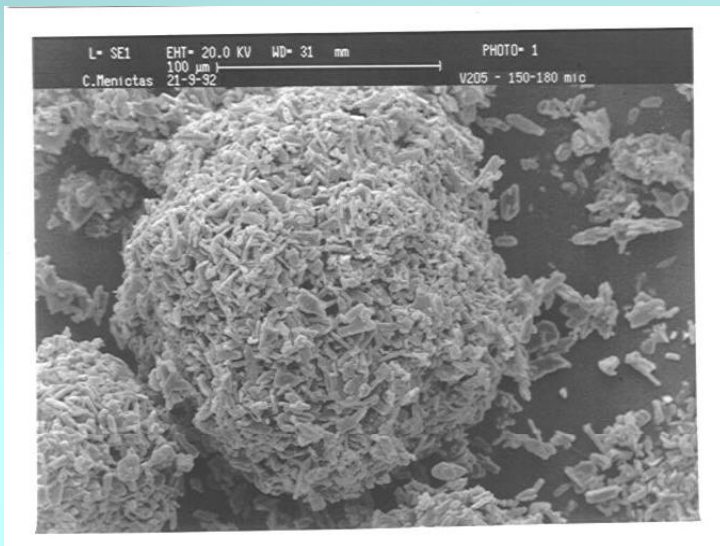
- Soaking treatments found to provide temporary improvement.



Vanadium Electrolyte Production

Investigation of V_2O_5 :

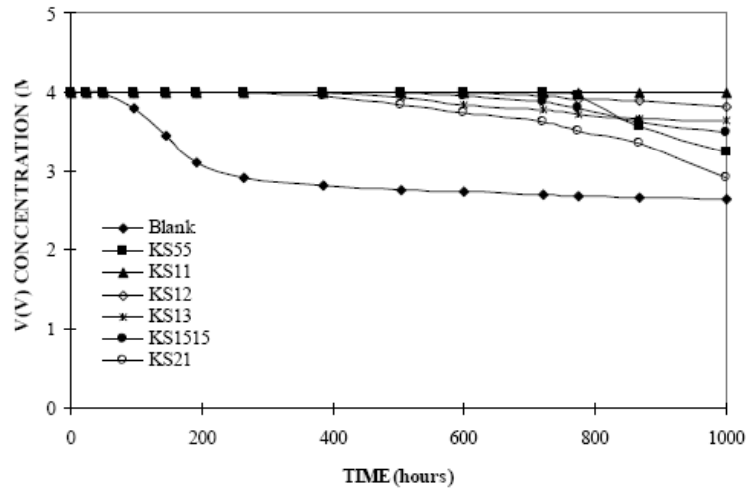
- chemical reduction
- leaching
- suspended powder electrolysis



From C. Menictas, 1993

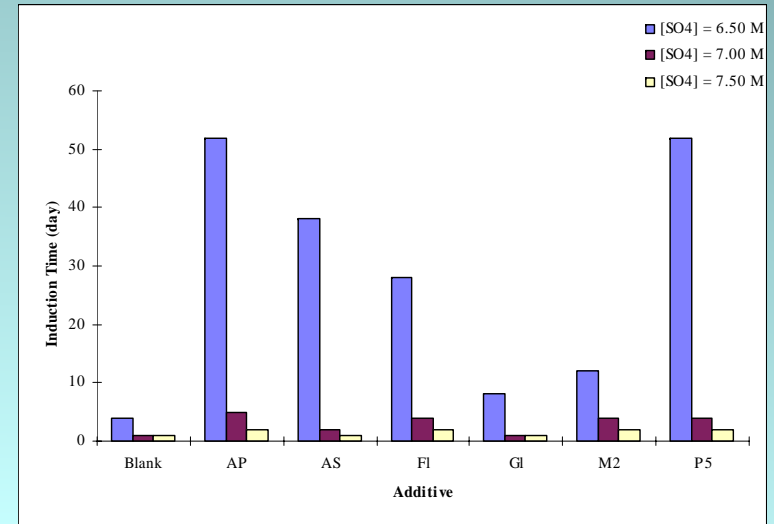


Electrolyte Stabilising Agents



Effect of different blends of formulation KS on precipitation of V(V) solution at 40°C.

(Ref: F. Rahman)



Induction times for 2.0 M V(III) solution with different total sulfate concentrations, T = 1.0 °C.

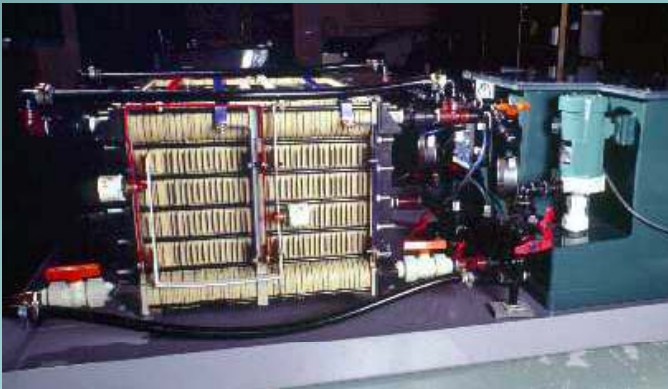
(Ref: A. Mousa)



Demonstrations of G1 VRB Technology 1993 to present



VRB Demonstration Projects at UNSW



Emergency Back-up Battery for Submarines (1995)



Vanadium Battery Powered Solar House in Thailand (1993)



UNSW vanadium battery powered golf-cart (1996)

VRB Installations by Sumitomo Electric Industries

Place	Applications	Specifications	Delivery
Office building	Load leveling (Demonstration)	100kW x 8h	2000
Wind power station	Stabilization of wind turbine output (Field test)	170kW x 6h	2000
Semi-conductor factory	1) Voltage sag protection 2) Load leveling	1) 3000kW x 1.5sec. 2) 1500kW x 1h	2001
Golf course	Load leveling (Photovoltaic hybrid system)	30kW x 8h	2001
South Africa	Load leveling (Field Test)	250kW x 2h	2001
Wind Farm	Wind storage	4 MW x 1.5 h	2006
Italy	Load leveling (Field Test)	42kW x 2h	2001

Back-up power

1.5MW-1Hrs/3.0MW-1.5sec VRB System



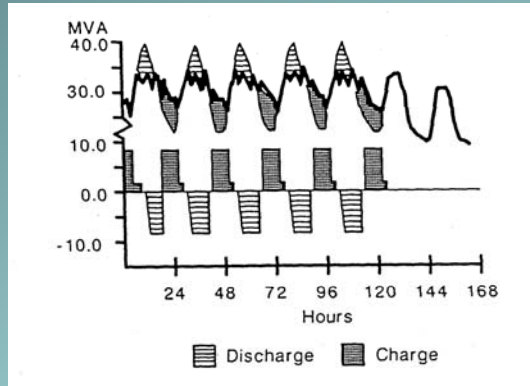
Battery boxes



Electrolyte Tanks

Courtesy Sumitomo Electric Industries

VRB Load-Leveling Installations



2 VRB load-leveling installations in Japan:

- 200 kW/800 kWh VRB at Kashima-Kita Power Station
- 450 kW/900kWh VRB at Kansai Power Station (built by SEI)
- Energy Efficiency of 80%



G1 VRB Wind Energy Storage Demonstrations

Tomomae wind farm on Hokkaido:
– 30.6 MW rated output

VRB demonstration system:
- Sumitomo / J-Power
- 4 MW / 6 MWh

NEDO funding for optimisation of control system

After 3 year operation more than 200,000 cycles completed



Early Challenges:

- High cost membranes used by SEI and VRB Power
- Limited to operation between 10 and 40 °C
- Energy density too low for mobile applications



G1 VRB Membrane Requirements

- Chemical stability in vanadium electrolyte
- Stable to strong V(V) oxidising agent
- Low electrical resistivity
- High conductivity to hydrogen ions
- Low permeability to V ions
- Low cost
- Good mechanical properties

Recent Membrane Developments

- New low cost membrane and pre-treatment process patented by V-Fuel Pty Ltd. Cost less than $\frac{1}{4}$ current price of Nafion and excellent performance and long-term stability
- Several research groups in China and USA currently investigating new “low cost” membranes,

eg: sulfonated polyphenylsulfone (PNNL/Pen State); poly(vinylidene fluoride)-graft-poly(styrene sulfonic acid) (PVDF-g-PSSA) membrane (Tsinghua Uni); poly(arylene thioether ketone) (PTK) and poly(arylene thioether ketone ketone) (PTKK) (*Sun Yat-Sen Uni*); sulfonated poly fluorenyl ether ketone (SPFEK) (various groups).

Some Good comparative performance vs Nafion BUT

- No real cost figures have been provided
- No long term cycling
- No long term stability data in V(V) solution



Energy Density and Electric Vehicle Applications

- Redox Flow Batteries are only batteries that allow BOTH electrical recharge and “instant” recharge by mechanical refuelling
- Spent solutions can be recharged overnight with off-peak power
- Eliminates need for new power stations to meet increased load from electric cars
- Energy density for G1 VRB limited by solubility limits of different vanadium ions at high and low temperature.
- Current G1 energy density too low for EV applications.





Generation 2 Vanadium Bromide Redox Cell

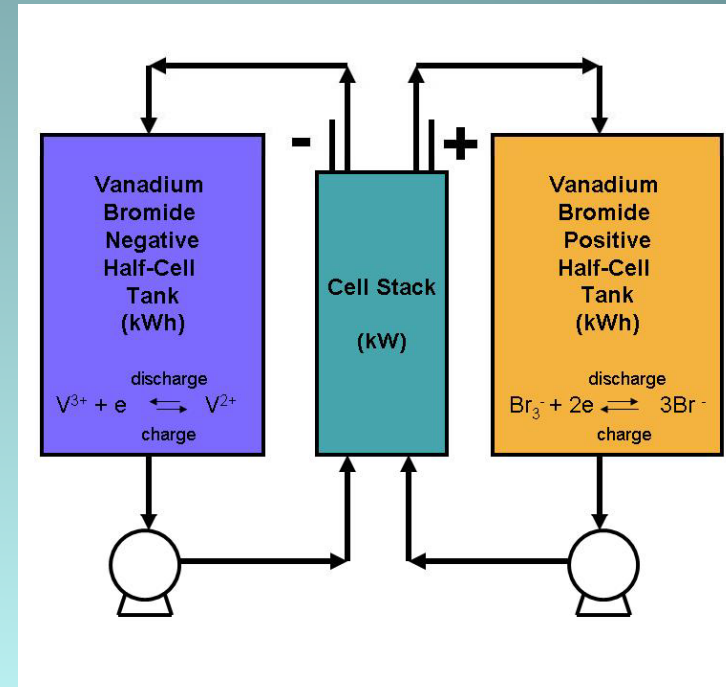
- Patented by UNSW in 2001.
- While G1 VRB employs solution of Vanadium Sulphate in Sulphuric Acid on both sides, the G2 V/Br employs a Vanadium Bromide solution in both half-cells.
- Higher solubility of vanadium bromide allows energy density to be almost doubled (to around 50 Wh/kg)
- Higher energy density opens market for electric vehicle applications with refueling station option
- Higher solubility of vanadium bromide also allows lower temperature operation of Generation 2 V/Br system
- No V(V) produced, so no thermal precipitation
- Initial challenge to identify low cost, long-life, high performance carbon felt and membrane





G1 VRB vs G2 V / Br

	G1	G2
Electrolyte	V/Sulphate in both Half-cells	V/Br in both half-cells
Negative couple	V^{3+} / V^{2+}	V^{3+} / V^{2+}
Positive couple	V(IV)/V(V)	Br^- / Br_3^-
Specific Energy (energy / kg)	15-25 Wh/kg	25-50 Wh/kg
Energy density (energy / litre)	20-33 Wh/l	35-70 Wh/l



G2 V/Br Challenges:

1. Stable, low cost membrane and electrode materials already identified
2. Low cost complexing agents to bind bromine and prevent vapour emissions



Bromine Complexing Agents

- Considerable development already achieved with bromine complexing agents for Zn/Br battery
- Mainly based on quaternary ammonium compounds
- Bind with bromine to form organic liquid layer and 2-phase electrolyte with all bromine bound in lower organic layer in electrolyte tank



Evaluation of Bromine Complexing Agents:

Appearance of red organic layer with different combinations of complexing agents

Solution Number	V(IV), Br ₂ conc M, M	A & B conc M	After 7 days at 11 °C	After 7 days at room temp	After 7 days at 40°C
1	2, 1	1, 0	Solid	Solid	Solid
2	2, 1	0.75, 0.25	Liquid	Liquid	Liquid
3	2, 1	0.5, 0.5	Liquid	Liquid	Liquid
4	2, 1	0.25, 0.75	Solid	Solid	Liquid
5	2, 1	0, 1	Solid	Solid	Liquid

(Grace Poon, MSc Thesis, UNSW, 2007)



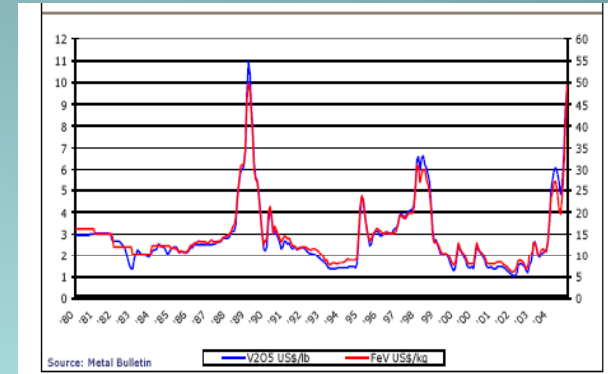
Further Studies with Complexing Agents

- Cell cycling studies to be conducted with 3M V solutions and complexing agents
- Optimisation of cell design and electrolyte flow system required for uniform 2-phase electrolyte flow distribution
- Improved membrane to be further evaluated with complexing agents
- BUT, Br_2 complexing agents currently used are too expensive. Need cost reduction or novel low cost alternatives.

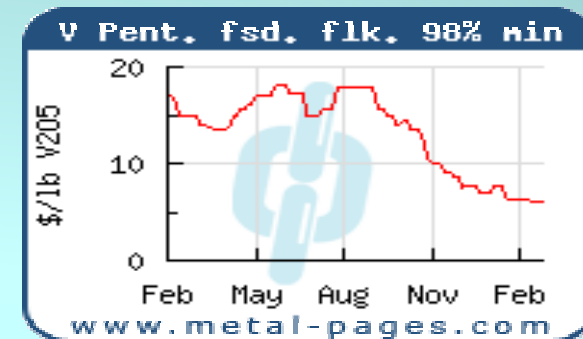


Cost Considerations

- G1 VRB technically proven in range of applications, but future commercial implementation linked to vanadium prices
- Current world vanadium production inadequate to meet demand from VRB commercialisation needs
- Recent price instability creating insecurity for VRB investors – eg VRB Power collapse
- Investment in new vanadium mines essential for VRB future price stability



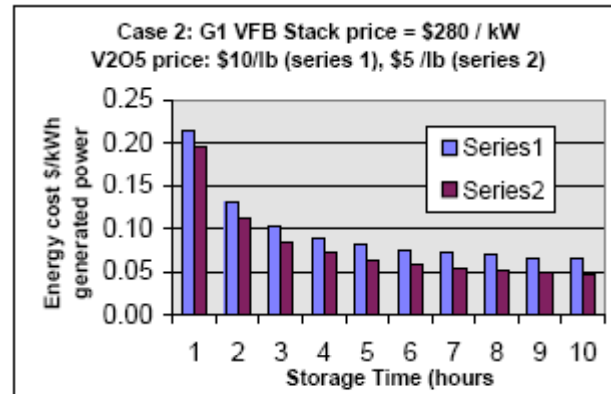
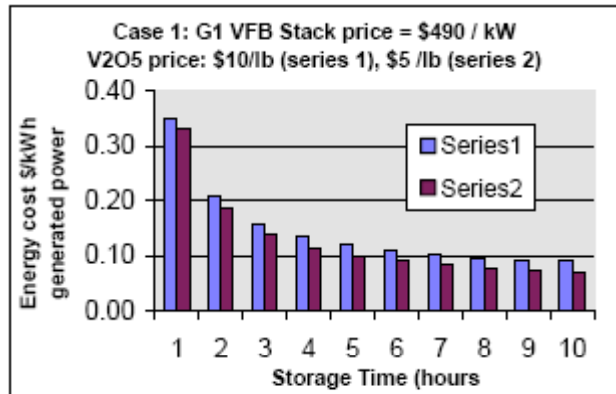
(a) Period 1980 – 2004



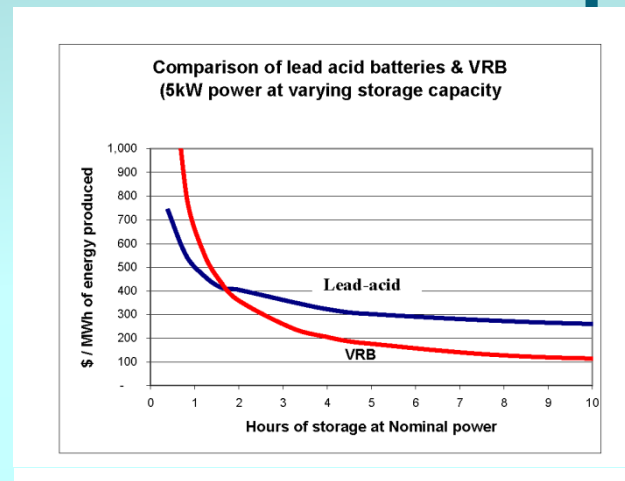
(b) Period : Feb 08 to Feb 09



G1 VRB Cost Estimates



Pd-Acid Cost Comparisons



VRB assumptions: \$500 /kW stack cost, \$5/lb V2O5 cost



Summary

- R&D relating to electrodes, membranes, electrolytes and stack design optimisation for All-Vanadium Redox battery at UNSW since 1984
- G1 VRB being commercialized in many stationary applications
- New improvements in energy density of Vanadium Bromide Cell should extend stationary applications and open mobile
- New low cost, high performance membranes identified for G1 and G2
- Membrane pre-treatment processes optimised for good overall energy efficiencies without membrane degradation
- Excellent performance with 5-10 kW stacks using G1 electrolyte
- Membrane and electrodes compatible with G1 and G2 electrolytes
- Bromine complexing agents for G2 V/Br produce stable organic bromine oil and eliminate vapours, but are currently too expensive
- Vanadium supply and price stability crucial for VRB implementation

Thank You



Questions?