40 Years of Vanadium Flow Battery Research and Development at UNSW

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The original seed – NASA's Fe/Cr flow cell project by Martin Green's Student Bob Brand



Larry Thaller (NASA)





Bob Brand

ELECTRICAL ENGINEERING SCHOOL LIBRARY

A REDOX BATTERY FOR REMOTE ENERGY STORAGE

Martin Green

R. E. BRAND

Supervisor : Dr. M. A. Green

This thesis is submitted to the School of Electrical Engineering and Computer Science in partial fulfilment of the requirements for the degree of Bachelor of Engineering.

University of New South Wales

November, 1982



Fe²⁺ Fe³⁺ Cr³⁺ Cr²⁺





First Electrochemical Experiments of Vanadium Redox Couples – Elaine Sum 1984



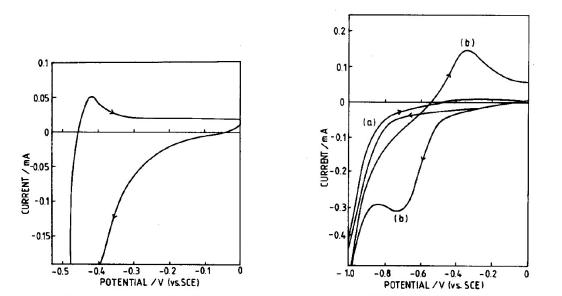


Fig. 1. Voltammogram of gold (area 0.45 cm^2) in $0.015 \text{M VCl}_3 + 0.1 \text{M H}_2\text{SO}_4$; sweep rate 2 V min⁻¹.

Fig. 2. Effect of electrode polishing on voltammograms for glassy carbon in $0.08M \text{ VCl}_3 + 1.8M \text{ H}_2\text{SO}_4$; scan rate 5 V min⁻¹. (a) Electrode prepared with P1200 sandpaper, 0.3 μ m alumina, 45 min ultrasonic cleaning; (b) electrode polished on P1200 sandpaper.

A study of the V(II)/V(III) redox couple for redox flow cell applications, E. Sum and M. Skyllas-Kazacos, J. Power Sources, **15**, 179-190 (1985).

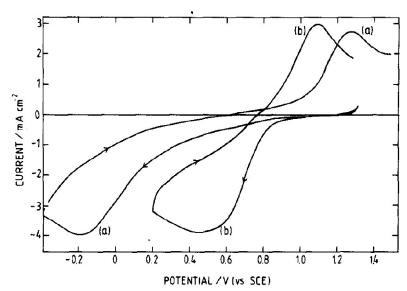
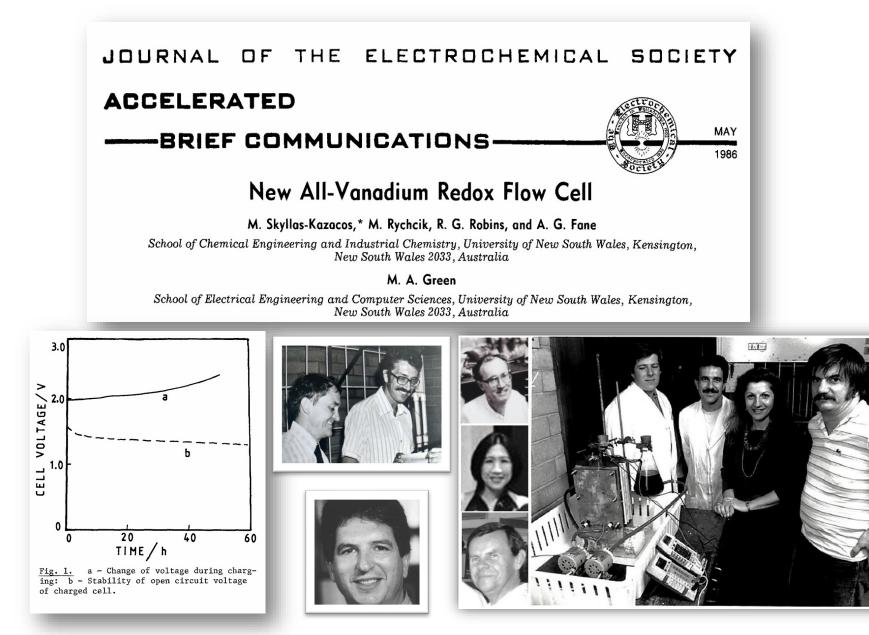
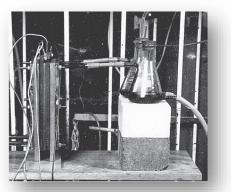


Fig. 2. Effect of surface preparation on voltammograms for glassy carbon in 0.055 M $V(V) + 1.8 \text{ M } H_2 \text{SO}_4$ solution; scan rate = 4 V min^{-1} . (a) Electrode prepared with P1200 paper, 0.3 μ m alumina, and ultrasonic cleaning for 1.5 h. (b) Electrode polished with P1200 paper.

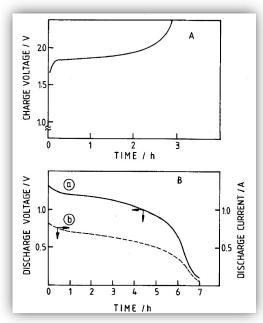
Investigation of V(V)/V(IV) system for use in positive half-cell of a redox battery, E. Sum, M. Rychcik and M. Skyllas-Kazacos, J. Power Sources, **16**, 85-95 (1985).

First Flow Vanadium Cell Tests





First All-Vanadium Flow Cell fabricated by Franz Grossmith in 1986



Efficient vanadium redox flow cell, M. Skyllas-Kazacos and F. Grossmith, J. Electrochem. Society., **134**, 2950 (1987).

1987 - Discovered by the media and 1st licence

No. 232 (No. 12 of 1987) Published fortnightly by the Public Affairs Unit Registered b UNSW team invents a promising new storage battery Electric vehicles to fill up with vanadium? Researchers at UNSW have invented a new rechargeable storage battery which they believe may be one of the most promising energy storage systems currently under development. Unisearch Limited the University's research and devel opment company, has negotiated a world wide licence agreement with Agnew Clough Limited to develop and market the invention. Not only is the battery ideal fo load-levelling and sturing energy in remote areas, but also as a power source for electric vehicles. Loadevelling allows power generators to be smaller because stored battery power could cope with peak demand. The battery is based on the "NASA redox flow cell concept "NASA refort flow refil concept which employs two different redox solutions pamped separately holy or autocompanies of the separately relations provide reference and relations provide reference and relations provide reference and barressen dersons. When the reference barresen dersons and the reference barresen makes the UNSW battery so differ-ent in terms of concentional batteries, such as the lead-acid batteries, is the use of a solution in water of a compound of the cloment vanadium. Energy is stored in the vanadium. It differs from the existing NASA cell which employs solutions of iron and chromium compaunds thas suffering from cross-contami-nation as the two different solutions Dr Maria Skyllas-Kazacos and Dr Miron Rychcik with the experimental battery diffuse across a membrane separat-ing the half-cells. UNSW's cell does not experience cross-contamination because it employs two separate vanadium solutions, which differ only in their oxidation statu (i.e. the electrical charge carried by the 'lons', o charged particles of vanadium' Vanadium solution The vanadium battery works in the following way (see diagram). Vanadium solutions are stored in two separate small tanks and the solutions are pumped through a two-compartment cell. One part of the cell is positive, the other negative. Here the vanadium can be charged and discharged. A key to the operation of the battery is the use of a membrane which is used to keep the two solutions apart. The membrane currently used in laboratory tests i a controcretial material made o polystyrene sulphonic acid. Th

Exclusive world-wide licence being granted to Agnew Clough Pty Ltd. Company funded further research at UNSW for 3 years, but relinquished licence during Asian financial crisis.



Sir Robert David Garrick Agnew, CBE (21 September 1930 – 3 August 1987) . Australian competition swimmer and businessman. Represented Australia at the 1948 and 1952 Summer Olympics, as well as the 1950 British Empire Games. After retiring from swimming he entered business, becoming involved in resources industry in Western Australia. Partnered with Clough to establish Agnew Clough Pty Ltd – vanadium mine in WA.



The UNSW All-Vanadium Flow Battery

- 1984: First practical VFB demonstrated at the University of NSW
- **1986**: Patents filed in Australia, USA and Japan
- **1984-2000**: Extensive R&D effort at UNSW covering all aspects of cell materials, electrolyte characterisation and production, stack design, modelling, fabrication and testing, sensor and control system development etc.
- Early UNSW field trials in solar house in Thailand, electric golf cart and submarine applications in mid-1990s.
- Early projects funded by Australian national and state government bodies interested in energy storage for remote area power systems (NERDDC, ERDC, NSW Office of Minerals and Energy, ARC).
- Initially licensed to Thai Gypsum, Mitsubishi Chemical Corporation in mid-1990s and Sumitomo Electric Industries in 2001.







VRB Progress at UNSW 1984-1990

- First All-Vanadium Flow Battery patent filed by UNSW in 1986
- Basic chemical and electrochemical studies
- Screening, characterisation and selection of membranes, electrodes, cell materials
- Development of vanadium electrolyte processes.
- Early stack design and development

Rui Hong, Jim Wilson, Dennis Yan, Michael Kazacos, John Chieng, Djen Kasherman, Peter Wegner



First VFB flow cell: 1986



Early VFB multi-cell: 1988



First 1 kW VFB multi-cell stack: 1988





First 2.5 kW VFB stack: 1989





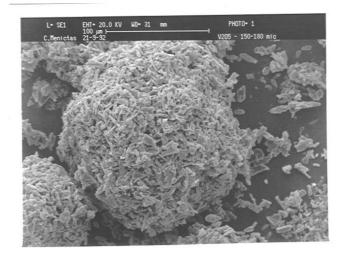
Early UNSW R&D Projects: Vanadium Electrolyte Production

Investigation of $V_2 O_5$ processes:

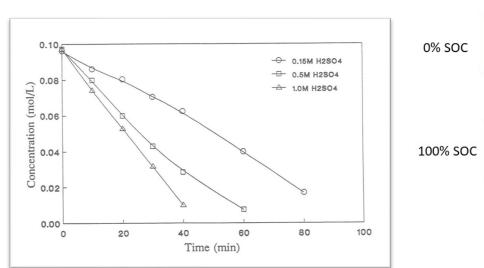
- Suspended powder electrolysis
- Chemical reduction eg H_2SO_3 , oxalic acid
- Leaching eg with V(III)
- V205 + V203 reactive dissolution

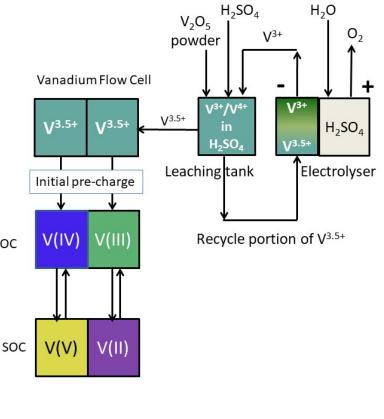
"Vanadium salt dissolution process", M. Skyllas-Kazacos, R. McDermott and M.Kazacos, Patent Appl. No. PCT/AU88/00471.

"Vanadium Redox Battery Electrolyte Process" M.Skyllas-Kazacos, Prov. Patent Application, PR 5143, 21 May, 2001, PCT Application, PCT/AU02/00613, May, 2002, US Applic No 2004/0241552 A1.



C. Menictas PhD thesis, UNSW, 1993





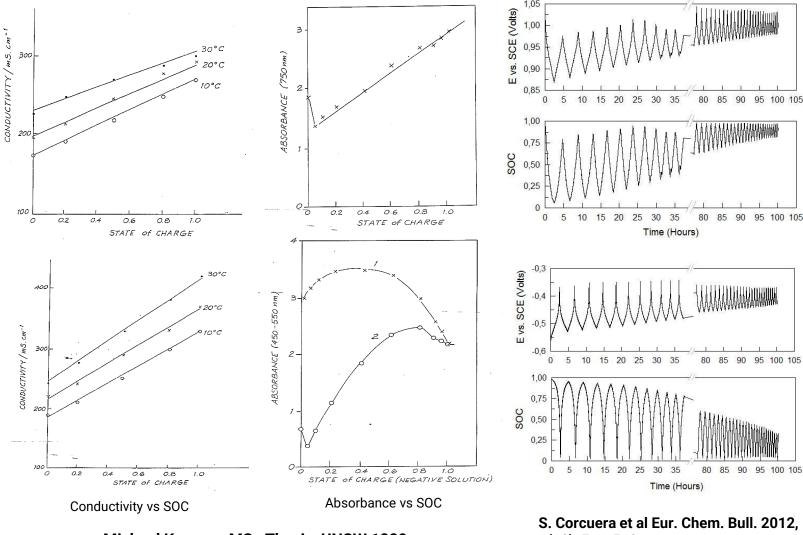
Chris Menictas, Rod McDermott, Rui Hong, Jim Wilson, Alex Stefos

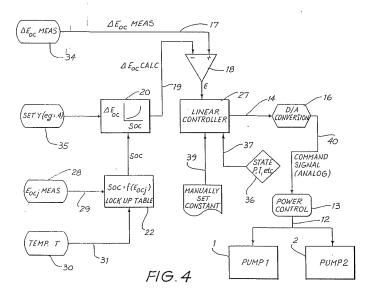


Early UNSW R&D Projects: SOC Monitoring and Control

95 100 105

95 100 105





"State-of-Charge of Redox Cell", by M. Skyllas-Kazacos, M. Kazacos, J. Joy and B.G. Madden, Patent Appl. No. PCT/AU89/00252, June 1989.

Battery Controller Development: Barry Early Madden, Rob Largent, Luke McDermott, Yifeng Li



S. Corcuera et al Eur. Chem. Bull. 2012, 1(12), 511-519



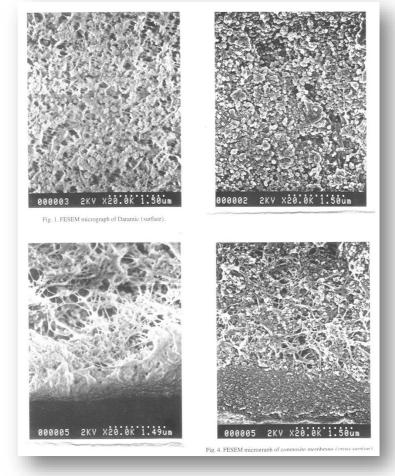
Early UNSW R&D Projects: Membrane Screening and Modification

Wide range of commercial membranes screened for:

 electrical conductivity
 permeability
 chemical stability in V(V)
 water transfer behaviour

- 2. Developed membrane modification processes to reduce water transfer
- 3. Novel low-cost composite membrane based on "Daramic" separator.
- 4. Developed methods to measure membrane diffusion coefficients

John Chieng, Toraj Mohammadi, Theresa Sukkar, Helen Prifti, George Kazacos (V-Fuel)



From T. Mohammadi PhD thesis UNSW, 1995

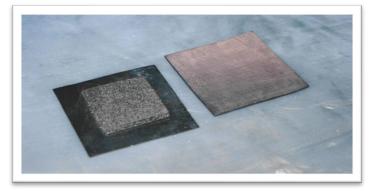


Early UNSW R&D Projects: Bipolar Electrode Development



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

S.Zhong, PhD thesis UNSW, 1992, V. Haddadi-Asl PhD thesis, UNSW, 1995 Jim Wilson, Michael Kazacos, Chris Menictas, Christoph Hagg, Nick Kazacos (V-Fuel)



End electrodes



Bipolar electrode



Graphite Felt Electrode

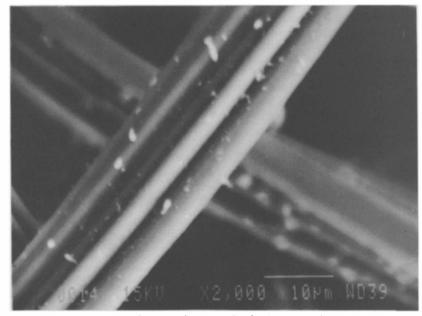
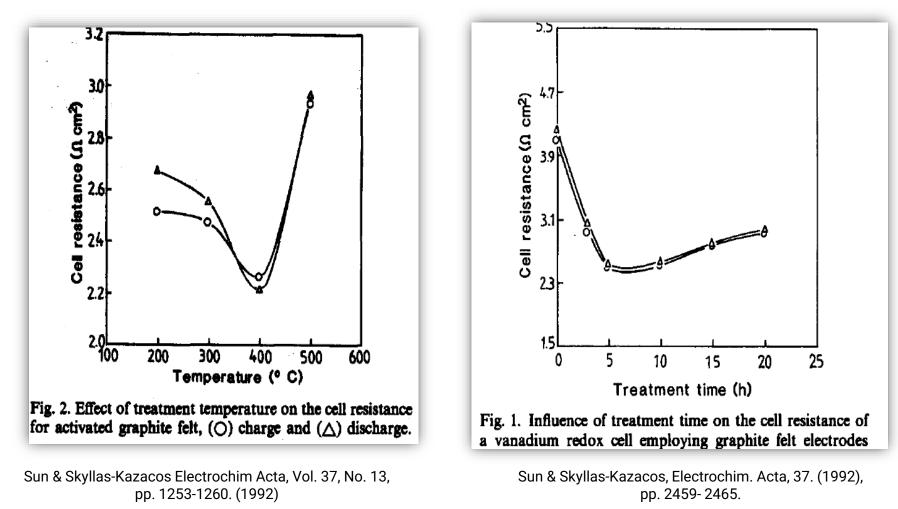


Fig. 6. The surface morphology of graphite felt treated at 400°C for 30 h.

Thermal, chemical and electrochemical treatments of graphite felt found to improve cell performance by introducing surface functional groups that provide active sites for the vanadium reactions and increasing hydrophilicity

Sun and Skyllas-Kazacos, Electrochemica Acta 1992

Graphite felts and felt activation (a)Thermal treatment (b) Acid Treatment



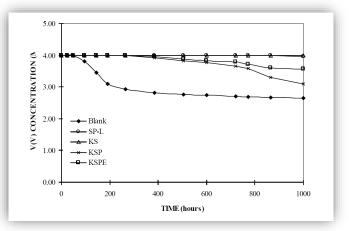




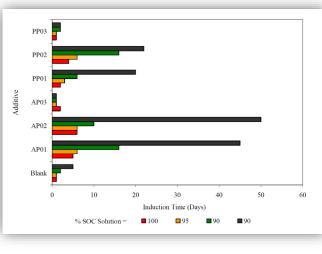
Improved G1 VRB with supersaturated solutions and precipitation inhibitors

- In mid 1990s, Skyllas-Kazacos and co-workers patented use of precipitation inhibitors to stabilise up to 4 M vanadium electrolytes concentrations and increase energy density (PCT/AU94/00711, 1994)
- Wide range of additives identified as good precipitation inhibitors to stabilise highly concentrated vanadium solutions over wide temperature range

Early precipitation inhibitor screening by Min Chen 1991, Michael Kazacos 1992, Chris Menictas 1995, Faizur Rahman 1998, Nadeem Kausar 2002, Asem Mousa 2003



Faizur Rahman UNSW PhD thesis 1998



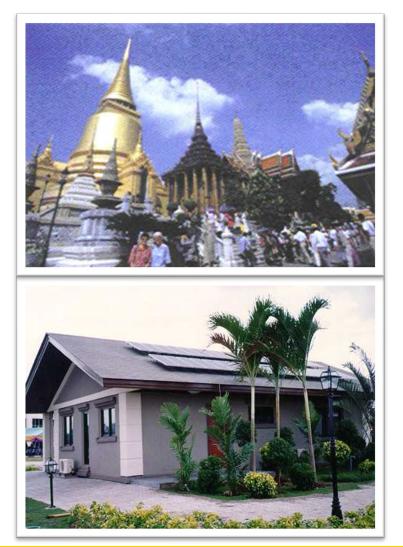
Nadeem Kausar, UNSW PhD thesis 2002

Solution	Induction	Degree of
D11-	time (day)	Precipitation
Blank	4	4
Ammonium Sulfate	38	1
Ammonium	> 52	Nil
phosphate†		
Ammonium oxalate	10	3
Phosphoric acid	10	2
Potassium	8	2
triphosphate		
Sodium	30	3
triphosphate		
Sodium	30	4
Pyrophosphate		
Potassium Sulphate	10	3
Potassium	9	2
persulphate		
Sodium Sulfite	30	3
Boric acid	5	5
Tungstic acid†	> 52	Nil
Sodium Tungstate†	> 52	Nil
M1*	10	3
M2*	14	1

Asem Mousa UNSW PhD thesis 2003



1992 - Moving out of the laboratory - first Thailand...



Vanadium battery agreement signed with Thai Gypsum

After seven years of research nitely; and batteries may be re charged instantaneously by pumping and development, Unisearch out spent electrolyte and replacing Ltd has signed an option agreement with Thai Gypsum Prowith charged electrolyte. Construction, running and maintenance costs ducts Co Ltd for development have been shown to be more than of its unique vanadium battery competitive with other power stortechnology. Unisearch is the research, develage systems.

opment, training and technology transfer company of UNSW and is tollectual Property Business the owner, by assignment, of the va-Manager, said: "The development of nadium battery technology that has this technology has received support been developed at UNSW. from government research funding and private industry in Australia. In return for a major investment in the commercial development of the technology, Thai Gypsum will

"Although this technology has enomous potential, we at Unisearch acquire a licence to make, market and UNSW have had, until now, difand develop the valuation battery for ficulty in attracting a major industrial end-user domestic applications in partner, so we are very pleased to be much of South-East Asia. able to collaborate with Thai Gyp-The agreement between Unisum

search and Thai Gypsum was "We are looking forward to working with Thai Gypsum and conreached after a recent visit to Australia by Mr Krisada Kampafidently expect the project to benefit natsanyakorn, the Managing both companies. We are also pleased Director of Thai Gypsum. that this association will establish The vanadium battery technolour battery technology on a large ngy was invented at UNSW by scale in South-East Asia, a region Associate Professor Maria where we see strong growth creating Skyllas-Kazacos of UNSW's great demand for this type of energy-School of Chemical Engineering and efficient and collution minimising Industrial Chemistry, Dr Myron technology. Rychelk and Professor Robert Robins.

High commercial viability

Other engineers and researchers who have played a significant role in Mr Krisada said: "With environmenthe development of the vanadium tal concern now a global issue, battery technology include Dr DJen renewable energy sources combined Kasherman, Michael Kazacos, with energy-efficient applications



Protured during an inspection of UNSW's Centre for Photovoltaic Devices and Systems laboratory (from left): Mr Ted Spooner, a Project Scientist from UNSW's Department of Electric Power Engineering; Ms Kirsten Murray, Projects Manager for Unisearch's Consulting and Research Division; Professor Robert Excell, Chairman of the Division of Energy Technology at the Asian Institute of Technology, Bangkok, Mr Krisada; Mr William Cecchini Project Director for Thai Gypsum; Mr Largent, Dr Sunt Techakumpuch, Chairman of Thai Engineering Consultants Co Ltd; Mr Hogg.

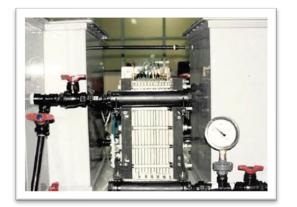
Thailand to test the battery under volts and will have a capacity of 15 cessing, provided technical assist-

INSV



Thai Solar House Project 1993-94





To save energy, pump control system designed to turn pumps on only when current > 20 A. When stack voltage dropped below pre-set value, pumps turned on for 3 minutes to replenish solution in stack.



Improved PV System Performance Using Vanadium Batteries" by Robert L. Largent, Maria Skyllas-Kazacos and John Chieng, Proceedings IEEE, 23rd Photovoltaic Specialists Conference, Louisville, Ky., May 1993 Battery fabricated by Rui Hong, Chris Menictas, John Chieng, Michael Kazacos, Jim Wilson; Electrolyte produced with inhouse pilot process – controller designed and built by Rod McDermott; Battery controller designed and built by Rob Largent



...then Japan.



Vanadium battery receives backing

Continued from page 1

tion of Asia, Australia and New Zealand.

The intent of the agreement with Mitsubishi and Kashima-Kita is to bring the technology to the stage where it can be used for load levelling – storing electricity produced by power utilities during periods of reduced demand so it can be released at times of peak demand.

In the short term, this allows peak demand to be met without increasing electricity generating capacity. In the longer term it will postpone the need to build further expensive electricity generators.

Because the battery uses two liquid electrolytes, the battery's storage capacity can be raised by increasing the size of the storage tanks. The technol-



At the signing of the agreement between Unisearch and Mitsubishi Petrochemical and Kashima-Kita (standing, from left): Mr Hogg; Mr Kanji Sato, Chief Manager of Kashima-Kita's Vanadium Battery Development Division; Mr Hirokazu Takahashi, Power Systems Department, Mitsubishi Corporation; (and sitting from left) Mr Akira Shibata; Mr Richard Kaan, Managing Director of Unisearch; Mr Fuji Shigematsu, Representative Director of Kashima-Kita Electric Power Corp; and Professor Skyllas-Kazacos.





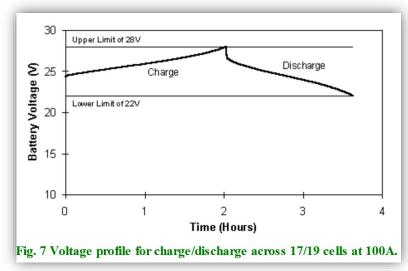






Australian Defence Department Project 1997





M. Skyllas-Kazacos and C. Menictas, Proceedings INTELEC'97, Melbourne, 19-23 October, 1997. (https://ieeexplore.ieee.org/document/645928/)

Tapping Cell Utilisation

- Two 19-cell stacks connected in parallel.
- Tapping cell in each stack at cell 17.
- Purpose to allow charging across 17 cells and discharging across 19 cells thus limiting the difference between charge and discharge voltages.
- Charging battery across 17 ensured total battery stack voltage < 28 V.
- Battery discharged across 19 cells until total battery stack voltage reached 22 V.
- Two tanks share common wall with anti-syphoning pipe to transfer solution back to other side whenever electrolyte level exceeded.
- Typical voltage profile for 17 cells charge 19 cells discharge at 100 A illustrated in Figure.

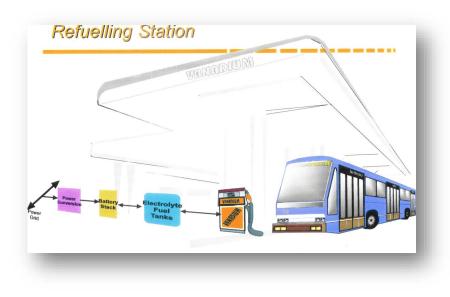
Design and fabrication team: Rui Hong, Chris Menictas, Denis Yan, Jim Wilson, Michael Kazacos



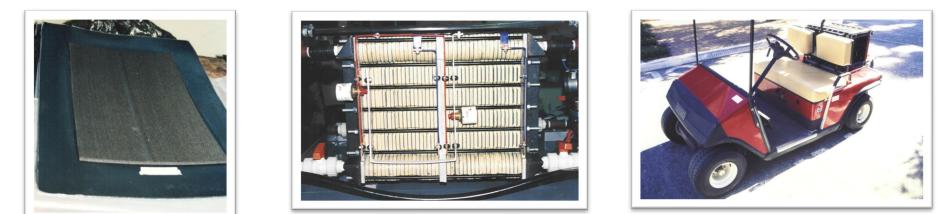
Bill Wentworth - Local advocate for UNSW VFB-powered light rail for Sydney in 1990s



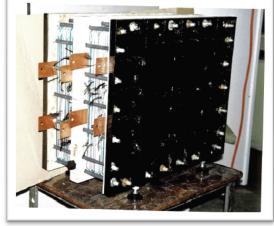




UNSW Electric golf cart project 1996-97



Conducting plastic electrode stack + 2 M electrolyte – typical Rcell = 3.2 ohm.cm2







Glassy carbon electrode stack + 3 M vanadium electrolyte – Rcell = 2 ohm.cm2

Team: Rui Hong, Dennis Yan, Jim Wilson, Chris Menictas, Michael Kazacos, David Hogg, Wal Lamberth Electrolyte Additives for 3 M solution: Michael Kazacos, Chris Menictas, Asem Mousa, Nadeem Kausar, Faiz Rahman, Sarah Roe



Exhibitions and Visitors























UNSW

VRB Technology moved off-shore

- UNSW VRB patents sold to Pinnacle in 1997.
- Hostile take-over in 2001, Pinnacle and VRB patents taken over by Canadian company VRB Power.
- 2001 VRB licensed by Pinnacle to Sumitomo Electric first began manufacturing and installing VRBs in 1990s.
- After Global Financial Crisis, Canadian company assets bought by Prudent Energy.
- Original UNSW VRB patent expired in 2006.



Gen 2 V/Br patented by UNSW in 2003

2005: Spin-off V-Fuel, established by Michael, Nicholas & George Kazacos with investment funding from CEGT and Newchris2010: V-Fuel folds due to lack of investment





Commercial VFB Systems & Installations in Early 2000s

REDOX FLOW SUMITON OEL ECTRIC



1 MW/5 MWh VRB - Sumitomo - Japan

1C



5 MW/10 MWh Rongke Power - China





Gildemeister - Germany



300 kW/3.6 MW Prudent - California



VFB SYSTEM FOR UNSW TYREE BUILDING

- \$129.7 million grant awarded to AGL Energy and First Solar under Solar Flagships Program in 2012
- \$40.7 million to University of Queensland and UNSW to conduct related research.
- Part of UNSW funds for installation of 30 kW/ 120 kWh VFB unit in new Tyree Energy Technology Building at UNSW
- Installation of Cellcube VFB completed June 2015
- VFB system used to store solar energy from PV array on roof of building, while also allowing research on different energy storage applications.











Sumitomo 60 MWh VFB in Hokkaido



30 MW/ 60 MWh VFB Location: Hokkaido, Japan Started: December 2015 Grid Use:

- Suppress WT and PV output fluctuations
- Load Frequency control
- Suppress long-period fluctuations
- Over generartion measures
- Hybrid operation of Long and Short period fluctuations

Shibata et al, IFBF 2017, Manchester UK.

UNSW Basic VFB patent expired in 2006, allowing universal freedom to operate.

Since 2006, VRB manufactured by companies in Japan, China, USA, Germany, Austria, UK, Canada, Korea, India.

But for next 15 years, market still not ready.

This changed in recent years and the UNSW VFB currently manufactured by more than 20 companies.

100s of MWhs of VFBs installed around the world. Several companies being established in Australia to manufacture and install VFB systems and produce vanadium electrolyte for local market.

Installed and Announced VFB installations in 2023





Largest VFB project in Australia to date

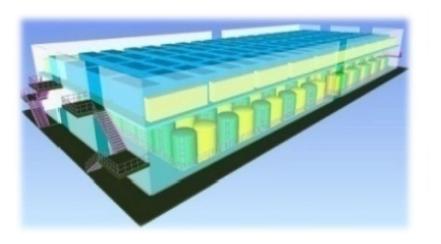


Invinity currently creating Australia's first dispatchable solar power plant with an 8 MWh (VFB), coupled with a 6MWp solar array in South Australia.



800 MWh Rongke Power Dalian Project and GigaFactory

200MW/800MWh VRFB Project



Location: Dalian City, CHINA

The first floor :Electrolyte tankThe second floor:Power unit + control unitThe third floor:PCS + Transformer

Huamin Zhang, IFBF 2017, Manchester, UK

First 100 MW/400 MWh system commissioned in 2022. Phase 2 under construction

Rated Power: 200 MW Rated Capacity: 800 MWh AC efficiency > 70%

Components:

Battery: 500 kW/2 MWh x 400



Rongke Power, LinkedIn 2024

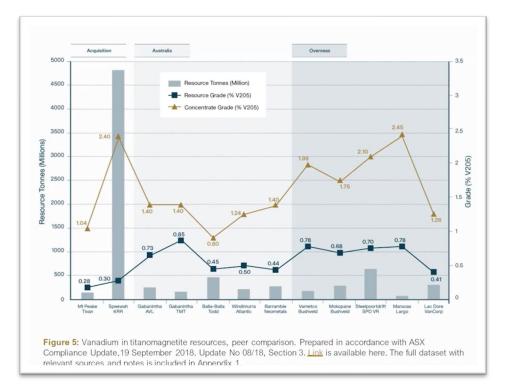
Many GWh of VFB storage projects in pipeline in China



Global Vanadium Production and

By 2030, the cumulative installed capacity of electrochemical energy storage will reach 100GW, and the market share of VFBs is estimated to be about 30%, which is 30GW. If the average storage time of VFBs is 6 hours, it will be about 180GWh.

The 180GWh electrolyte requires 1.5 (1.44 million) tons of V2O5.



- Prof Huamin Zhang, Vanitec Conference, China 2023

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Vanadium supply forecasts –
Tivan Pty Ltd
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Australia can be a major global supplier of this critical mineral and potentially establish a significant battery manufacturing capability

40 years of team effort



Bob Robins and Tony Fane



Martin Green



Rob Burford



Tuti Lim



Bob Brand











Miron Rychcik



Franz Grossmith, Michael Kazacos, Maria S-K, Rod McDermott



and many many more...





Jim Wilson

Jie Bao



Rob Largent



Peter Wegner



Chris Menictas





Bao, Jie Brungs, Mike Burford, Rob Brand, Bob Chau, Andrew Dobrinski, Elizabeth Fane, Tony Fell, Chris Fletcher, John Fynch, Mike Giddy, Alan Green, Martin Hogg, David Howe, Russell Lamberth, Wal Largent, Rob. Lim, Tuti Liyadipitiya, Gamini McCann, John Meng, Ke Menictas, Chris Nasev ,Katia Tomazic Gerd Tran, Tam Trimm, David Wainwright, Mark Walker, Richard Welch, Barry

Adam, Jeffrey Akter, Md. Parvez Alvin, Leonhard Arcidiacono, Alfio Banzato, Amadeo Becker, Ashley Benson, Craig Borman, Michael Cao, Liuyue Channing, Amanda Chau, Andrew Hung Che Mat, Norfamila Cheng, Min Cheung, Winnie Cheuk Chieng, S.C. John Choi, Nak Heon Choong, Petrina Cohen, Elizabeth Corcuera, Sara Eadie, Ben Estornés, Jon Furner, Nicholas Gerber, Anthony Godiwala, Shail Goh. Leesean Goulet, Marc-Antoni Grossmith, Franz Guan, Xinjie Haddadi-Asl, Vahid Hagg, Christoph Holme, Sue Hong Anh, Wendy

Hong, Rui Jeffrey, Adam Joy, Jaqui Ju, Jesse-Yizhou Kasherman, Djen Kausar, Nadeem Kazacos, Michael Kazacos, Nicholas Kazacos, George Kenyon, Rebecca Kiat, Meng Koh, Bing Sen Kronander, Anders Lee, Anna Lee, En Leng Leonardi, Alvin Leong, Tween Teng Li. Jui-Ko Li, Jun Li, Yifeng Liao, Hannah Lim, Tuti Limantri, Yuni Ling, Lionel Lisinio, Lisboa Llewellyn, Paul Ma, Elisha Marston, Susan McAuley, Robert McDermott, Luke McDermott, Rod McKay, David McCloy, Ryan

McKinley, Sarah Milne, Nicholas Mohammadi, Fereidoon Mohammadi, Toraj Morabito, Joe Moses, Michael Murphy, Kristina Navaphol, Tharathon Olansathit, Janephum Olney, Kathryn Padeste, C. Peng, Christina Pennisi, Paul Poon, Grace Priest, Matthew Prifti, Helen Vafiadis Rachmat, Ryana Rahman, Faizur Reid, Nicola Risbud, Mandar Roe, Sarah Rychcik, Miron Saeed, Mohammed Kahlid Sani, Agus Shu, Bing Sim, Yaw Lim Siyu, Yuan Smith, Andrew Stefos, Alex Stiel, Andrew Sukkar, Theresa Suld, Sulide

Sum, Elaine Sun. Biantin Sun, Longgang Tang, Ao Tang, Chung Hang Tham. Andrew Tian, Yuheng (Carolyn) Timbrell, P. Ting, Simon Tio, Kitiono Tjokrowidjaja, Mariana Trinh, Phan Tuerah, Mery Turney, Robert Veersema, Hugh Vierkant, John Vijayaratnam, Pujith (PJ) Wah, Tay Kian Weber, Logan Wegner, Peter Wei. Lai Wen, Bingyi Widjaja, Melinda Wilson, Jim Xie, Jiangzhou Yan, Yitao Yan, Z.H. Dennis Ye, Zuyu Yi, Zuyu Zhang, Xinan Zhong, Shihuang



Thank you



Maria, Nick, George, Michael and Anthony Kazacos



Nick, Michael, Maria, Anthony and George Kazacos





