Development of Highly Efficient Electrode for Vanadium Redox Flow Battery

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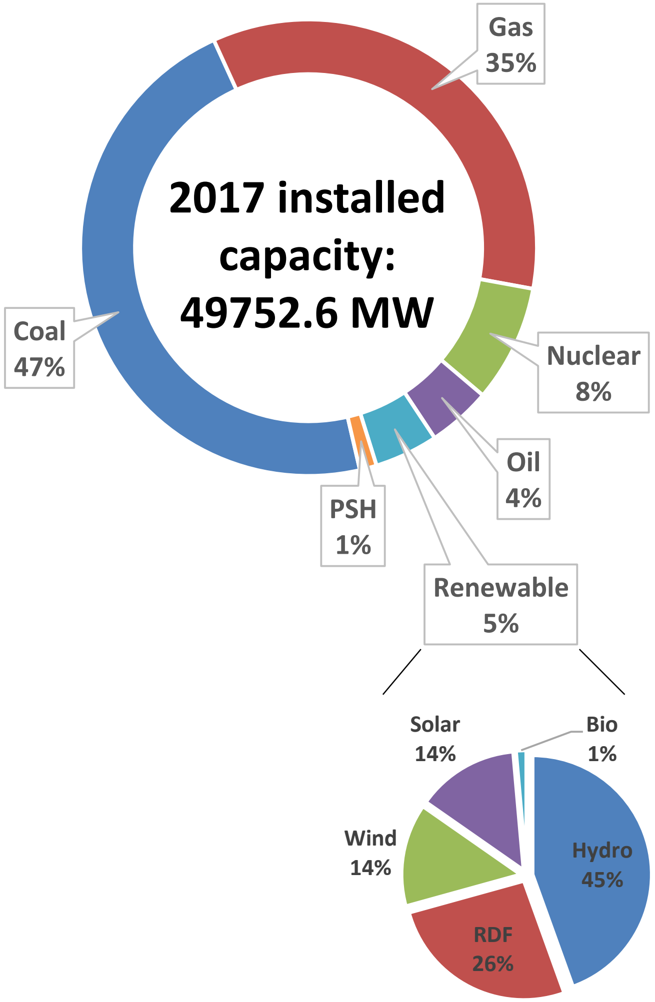
The importance of energy storage system (ESS)

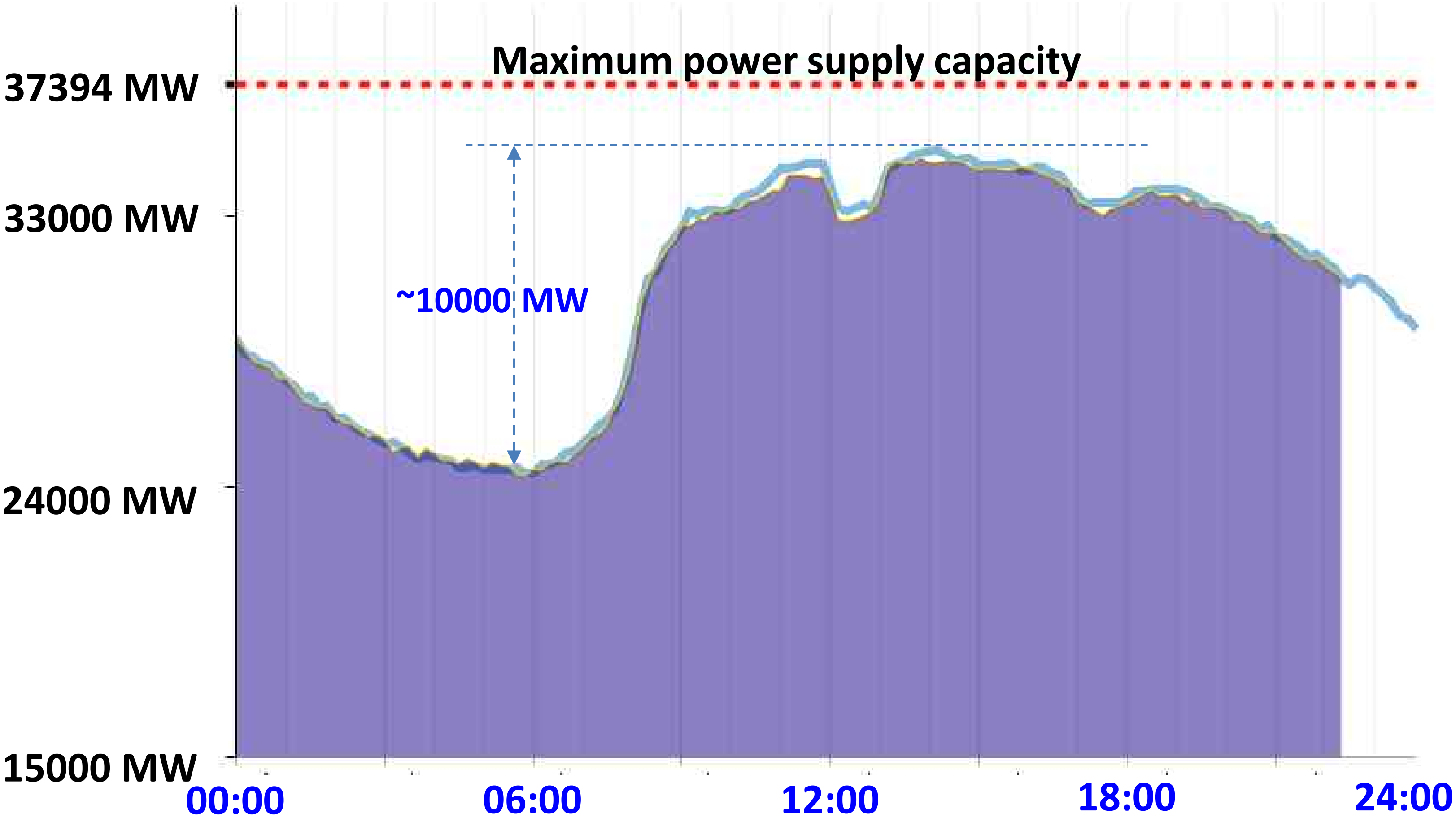
Power Stations in Taiwan

○ 核能電廠 Nuclear power plant
○ 核能計畫 Nuclear power (plan)
○ 火力電廠 Fossil fuel power plant
○ 火力計畫 Fossil fuel power plant (plan)
○ 水力電廠 Hydroelectric power plant



https://www.taipower.com.tw/tc/page.aspx?mid=37

Power Supply in Sep. 19, 2018



10000 MW means…


Taichung Power Plant
5824 MW

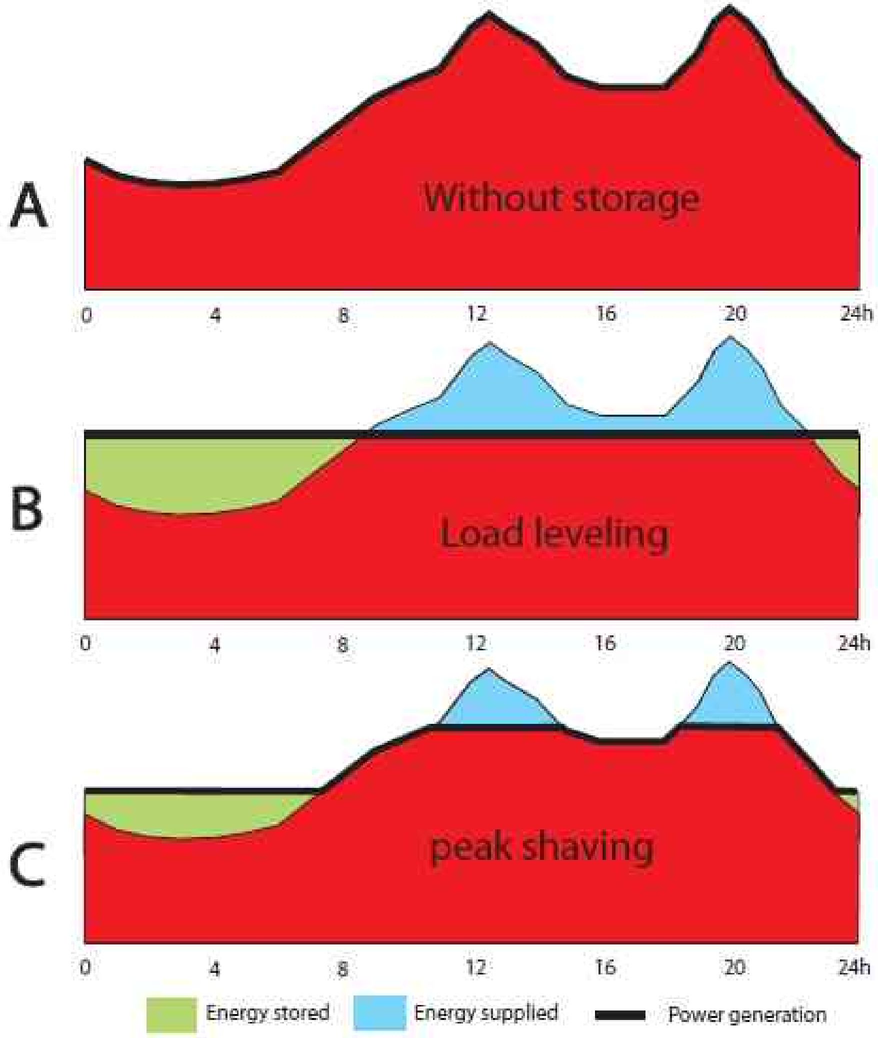
The 2nd largest plant in the world

×2


Maanshan Nuclear Power Plant
1902 MW

×5

The Benefits of Eenergy Storage

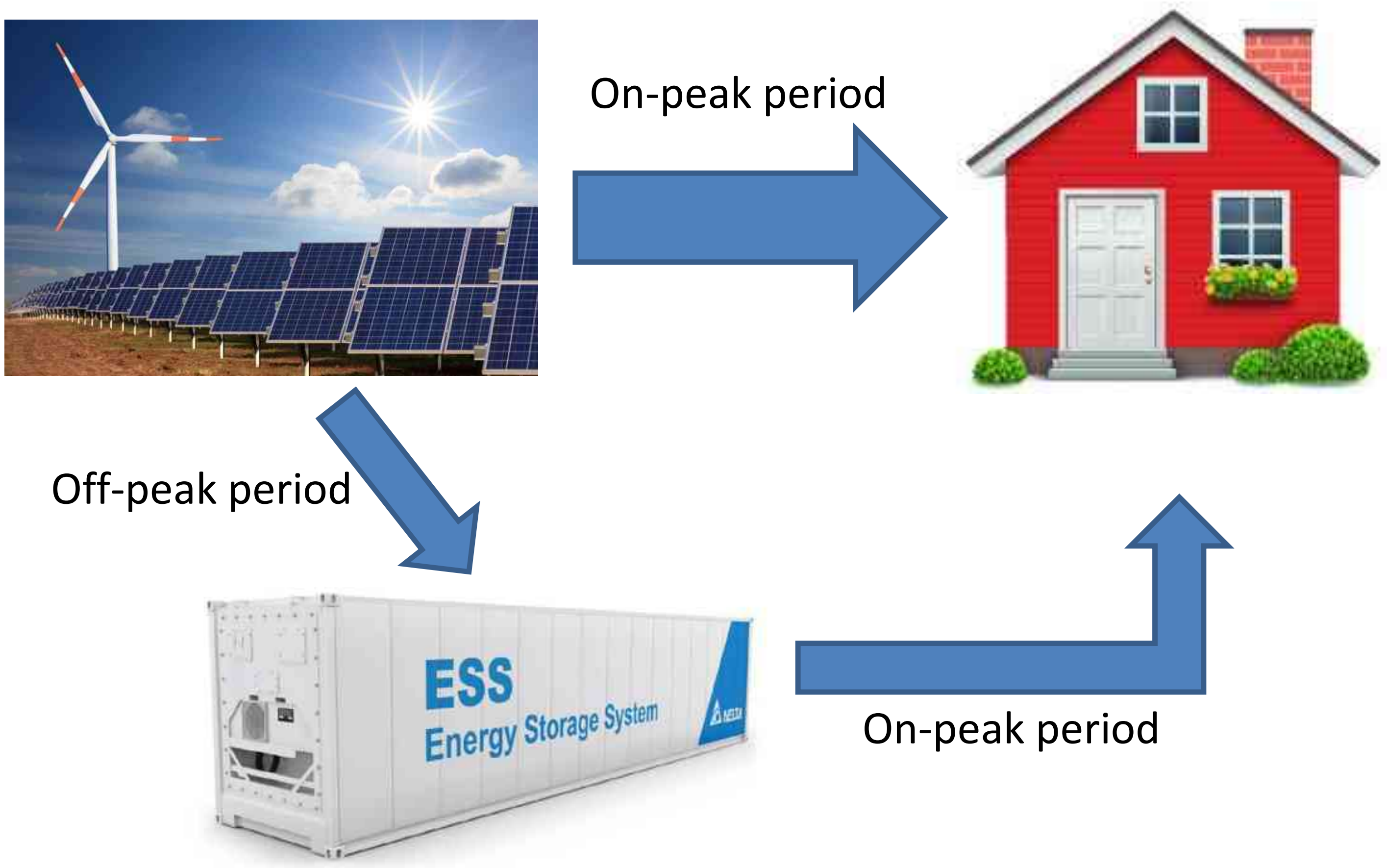


The **time-of-use** electricity cost management is an important issue, which electricity prices are divided into **off-peak, mid-peak and on-peak** with different **prices** for different periods.

Load leveling is a good example of time-of-use cost management.

This application is called **peak shaving** and consists of storing electricity during low demand period and using it during the peak period to reduce the **peak height**.

Sustainable Energy Integrated with Energy Storage System (ESS)



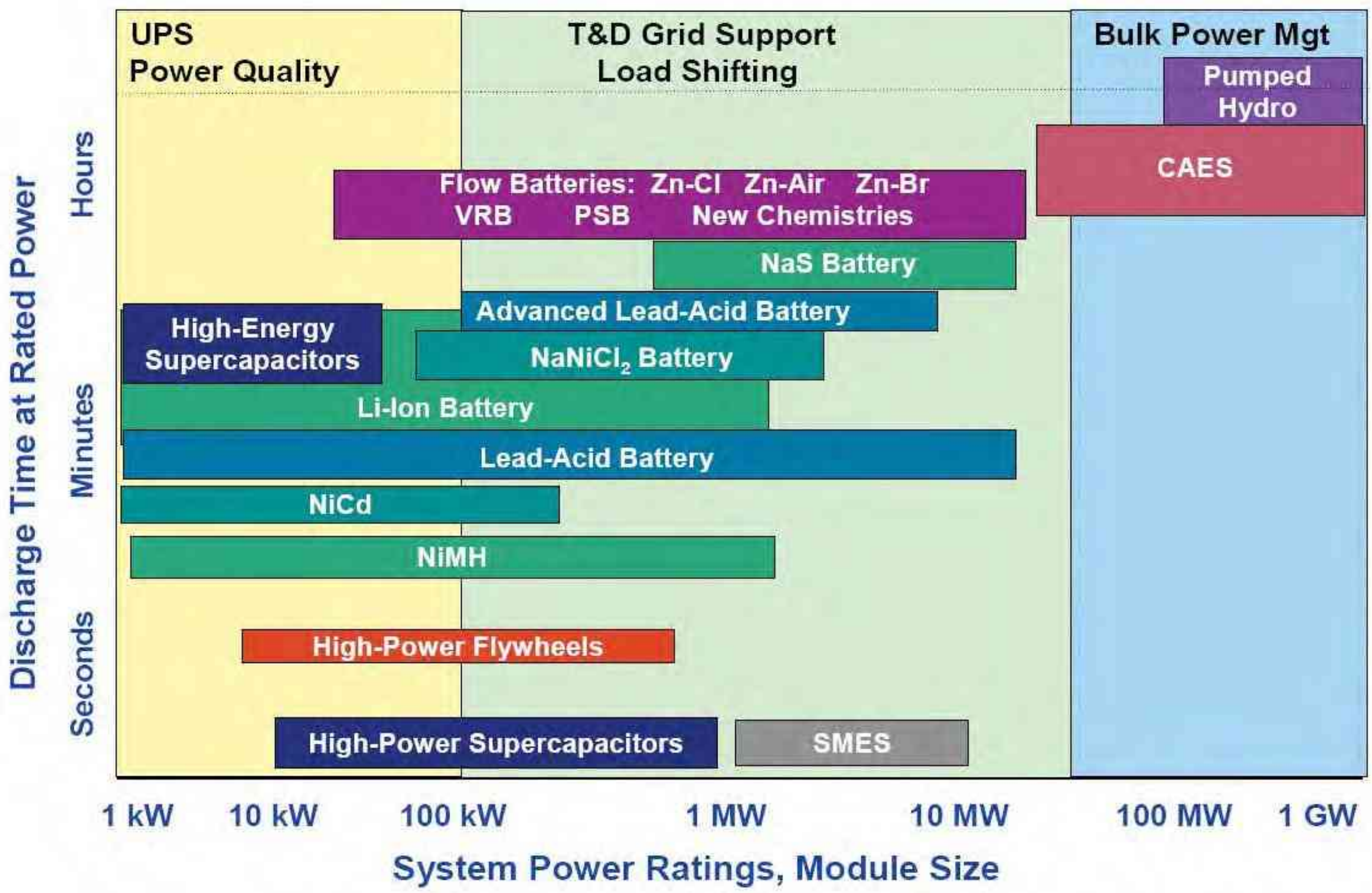
On-peak period

Off-peak period

On-peak period

https://www.vox.com/energy-and-environment/2017/8/30/16224582/wind-solar-exceed-expectations-again
https://www.fastsalehomes.co.uk/selling-your-home/
http://www.deltaww.com/Products/CategoryListT1.aspx?CID=1805&PID=3396&hl=en-US&Name=Container+20ft%2f40ft

Rated Power and Module Size of ESS



Trend of The Word Largest ESS

Before 2015, the world largest ESS is **VRFB** with 60 MWh in Hokkaido, Japan, installed by Sumitomo.

In 2017, the world largest ESS is **LiB** with 129 MWh in Australia, installed by Tesla.

The largest planned ESS is **VRFB** with 800 MWh in Dailen, China, installed by Rongke Power.

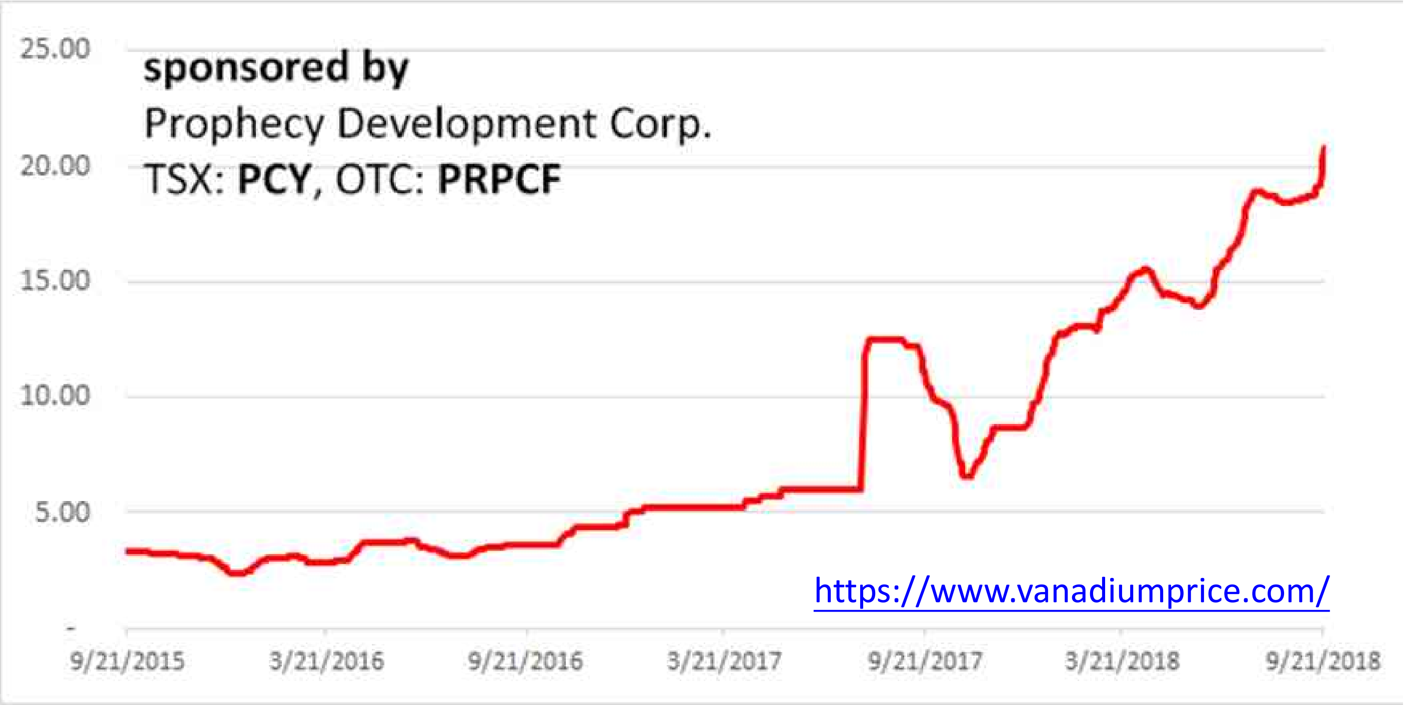
Small VRFB System

REDT 5 kW x 6hrs system - ENIFY

A total storage capacity of 1.1 MWh system - Gildemeister

Vanadium Price Going Higher

Vanadium Pentoxide (V_2O_5) 98% min China USD/lb – 3 years



sponsored by
Prophecy Development Corp.
TSX: **PCY**, OTC: **PRPCF**

https://www.vanadiumprice.com/

Vanadium redox flow battery (VRFB)

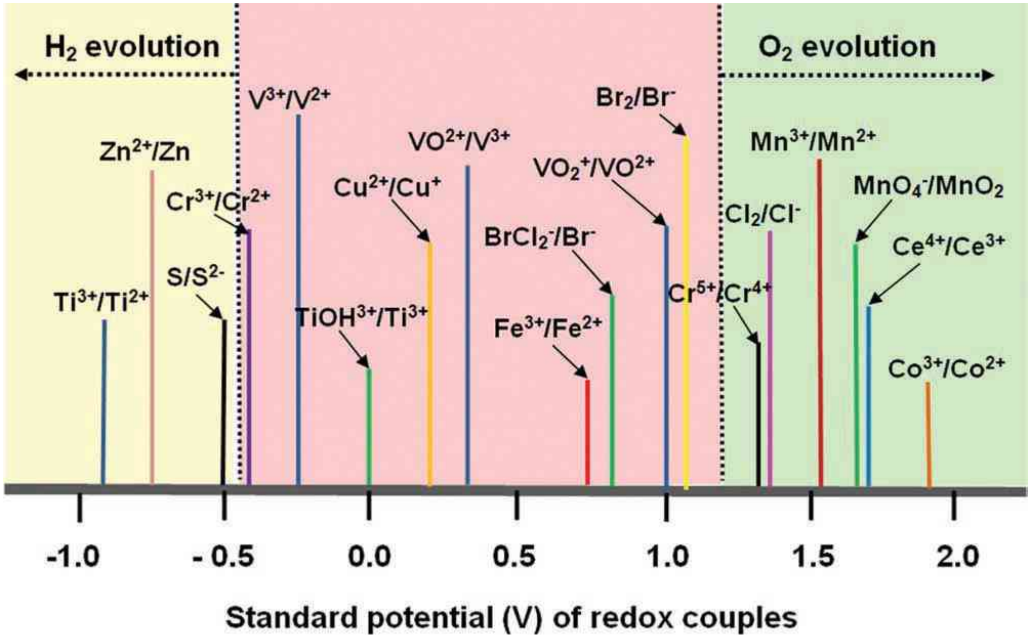
Static Battery vs. Flow Battery

- **Static battery**
  - Lack of flowing electrolyte
  - Electrolyte stored within the same housing as the electrodes
  - Energy content constrained by the volume of the packaging
- **Flow battery**
  - Flowing electrolyte
  - Electrolyte stored external to conversion volume
  - Energy content constrained by the size of external tanks

©E-ONE Moli Energy Corp.

©ENIFY

Redox Flow Battery



Redox couples	Anode	Cathode	E^0 (V) vs. SHE	Performance E (V) vs. SHE	Performance Efficiency
V/V, VRFB	$V^{3+} \rightarrow V^{2+} + e^-$	$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.26	1.35 (50% SOC)	>80%
Fe/Cr	$Cr^{2+} \rightarrow Cr^{3+} + e^-$	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	1.18	0.95 (50% SOC)	~86%
V/Fe	$V^{3+} \rightarrow V^{2+} + e^-$	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	1.02	1.02 (Dis. OCV)	~80%
V/Ce	$V^{3+} \rightarrow V^{2+} + e^-$	$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.93	1.87 (Dis. OCV)	~68%
V/Mn	$V^{3+} \rightarrow V^{2+} + e^-$	$Mn^{3+} + e^- \rightarrow Mn^{2+}$	1.77	1.66 (Dis. OCV)	~63%

Sandia National Laboratories, 2013

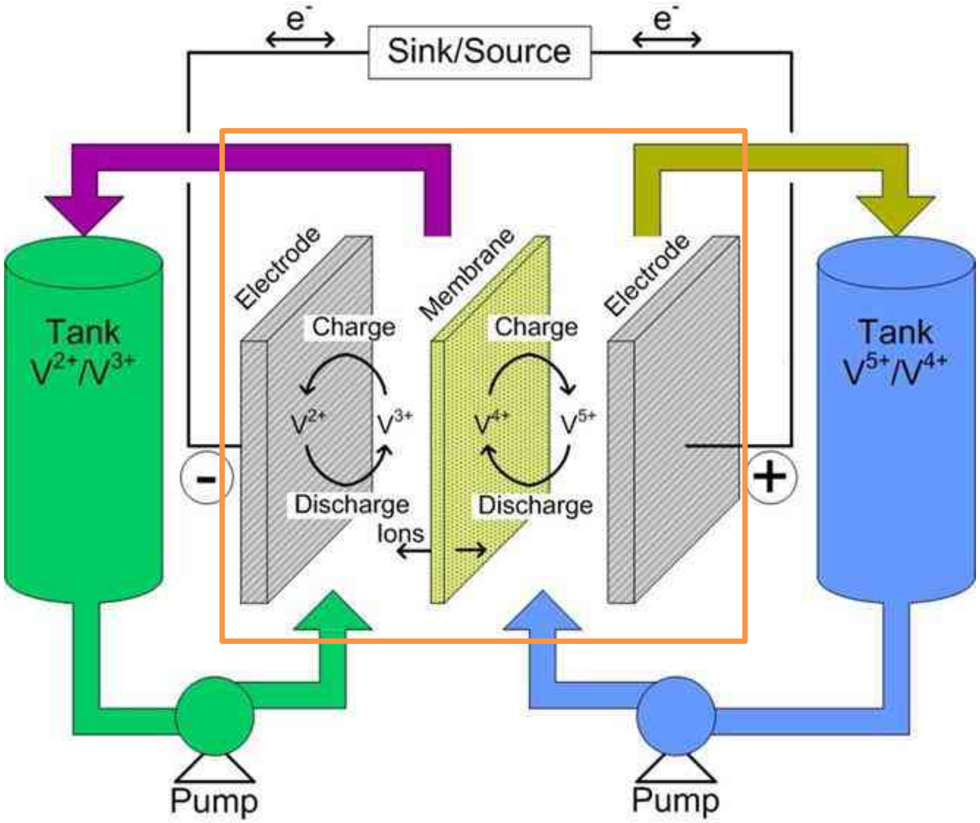
[1] P. Leung, X. Li, C. Ponce De Leon, L. Berlouis, C.T.J. Low, F.C. Walsh, RSC Advances, 2 (2012) 10125-10156.
[2] G. Nikiforidis, L. Berlouis, D. Hall, D. Hodgson, J. Power Sources, 243 (2013) 691-698.
[3] C. Tang, D. Zhou, Electrochim. Acta, 65 (2012) 179-184.

Several Chemical Energy Storage System

	Vanadium Redox Flow Battery	Zn-Br Battery	Li-ion Battery
Calendar & Cycle life	★ > 25 yrs	> 15 yrs	6 – 10 yrs
Scalability	★ 1 MWh – 1 GWh	10 kWh – 10 MWh	1 MWh – 100 MWh
Cost (US$/kWh)	600 – 800	700 – 900	★ 500 – 1200
LCOE (US$/kWh)	★ 0.02 – 0.04	0.08 – 0.12	0.25 – 0.70
Application time range	★ Hrs/days	Hrs	Hrs
Round trip efficiency	80%	70%	★ 90%
EOL value	★ Yes	Limited	Negative Needs disposal
Safety	★ Safe	Dangerous	Dangerous
Constrains	Needs scale	Safety, lifetime, needs scale	Safety, lifetime

LCOE: Overall Levelized Cost of Energy
EOL: End-of-life

Vanadium Redox Flow Battery (VRFB)



Positive electrode (Charging mode)

$$VO^{2+} + H_2O \rightarrow VO_2^{+} + 2H^{+} + e^{-} \rightarrow E^{0} = 1.00\,V$$

Negative electrode (Charging mode)

$$V^{3+} + e^{-} \rightarrow V^{2+} \quad E^{0} = 0.255\,V$$

Net reaction (Charge Mode)

$$VO^{2+} + H_2O + V^{3+} \rightarrow {VO_2}^{2+} + 2H^{+} + V^{2+} \quad E^{0} = 1.255\,V$$

Ding.et.al., J. Phys. Chem. Lett., 4 (2013) 1281–1294

Advantages of VRFB

1) **Long cycle life, cycle stability (> 10,000)**
2) **Efficiency >75 % is possible**
3) **Avoid cross-contamination**
4) **Greater design flexibility**
5) **Environmental friendly & safety**
6) **Low maintenance cost**

V is the only element which possesses four adjacent oxidation states that are all stable in aqueous solutions.

$$\begin{array}{c|c|} \cline{2-2} + & V(4) \underset{D}{\overset{C}{\rightleftarrows}} V(5) \\ \cline{1-2} - & V(3) \underset{D}{\overset{C}{\rightleftarrows}} V(2) \\ \cline{2-2} \end{array}$$

Ki Jae Kim et, al. J. Mater. Chem. A, 3 (2015) 16913–16933
https://www.chemicool.com/elements/vanadium.html

Energy Density

Calculate the energy density 1 M of V(4)

$$\boldsymbol{E = n \times C \times F \times V}$$

Energy density = Electron-transfer number × Conc. × Faraday const. × Voltage

$$E\left(\frac{Wh}{L}\right) = 1 \times 1\frac{mol}{L} \times 96485\frac{C}{mol} \times 1.2\,V \div 3600\frac{Ah}{C} = 32.16\frac{Wh}{L}$$

Positive electrode (Charging mode)

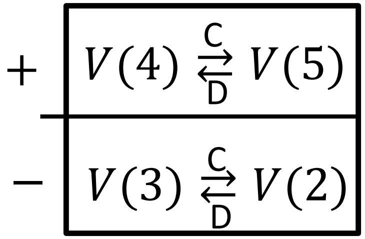
$$VO^{2+} + H_2O \rightarrow VO_2^{+} + 2H^{+} + e^{-} \rightarrow E^0 = 1.00\,V$$

Negative electrode (Charging mode)

$$V^{3+} + e^{-} \rightarrow V^{2+} \quad E^0 = 0.255\,V$$

Net reaction (Charge Mode)

$$VO^{2+} + H_2O + V^{3+} \rightarrow VO_2{}^{2+} + 2H^{+} + V^{2+} \quad E^0 = 1.255\,V$$



$$+ \quad V(4) \overset{C}{\underset{D}{\rightleftarrows}} V(5)$$

$$- \quad V(3) \overset{C}{\underset{D}{\rightleftarrows}} V(2)$$

Increasing Energy Density of VRFB

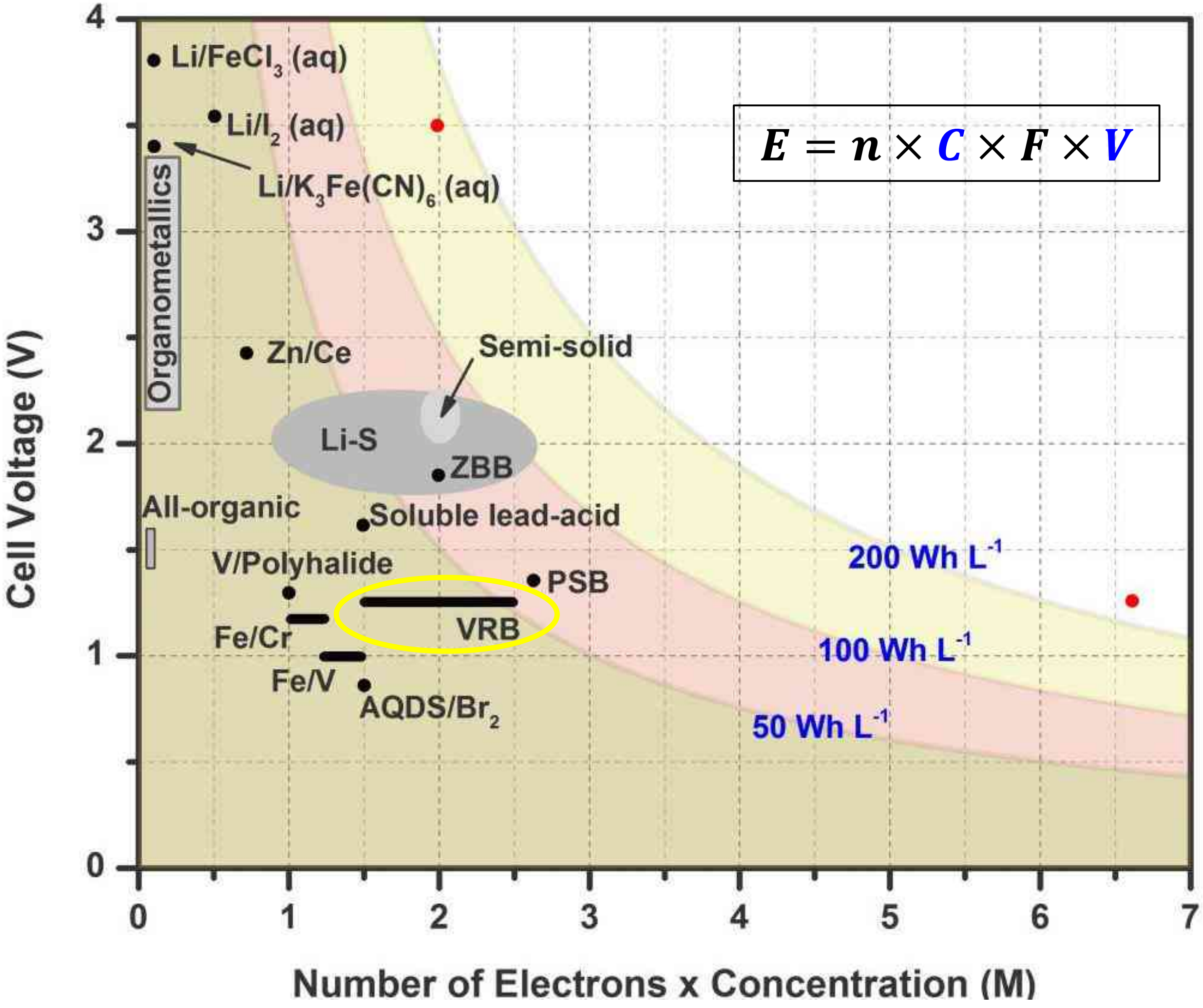
Energy density = Electron-transfer number × Conc. × Faraday const. × Voltage

$$E = n \times \boxed{C} \times F \times \boxed{V}$$

Increase the solubility of vanadium ion

Reduce overpotential and polarization of electrode

Energy Density of Various RFBs



$$E = n \times C \times F \times V$$

Factors Affecting VRFB Efficiency

Energy efficiency = Coulombic efficiency x Voltage efficiency

Electrode engineering

- **Redox kinetics**
  - The redox kinetics of the VRFB electrolytes at electrode surfaces and the mass transport processes of the vanadium electrolytes in the porous electrodes determine kinetic and transport polarizations, respectively, which affect energy efficiency.
- **Side reaction**
  - Side reactions such as hydrogen evolution reaction lower coulombic efficiency.

Electrolyte engineering

- **Ionic conductivity**
  - The ionic conductivity of VRFB electrolytes influences ohmic polarization of VRFB and consequently voltage efficiency.

Stack engineering

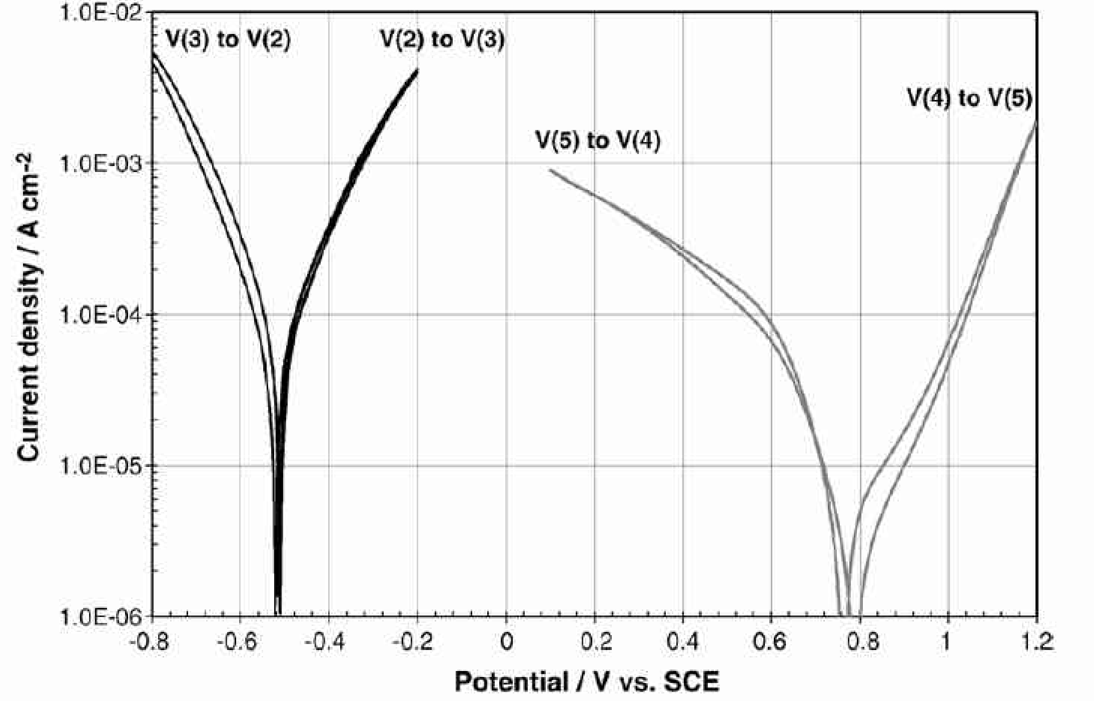
- **Shunt current**
  - Shunt current via vanadium electrolyte phases in a bipolar stack lowers energy efficiency
- **Vanadium crossover and water crossover**
  - Vanadium crossover and water crossover lead to a capacity imbalance, resulting in a lowered coulombic efficiency and capacity decay with a repeated cycling.

Renewable and Sustainable Energy Reviews, 69 (2017) 263-274

Kinetics of Vanadium Redox Reaction

$V^{3+} + e^- \rightleftarrows V^{2+}$

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



- **The V(II)/V(III) reaction is controlled by electron transfer, whereas a certain chemical step seems to play the dominant roles during another V(IV)/V(V) reaction.**

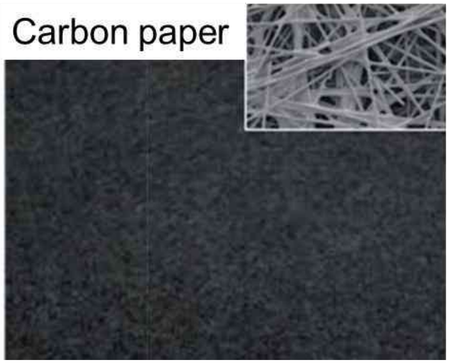
M. Gattrell et al., Electrochimica Acta 51 (2005) 395–407
G. Oriji et al., Journal of Power Sources 139 (2005) 321–324

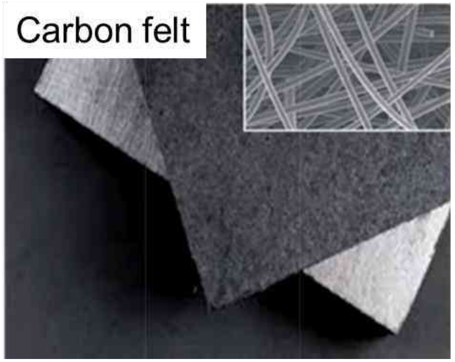
Carbon-based electrode used in VRFB

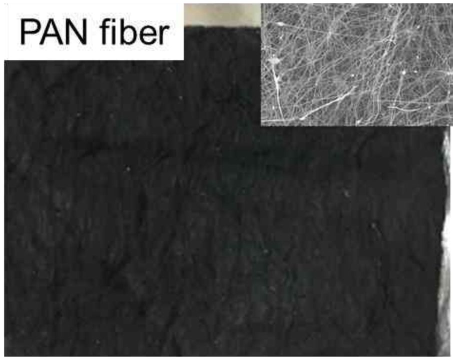
Carbon-based Electrodes

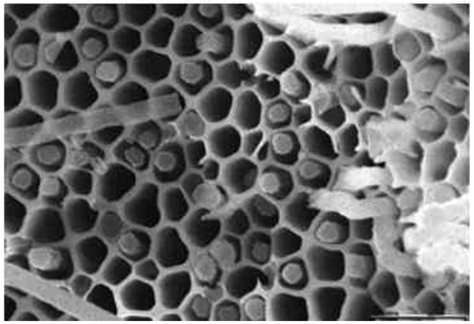
They play the role of three major functions in VRFB:
1. Mono/bipolar plates. 2. Liquid-diffusion layer. 3. Catalytic sites.

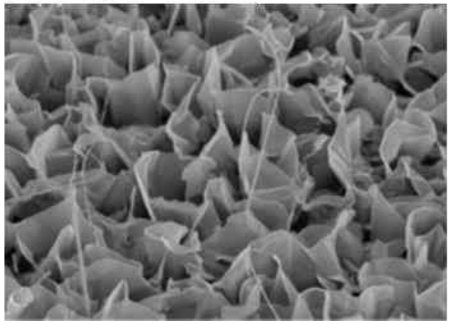

Carbon cloth

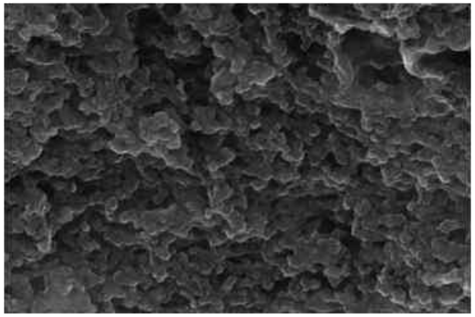

Carbon paper

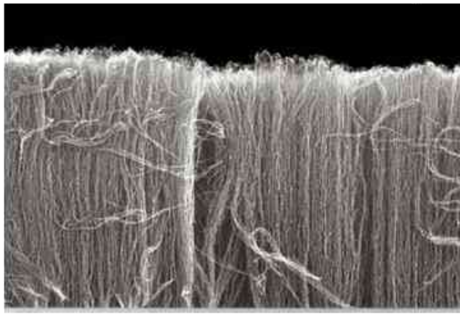

Carbon felt


PAN fiber

Mesoporous carbon


Graphene


Carbon black


Carbon nanotube


Modifications of carbon-based electrode include oxidation treatment, nitrogenization treatment, and introduction of an catalyst.

Hartmann.et.al., J. Phys. Chem. Lett., 4 (2013) 1281−1294

Modifications of Carbon-based Electrodes

- **Functionalization of carbon-based materials**

  thermal, acid, plasma, & microwave treatment

  (enhance electrochemical activity of electrode)

- **Additive**

  graphene, graphene oxide, & carbon nanotube

  (increase surface area & reaction active site of electrode)

- **Dopant**

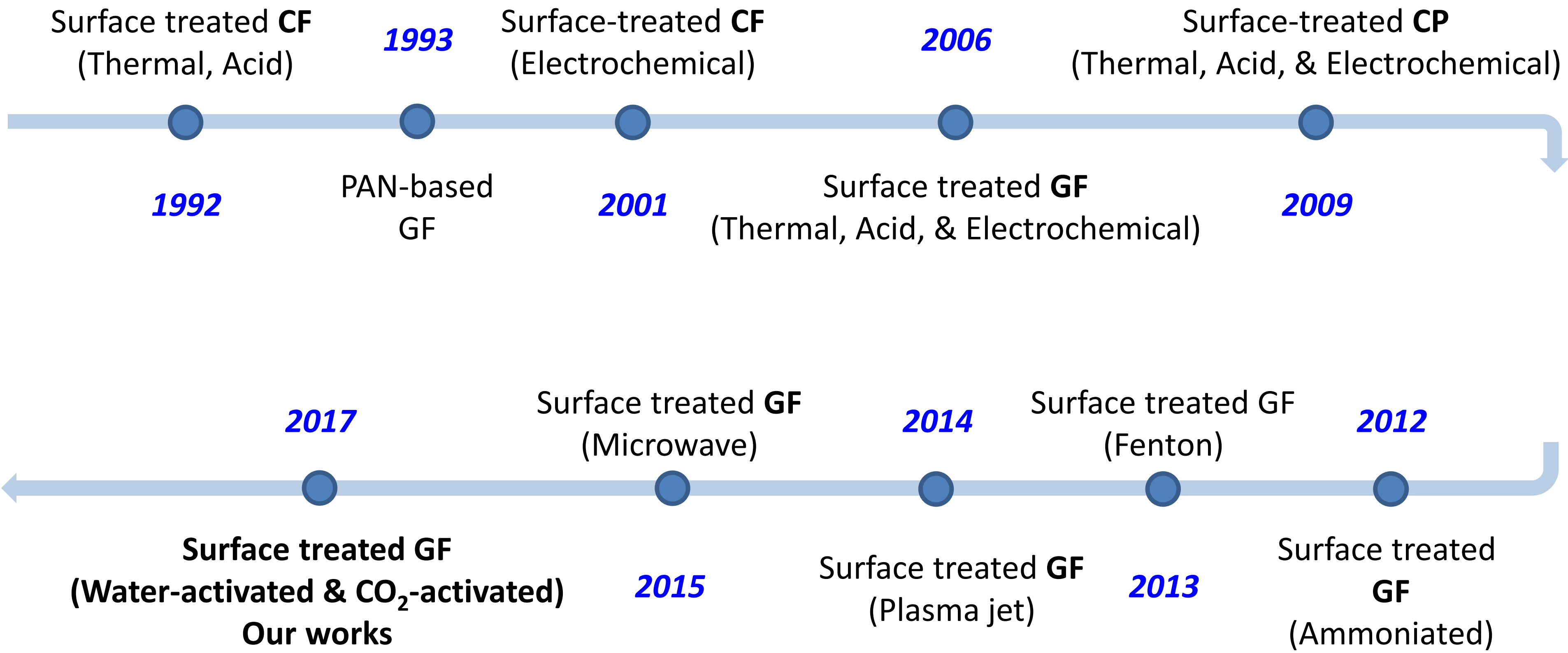
  N-doped, S-doped process

  (introduce other active element)

Historical Flow Chart for Development on Carbon Based Electrodes

CF: Carbon felt
GF: Graphite felt
CP: Carbon paper

Functionalization of carbon-based materials



1992 Surface treated **CF** (Thermal, Acid)

1993 PAN-based GF

2001 Surface-treated **CF** (Electrochemical)

2006 Surface treated **GF** (Thermal, Acid, & Electrochemical)

2009 Surface-treated **CP** (Thermal, Acid, & Electrochemical)

2012 Surface treated GF (Ammoniated)

2013 Surface treated GF (Fenton)

2014 Surface treated **GF** (Plasma jet)

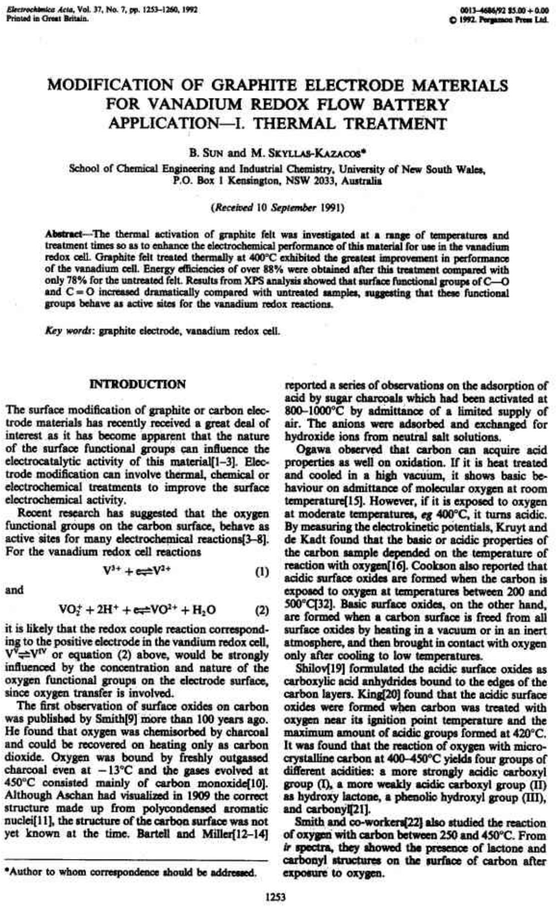
2015 Surface treated **GF** (Microwave)

2017 **Surface treated GF (Water-activated & CO_2-activated) Our works**

K.J. Kim, M.-S. Park, Y.-J. Kim, J.H. Kim, S.X. Dou, M. Skyllas-Kazacos, J. Mater. Chem. A, 3, (2015) 16913-16933

Functionalized Graphite Felt Electrode

First paper demonstrated surface modification of carbon felt and claimed the mechanism between *V atom and C-O functional groups of vanadium redox reaction*.



Electrochimica Acta, Vol. 37, No. 7, pp. 1253–1260, 1992
Printed in Great Britain.

0013–4686/92 $5.00 + 0.00

MODIFICATION OF GRAPHITE ELECTRODE MATERIALS FOR VANADIUM REDOX FLOW BATTERY APPLICATION—I. THERMAL TREATMENT

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P.O. Box 1 Kensington, NSW 2033, Australia

(*Received* 10 *September* 1991)

Abstract—The thermal activation of graphite felt was investigated at a range of temperatures and treatment times so as to enhance the electrochemical performance of this material for use in the vanadium redox cell. Graphite felt treated thermally at 400°C exhibited the greatest improvement in performance of the vanadium cell. Energy efficiencies of over 88% were obtained after this treatment compared with only 78% for the untreated felt. Results from XPS analysis showed that surface functional groups of C—O and C=O increased dramatically compared with untreated samples, suggesting that these functional groups behave as active sites for the vanadium redox reactions.

Key words: graphite electrode, vanadium redox cell.

INTRODUCTION

The surface modification of graphite or carbon electrode materials has recently received a great deal of interest as it has become apparent that the nature of the surface functional groups can influence the electrocatalytic activity of this material[1–3]. Electrode modification can involve thermal, chemical or electrochemical treatments to improve the surface electrochemical activity.

Recent research has suggested that the oxygen functional groups on the carbon surface, behave as active sites for many electrochemical reactions[3–8]. For the vanadium redox cell reactions

$$V^{3+} + e \rightleftharpoons V^{2+} \qquad (1)$$

and

$$VO_2^{+} + 2H^{+} + e \rightleftharpoons VO^{2+} + H_2O \qquad (2)$$

it is likely that the redox couple reaction corresponding to the positive electrode in the vandium redox cell, $V^{V} \rightleftharpoons V^{IV}$ or equation (2) above, would be strongly influenced by the concentration and nature of the oxygen functional groups on the electrode surface, since oxygen transfer is involved.

The first observation of surface oxides on carbon was published by Smith[9] more than 100 years ago. He found that oxygen was chemisorbed by charcoal and could be recovered on heating only as carbon dioxide. Oxygen was bound by freshly outgassed charcoal even at −13°C and the gases evolved at 450°C consisted mainly of carbon monoxide[10]. Although Aschan had visualized in 1909 the correct structure made up from polycondensed aromatic nuclei[11], the structure of the carbon surface was not yet known at the time. Bartell and Miller[12–14] reported a series of observations on the adsorption of acid by sugar charcoals which had been activated at 800–1000°C by admittance of a limited supply of air. The anions were adsorbed and exchanged for hydroxide ions from neutral salt solutions.

Ogawa observed that carbon can acquire acid properties as well on oxidation. If it is heat treated and cooled in a high vacuum, it shows basic behaviour on admittance of molecular oxygen at room temperature[15]. However, if it is exposed to oxygen at moderate temperatures, *eg* 400°C, it turns acidic. By measuring the electrokinetic potentials, Kruyt and de Kadt found that the basic or acidic properties of the carbon sample depended on the temperature of reaction with oxygen[16]. Cookson also reported that acidic surface oxides are formed when the carbon is exposed to oxygen at temperatures between 200 and 500°C[32]. Basic surface oxides, on the other hand, are formed when a carbon surface is freed from all surface oxides by heating in a vacuum or in an inert atmosphere, and then brought in contact with oxygen only after cooling to low temperatures.

Shilov[19] formulated the acidic surface oxides as carboxylic acid anhydrides bound to the edges of the carbon layers. King[20] found that the acidic surface oxides were formed when carbon was treated with oxygen near its ignition point temperature and the maximum amount of acidic groups formed at 420°C. It was found that the reaction of oxygen with microcrystalline carbon at 400–450°C yields four groups of different acidities: a more strongly acidic carboxyl group (I), a more weakly acidic carboxyl group (II) as hydroxy lactone, a phenolic hydroxyl group (III), and carbonyl[21].

Smith and co-workers[22] also studied the reaction of oxygen with carbon between 250 and 450°C. From *ir* spectra, they showed the presence of lactone and carbonyl structures on the surface of carbon after exposure to oxygen.

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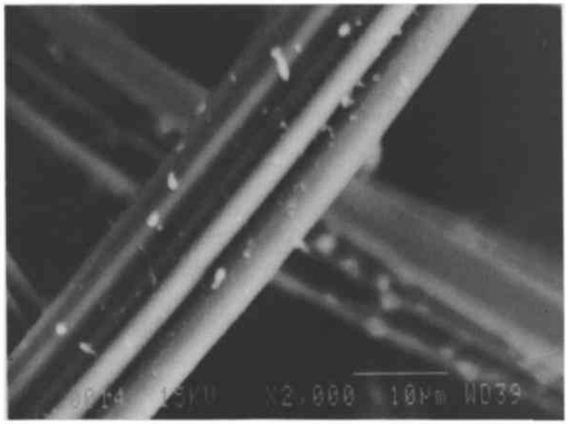
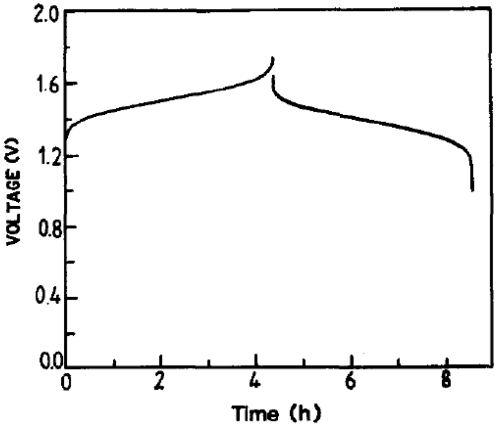
*Author to whom correspondence should be addressed.

The C-O functional groups on the electrode surface probably behave as **active sites**, catalyzing the vanadium species reactions. The mechanism of catalysis for reactions on the electrode surface can be **hypothesized.**



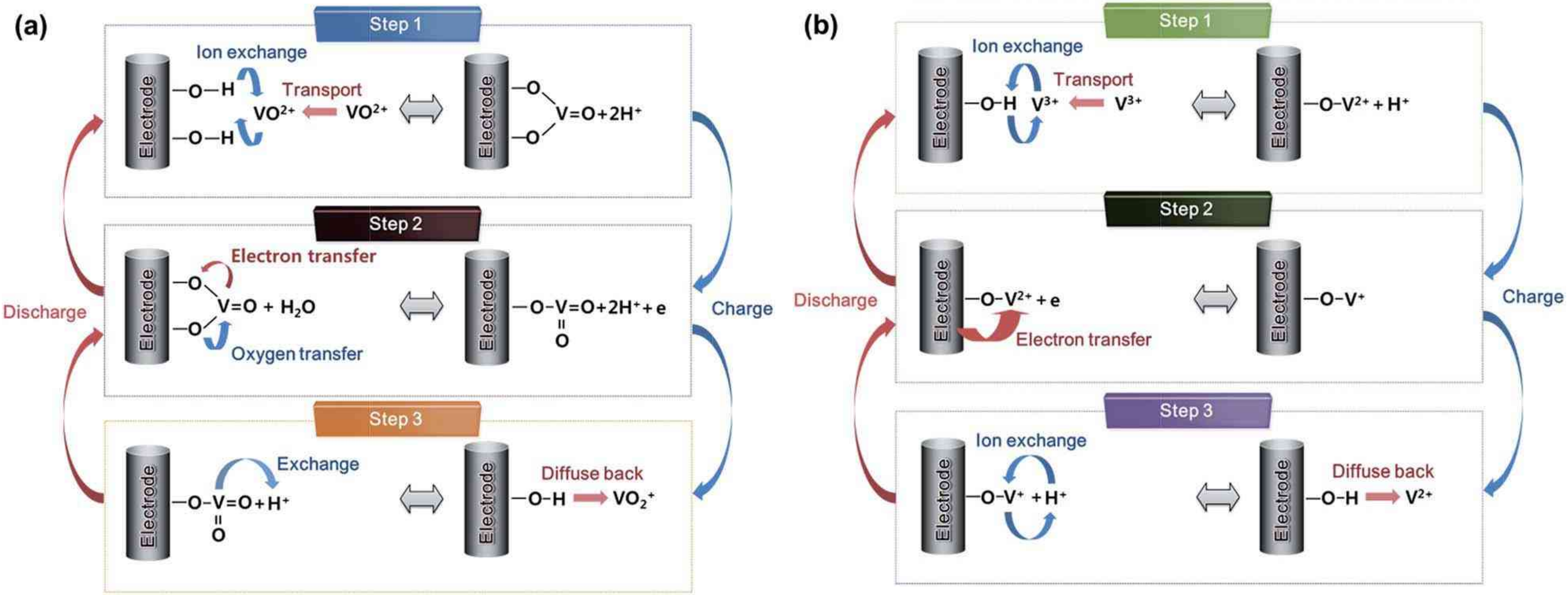


B. Sun & M. Skyllas-Kazacos, Electrochim. Acta, 36 (1991) 513–517.

General Mechanism for Redox Reactions of VRFB

VO^{2+}/VO$_2^+$ redox couple in the catholyte

V^{2+}/V^{3+} redox couple in the anolyte

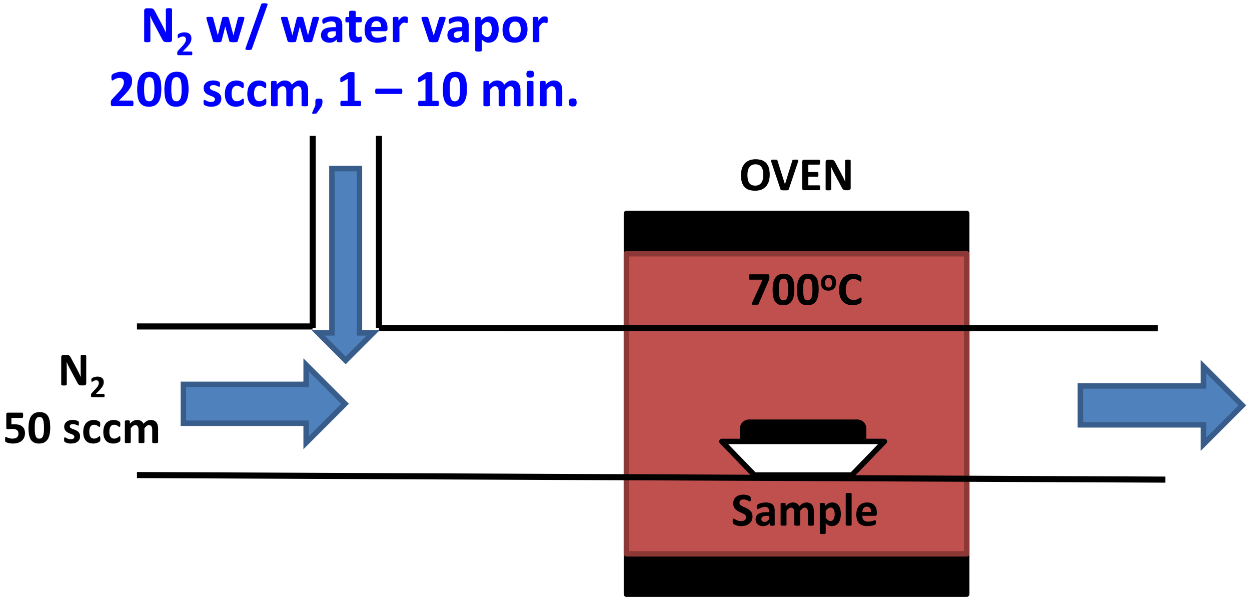


- C–OH functional groups behave as active sites for the redox reactions
- The positive electrode involve the transfer of an oxygen atom, which is likely to be the limiting reaction in the overall mechanism.
- By increasing the concentration of oxygen functional groups can enhance the oxygen transfer process

[1] K.J. Kim, M.-S. Park, Y.-J. Kim, J.H. Kim, S.X. Dou, M. Skyllas-Kazacos, J. Mater. Chem. A, 3 (2015) 16913-16933.
[2] B. Sun, M. Skyllas-Kazacos, Electrochim. Acta, 37 (1992) 2459-2465.

Water-activated Graphite Felt

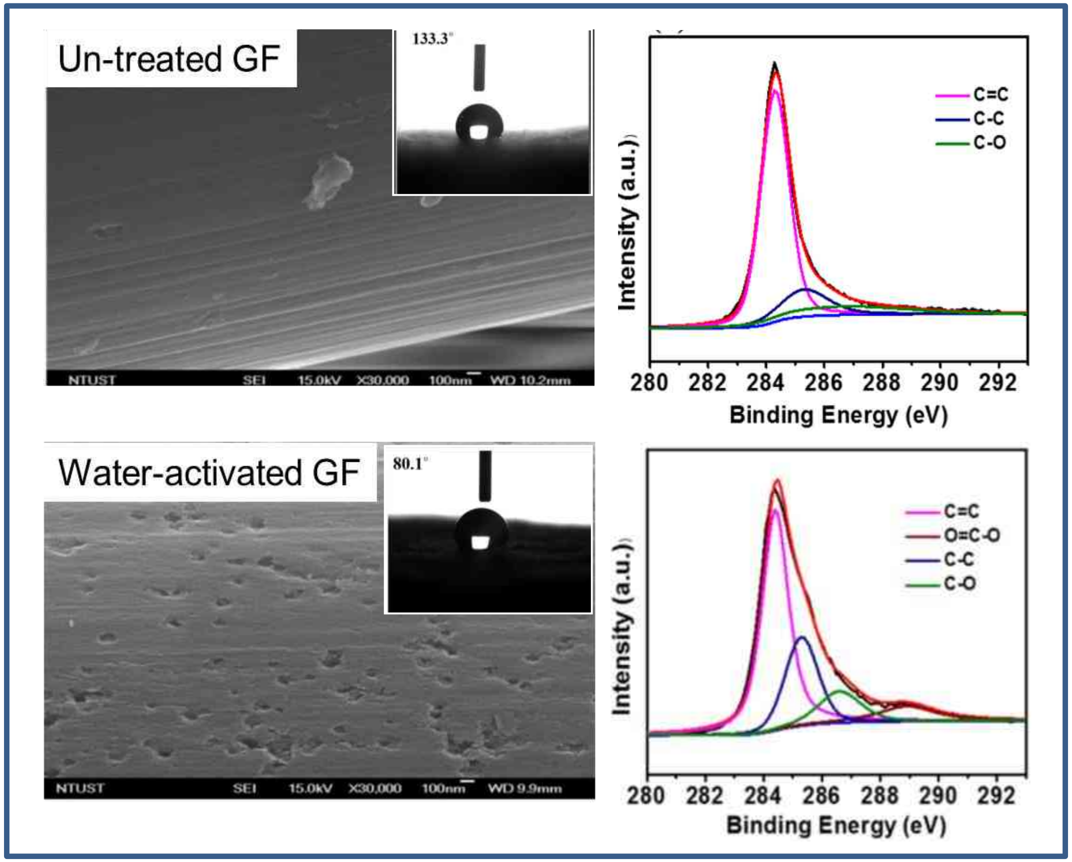
Wang* *et al.*, J. Power Sources, 341 (2017) 270-279

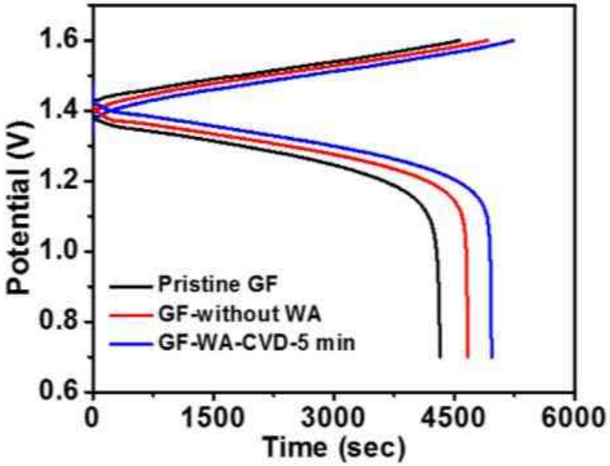


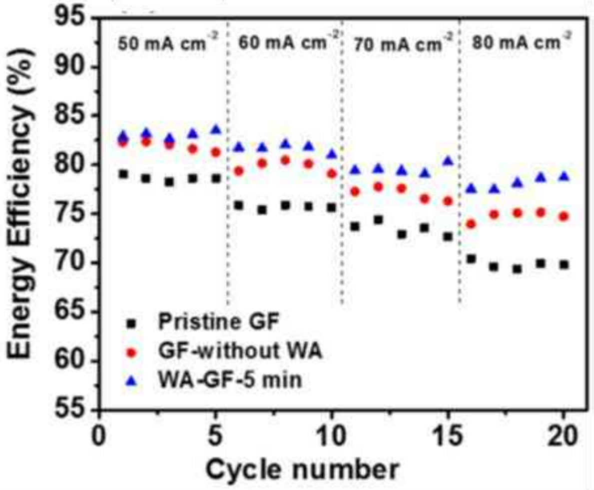
1) $C + H_2O \rightarrow CO + H_2 \quad \Delta H = +131\ kJ\ mol^{-1}$
2) $C + 2H_2 \rightarrow CH_4 \quad \Delta H = -75\ kJ\ mol^{-1}$
3) $CO + H_2O \rightarrow H_2 + CO_2 \quad \Delta H = -41\ kJ\ mol^{-1}$
4) $C + CO_2 \rightarrow 2CO \quad \Delta H = -393\ kJ\ mol^{-1}$

Water-activated Graphite Felt

- Improving the roughness of the fiber surface
- Getting more functional groups on fiber surface
- Increasing hydrophilicity of the fiber

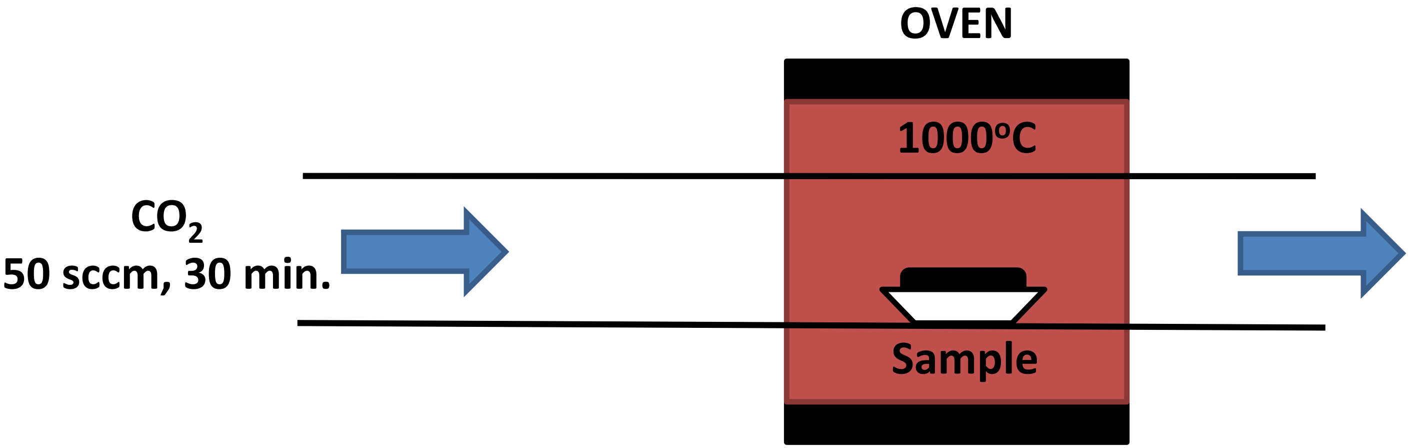






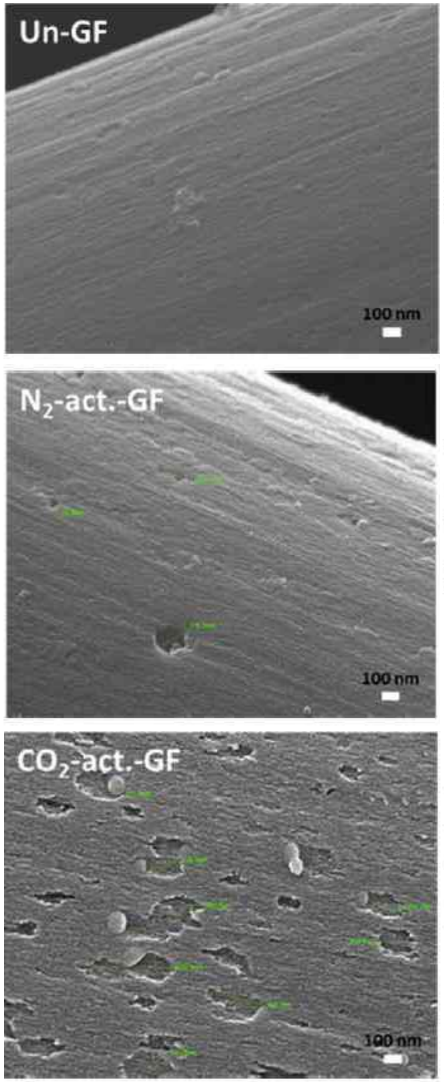
CO_2-activated Graphite Felt

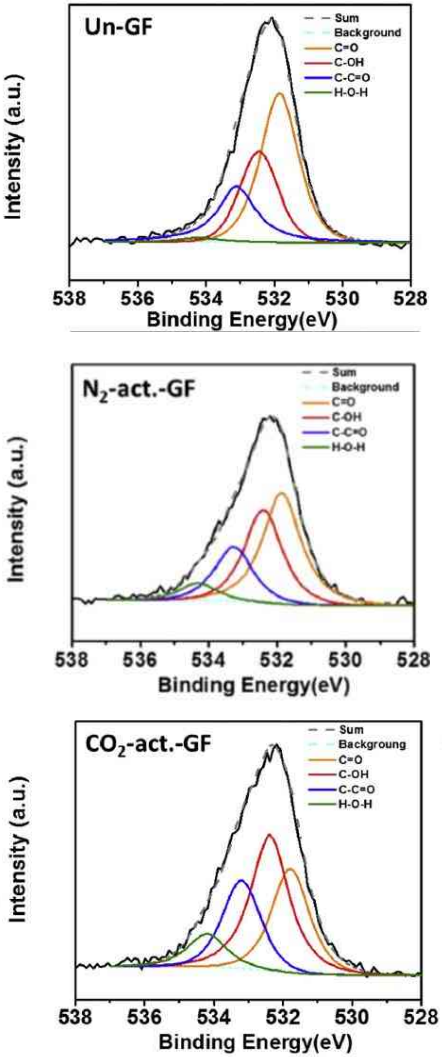
Wang* *et al.*, J. Power Sources, 364 (2017) 270-279

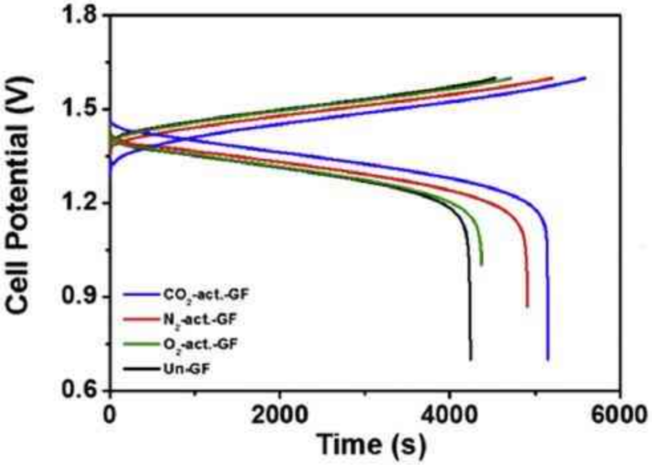


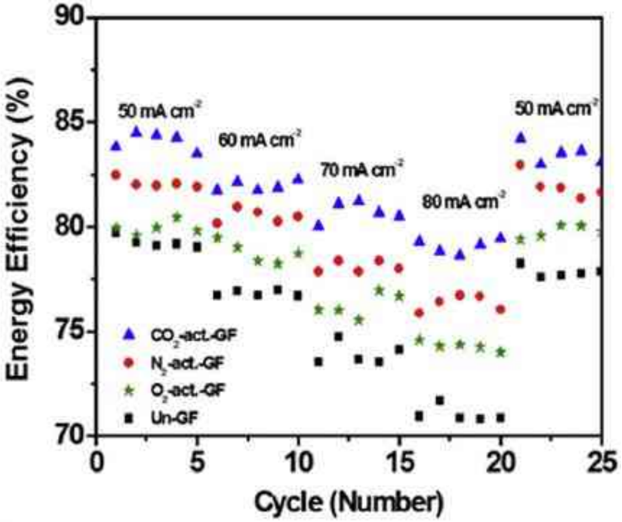
$$C + CO_2 \rightarrow 2CO \quad \Delta H = -393\ kJ\ mol^{-1}$$

CO_2-activated Graphite Felt









The efficiency enhancement is attributed to the higher number of oxygen-containing functional groups on the graphite felt.

Historical Flow Chart for Development on Carbon Based Electrodes

CF: Carbon felt
GF: Graphite felt
CP: Carbon paper

Carbon-based materials composite

Carbon polymer composite
1989

2008
Graphite/CNT

CNT/GF,
Graphite/graphite oxide
2011

2013
Graphite oxide/CNT
CF/CNF/CNT

Direct growth Bamboo-like
CNT/GF
Our works
2016

2018
Graphene nanoplate/CF

N-doped carbon materials electrode

N-doped
Mesoporous carbon
2010

2011
N-doped CNT/GF

N-doped Carbon
2012

2013
N-doped graphene

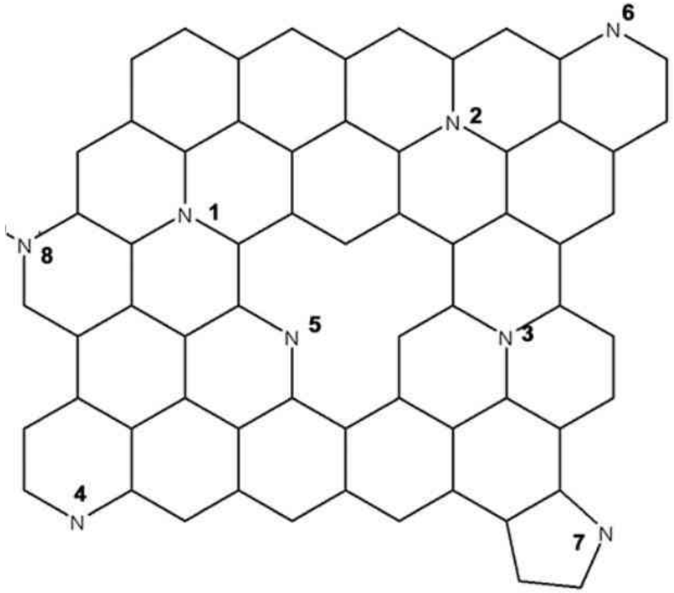
N-doped GF
2015

2017
Nitrogen-doped
porous graphene

K.J. Kim, M.-S. Park, Y.-J. Kim, J.H. Kim, S.X. Dou, M. Skyllas-Kazacos, J. Mater. Chem. A, 3 (2015), 16913-16933

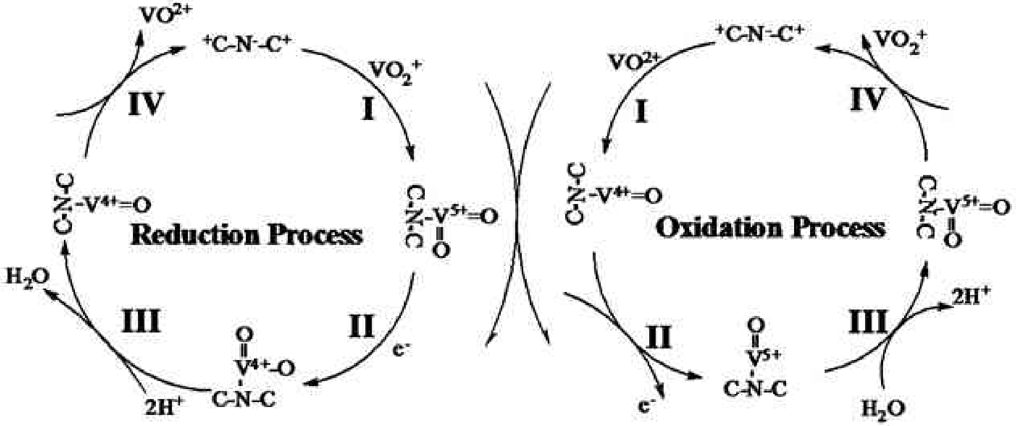
Mechanism of Redox Reactions of VRFB on N-doped Carbon-based Materials

The type of nitrogen bonding with carbon in the graphene sheets determines the catalytic activity of electrode.



1,2,3 quaternary nitrogen; 4,5,6: pyrridinic-like N; 7: pyrrolic-like N; 8: oxidic-N.

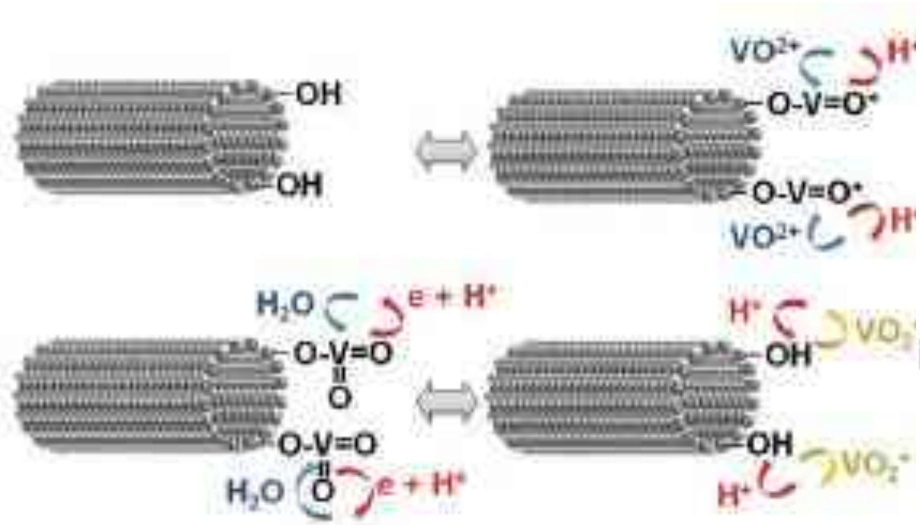
The quaternary nitrogen is more stable and serves as the active site for the $[VO]^{2+}/[VO_2]^{+}$ redox couple reaction.

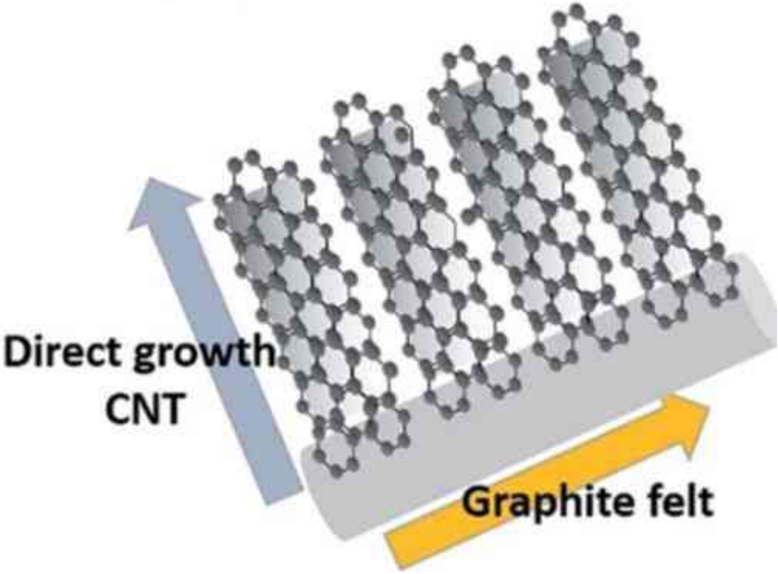


Jutao Jin, Xiaogang Fu, Qiao Liu, Yanru Liu, Zhiyang Wei, Kexing Niu, and Junyan Zhang, et al., ACS Nano 7 (2013) 4764–4773

CNTs on Functionalized Graphite Felt

1. **Edge plane of CNT as the active site**
2. **Enhance electrical conductivity**
3. **Reduce inner resistance**

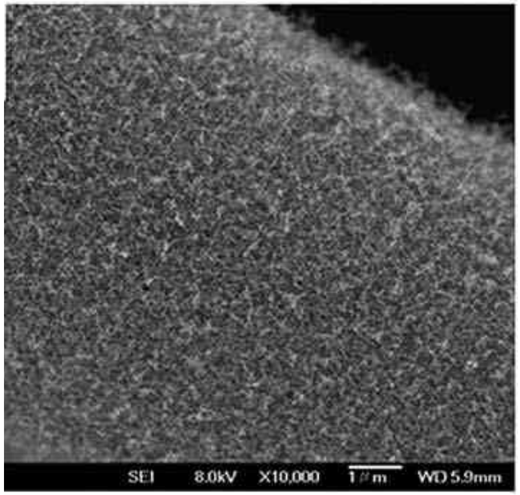


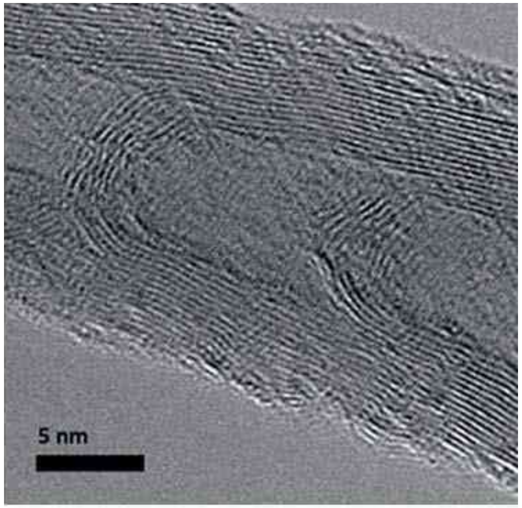


[1] RSC Adv., 6, (2016) 102068–102075
[2] Nir Pour *et, al.* J. Phys. Chem. C (2015) 119 5311−5318
[3] Ki Jae Kim *et, al*. Chem A (2015) 3 16913–16933

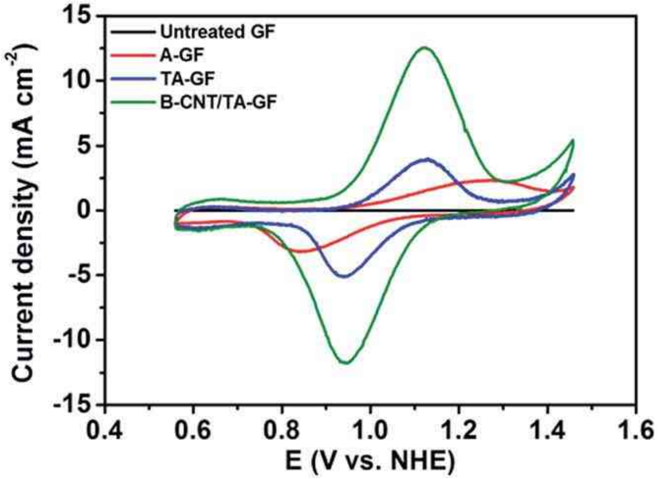
Bamboo-like CNTs on Functionalized GF

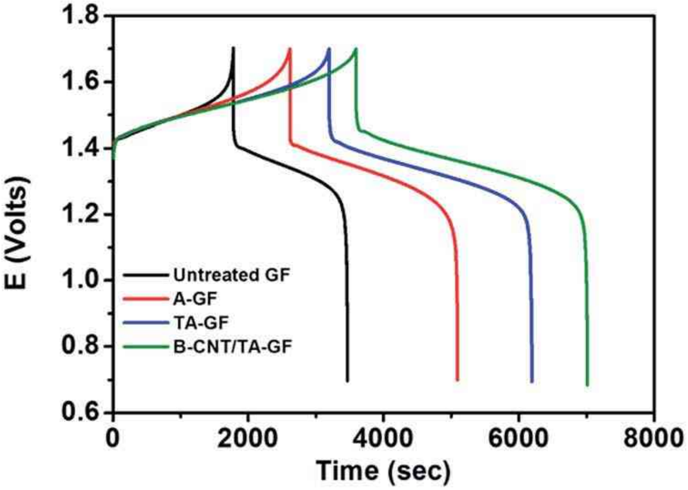
Wang* *et al.*, RSC Adv., 6 (2016) 102068–102075





B-CNT/TA-GF shows excellent activity and high reversibility. B-CNT/TA-GF also shows 81.0% energy efficiency, which is superior to those using untreated GF (68.3%).



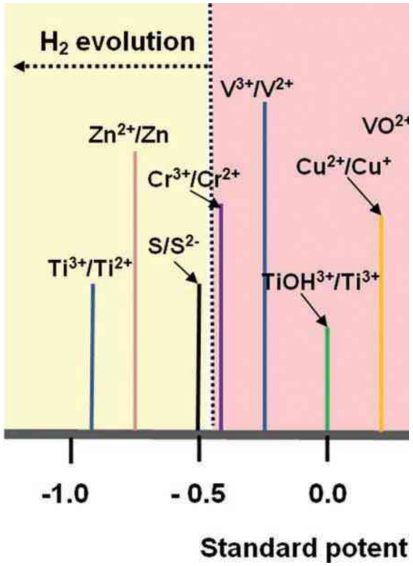


Samples	CE (%)	VE (%)	EE (%)
Un-GF	89.8	76.1	68.3
A-GF	94.8	81.7	77.5
TA-GF	93.8	81.1	76.1
B-CNT/TA-GF	95.0	85.3	81.0

Metal oxides/carbon-based Electrode used in VRFB

Metal Catalyst for VRFB

- **Metal catalysts perform the active sites to enhance the kinetics of the redox reaction.**
  - Metal-based catalysts: Pt, Pd, Ir, Au, Ru, Bi…
- **However, most of them are precious metals, which easily induce hydrogen evolution reaction before the redox reaction of V^{2+}/V^{3+}. Besides, their cost is concerned.**

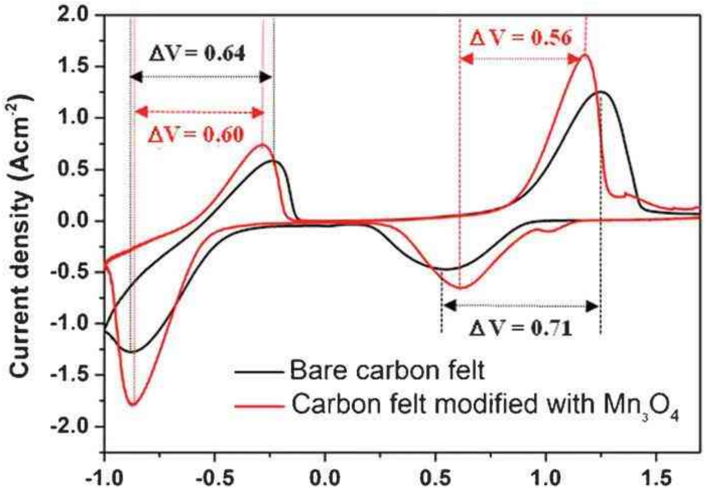


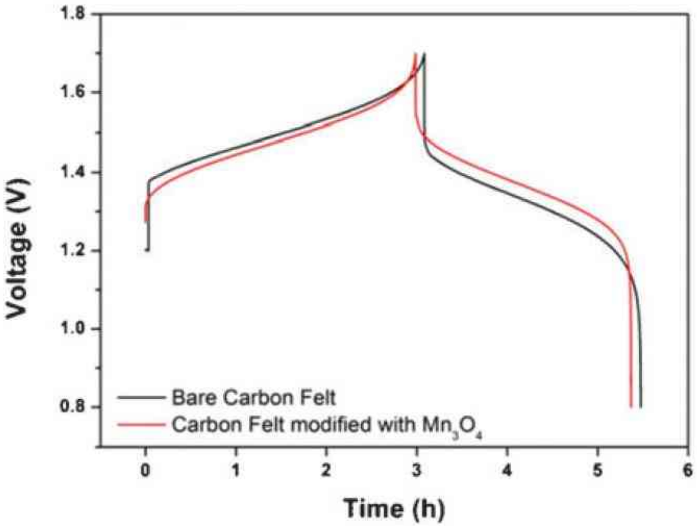
Metal Oxide Catalysts for VRFB

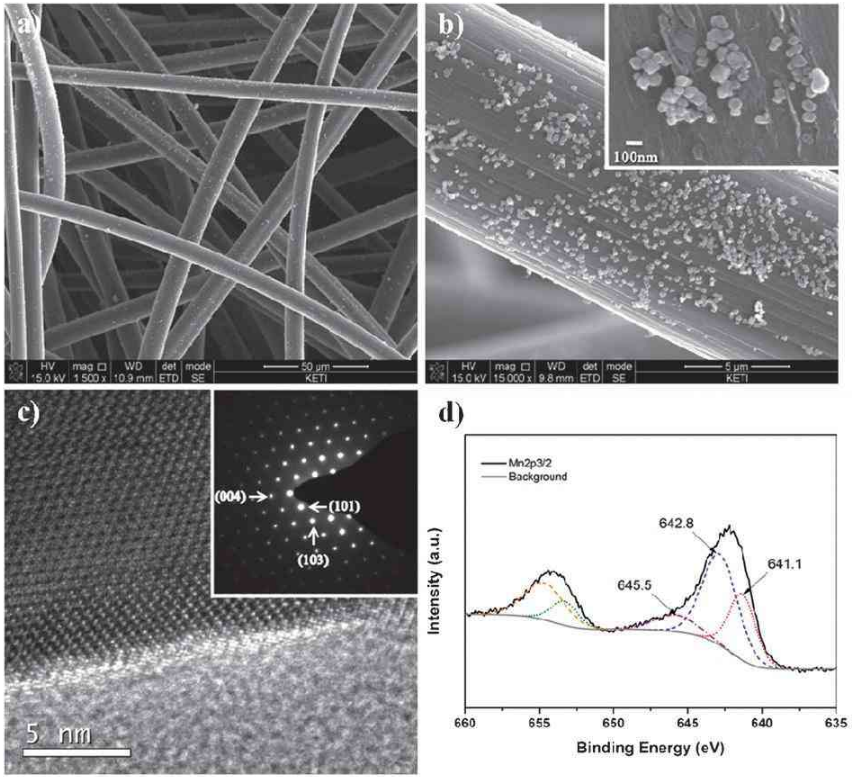
- **Metal oxide catalysts are considered to be applied in the VRFB due to their low cost and high stability in acid environment.**
  - Metal oxide-based catalysts: MnO_x, WO_3, PbO_2, Nb_2O_5…

Early Paper: Mn_3O_4 deposited on CF

Kim *et al.,* Chem. Commun., 48 (2012) 5455.







- Mn_3O_4 acts as the active site catalyzing the redox reaction of vanadium ions.
- Mn_3O_4 is very stable in the operation of VRFB.

Pure Metal Oxide as Catalyst

Electrode	Electrolyte	Membrane	Promoted redox couple	EE (%)	Ref
WO_3/SAC	1 M $VOSO_4$ in 3 M H_2SO_4	Nafion 1135	VO^{2+}/VO_2^+	76.6	J. Power Sources, 218 (2012) 455
Mn_3O_4/CF	2 M $VOSO_4$ in 2.5 M H_2SO_4	--	VO^{2+}/VO_2^+ and V^{3+}/V^{2+}	76.0	Chem. Commun., 48 (2012) 5455
MoO_2/MSU-FC	1 M $VOSO_4$ in M H_2SO_4	Nafion 212	VO^{2+}/VO_2^+	72.5	RSC Adv., 6 (2016) 17574
Nd_2O_3/CF	1.6 M $V^{3+}/^{4+}$ in 2 M H_2SO_4	Nafion 117	VO^{2+}/VO_2^+ and V^{3+}/V^{2+}	72.0	Electrochim. Acta, 268 (2018) 59

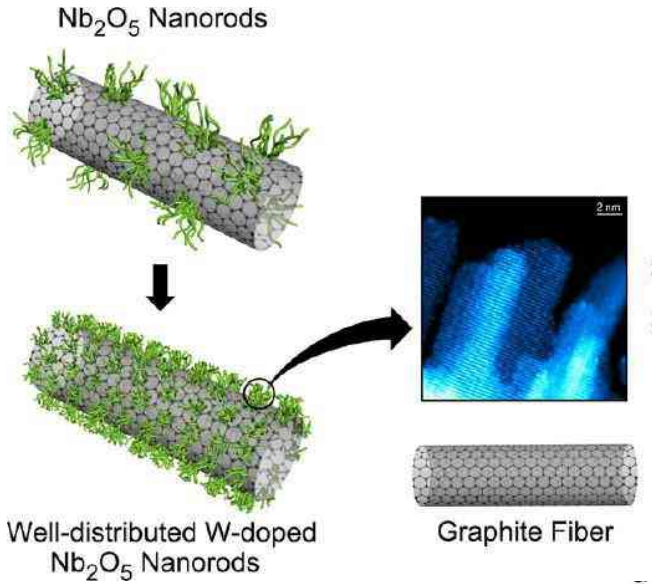
Advantages: Simple process

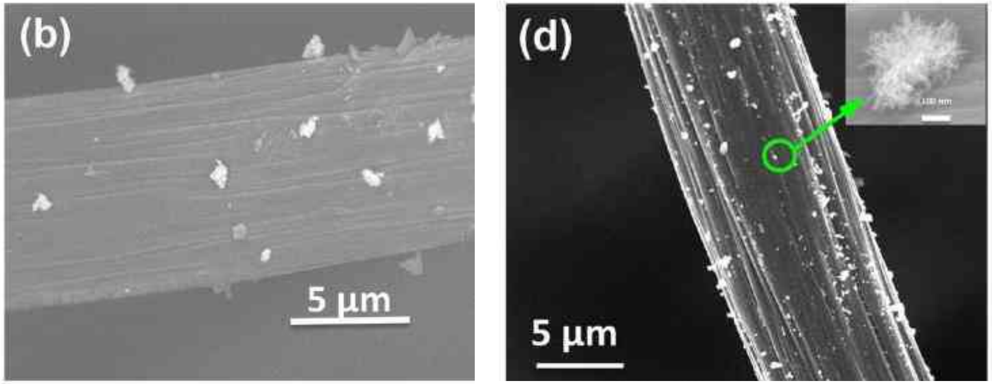
Disadvantages: Low conductivity ➡ High iR-loss and low EE!

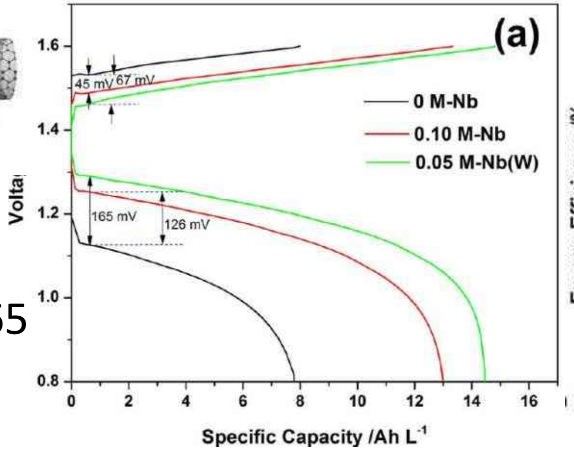
Dopants in Metal Oxides

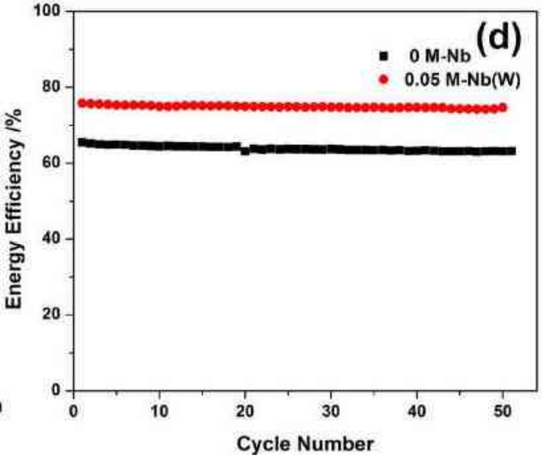
- **Characteristics of dopants in metal oxides for vanadium ion redox reaction in VRFB**
  - Producing moderate defect states, creating structural disorder, and forming oxygen vacancies
  - Increasing electrical conductivity
  - Improving distribution
  - Excellent stability

Heteroatom doping: W-doped Nb_2O_5









Li *et al.*, Nano Lett., 14 (2014) 158-165

Nb_2O_5 nanorod

1. **Low conductivity**
2. **Low activity**
3. **Agglomeration**

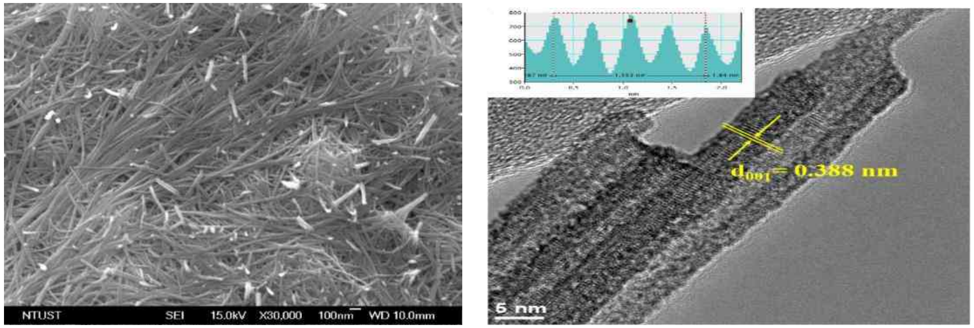
W-doped Nb_2O_5 nanorod

1. **Enhanced conductivity**
2. **Improved distribution**
3. **Excellent stability**

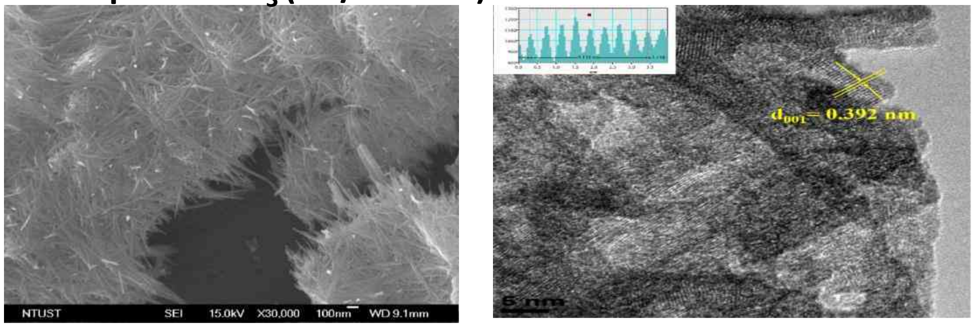
Nb-doped hexagonal WO_3 NW

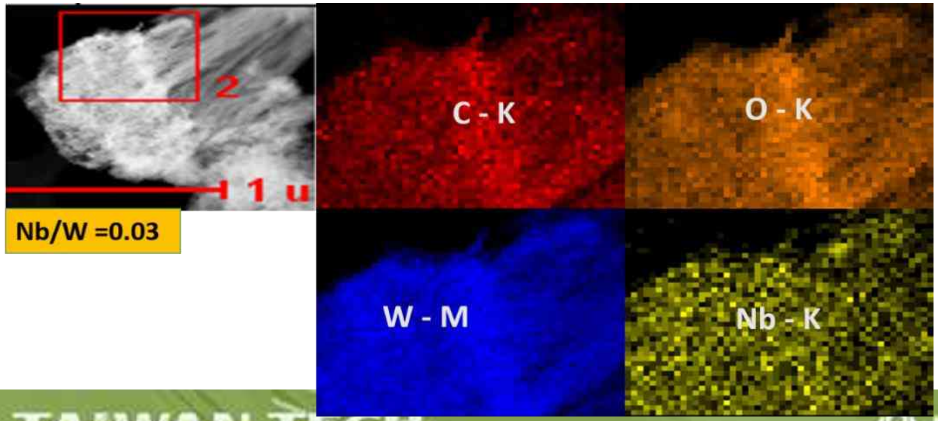
Wang* *et al.,* J. Mater. Chem. A, 4 (2016) 11472-11480

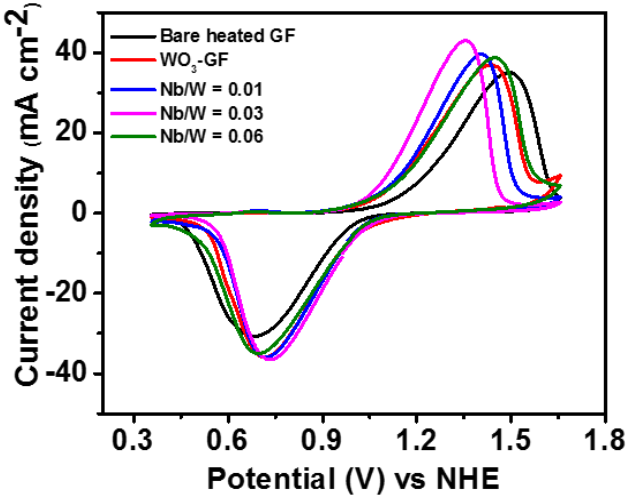
Undoped h-WO_3

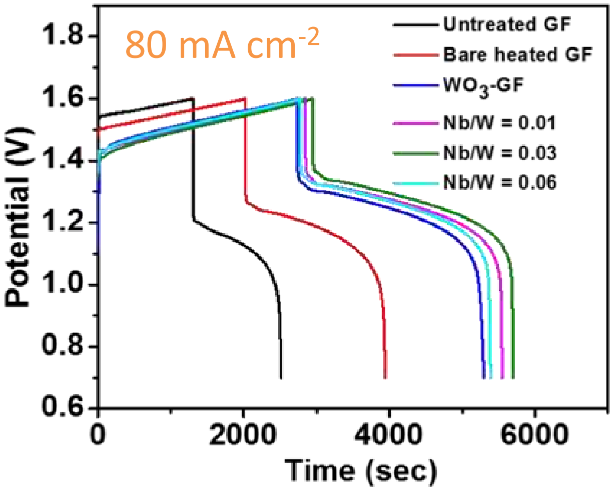


Nb-doped h-WO_3 (Nb/W=0.03)









Metal Oxide Supported by Graphene

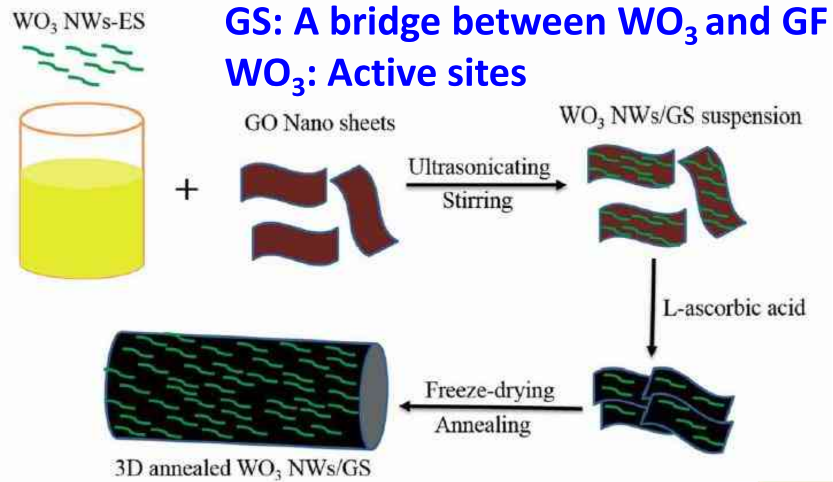
- **Characteristics of graphene composite**
  - Excellent conductivity
  - Good Stability
  - Large surface area
  - Beneficial to the distribution of metal oxide

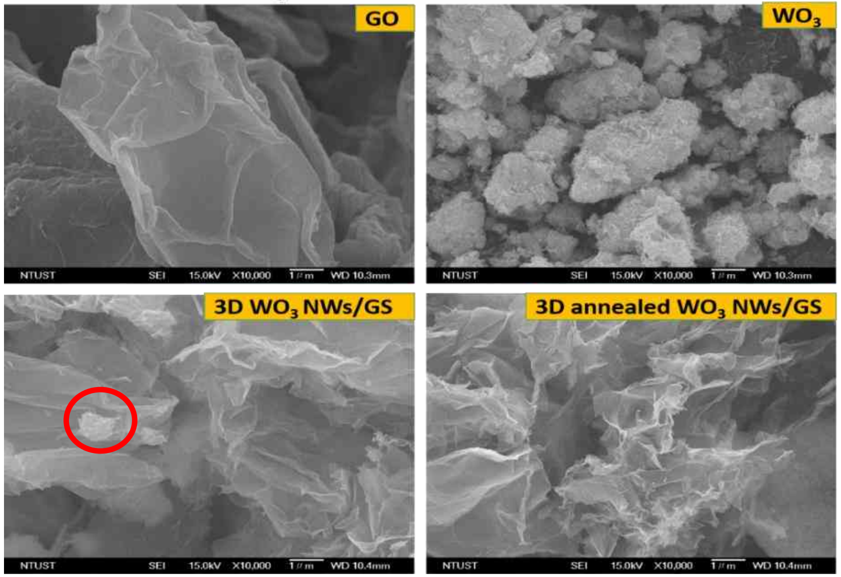
WO_3 NW/Graphene Nanosheet

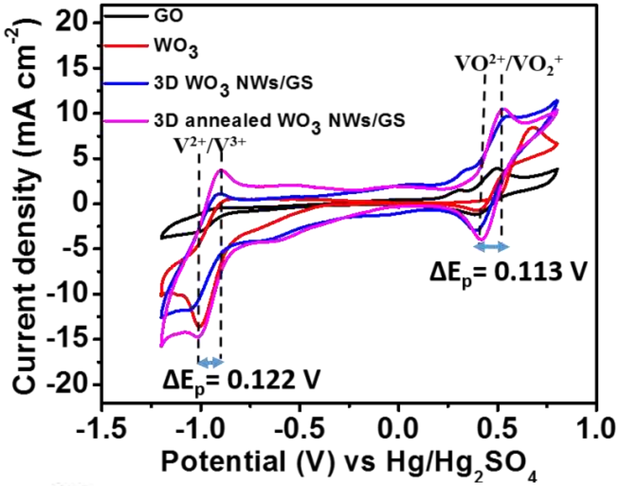
Wang* *et al.*, Sustainable Energy Fuels, 1 (2017) 2091-2100

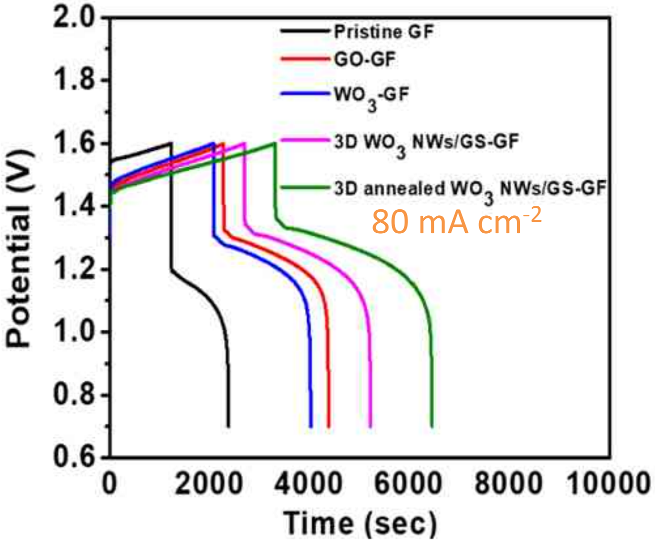
GS: A bridge between WO_3 and GF

WO_3: Active sites



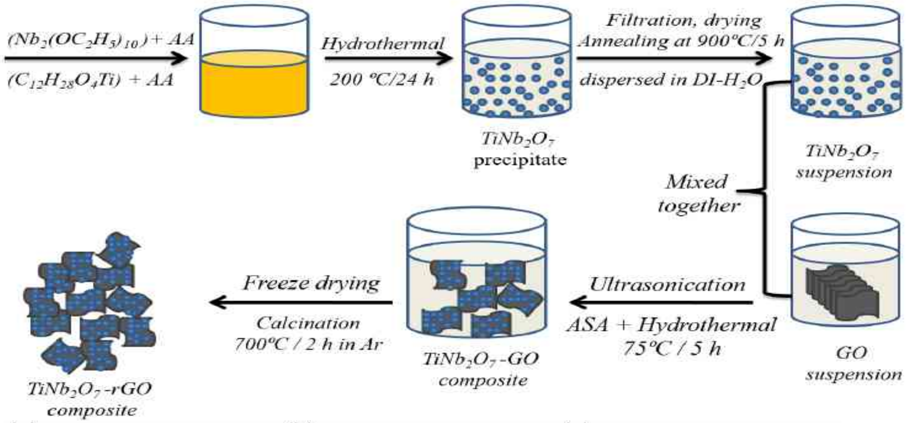


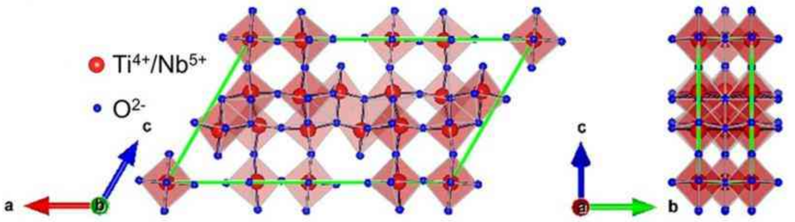




$TiNb_2O_7$/rGO

Wang* *et al.*, J. Mater. Chem. A, 6 (2018) 13908-13917

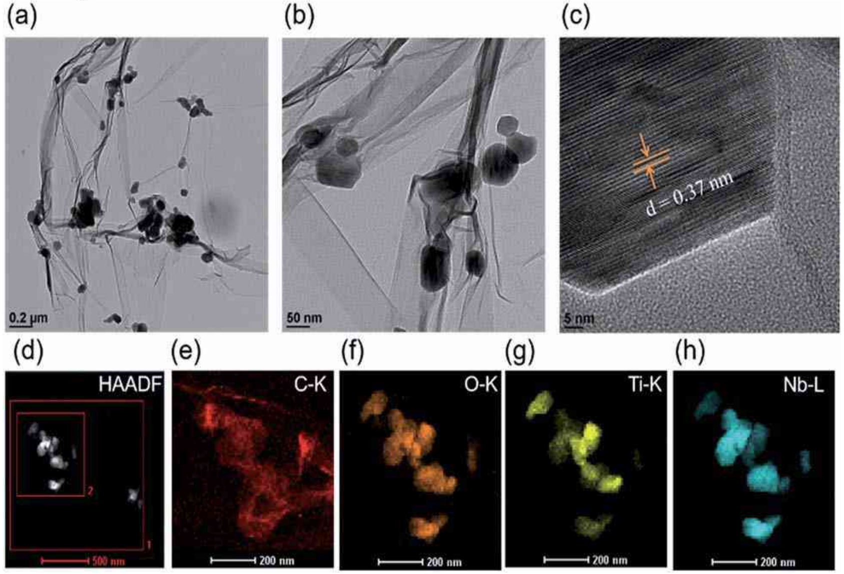


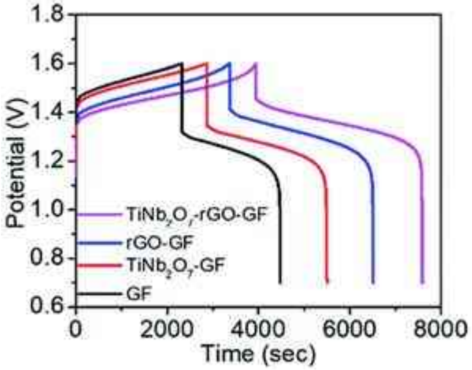


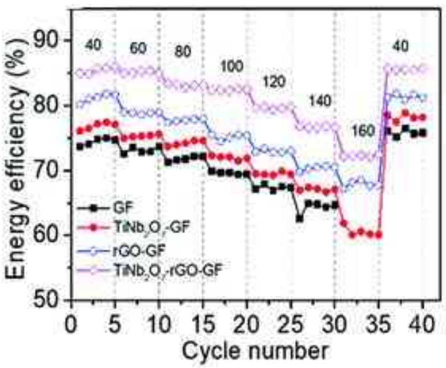
Sci. Rep., 5 (2015) 17836

Characteristics of $TiNb_2O_7$:

1) **Good conductivity, high stability, monoclinic layered structure for ion diffusion**
2) **Five electron transfers during the redox reaction of Ti^{4+}/Ti^{3+}, Nb^{5+}/Nb^{4+}, and Nb^{4+}/Nb^{3+} per formula unit**







Evaluation of Possible Electrodes

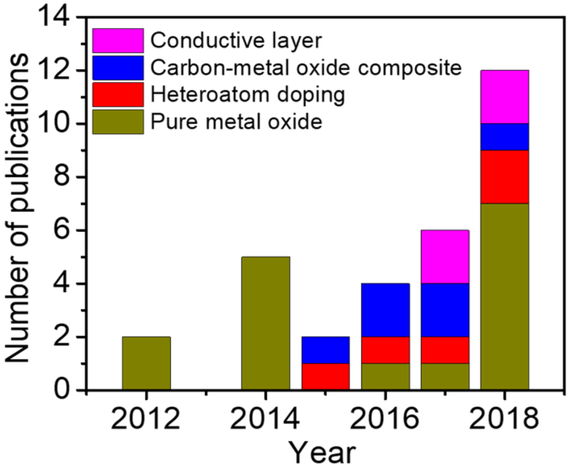
	Carbon-based Materials						Polymer	Metal-based Materials		
	CF	GF	CP	CNT	GO	Graphite	Carbon-polymer	Noble metal	DSA	Metal oxides
Activity	×	×	×	★	★	×	○	★	★	○
Conductivity	★	★	★	★	×	★	○	★	○	○
ECSA	○	○	×	★	★	○	★	★	★	○
Stability	○	○	○	★	★	★	×	★	★	★
Electrochemical window	★	★	★	○	○	★	★	×	×	★
Cost	★	★	★	×	×	×	★	×	×	○

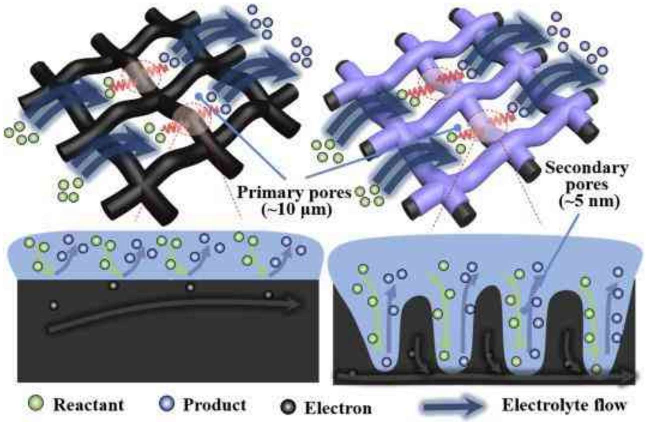
★: Excellent
○: Common
×: Poor

*DSA: Dimensionally stable anode
**The original table was originated from *H. Zhang eds., Redox Flow Batteries, CRC Press (2018), p. 132*.
***The current table has been revised by the presenter.

Future Development of Catalyst and Electrode in VRFB

- **Conductivity**
  - Formation of conductive layer onto catalyst
- **Surface area**
  - Avoid agglomeration
- **Heteroatom doping**
  - Defect, vacancy, and structural disorder
- **Stability**
  - Highly corrosion-resistant material
- **Electrode structure**
  - Diffusion





J. Power Sources, 325 (2016) 329-336

Chen-Hao Wang Ph.D. 王丞浩 博士

National Taiwan University of Science and Technology (NTUST)

Vice Dean, Office of Research and Development

Professor, Department of Materials Science and Engineering

Google scholar

H-index: 20

Total citation: 1539

Committee Service:

- Director of the Board, Taiwan Association for Coating and Thin Film Technology (臺灣鍍膜科技協會理事)
- Director of the Board, The Electrochemical Society of Taiwan (臺灣電化學學會理事)

Important Honors:

- Excellent Young Scholar Research Project, Discipline of Materials Science and Engineering, Ministry of Science and Technology (2015 – 2018 & 2018 – 2021)
- Outstanding Young Scholar Award, Taiwan Associate of Coating and Technology (2016)
- Outstanding Teaching Award (2016)
- Excellent Teaching Award (2012, 2013, 2014, 2015)

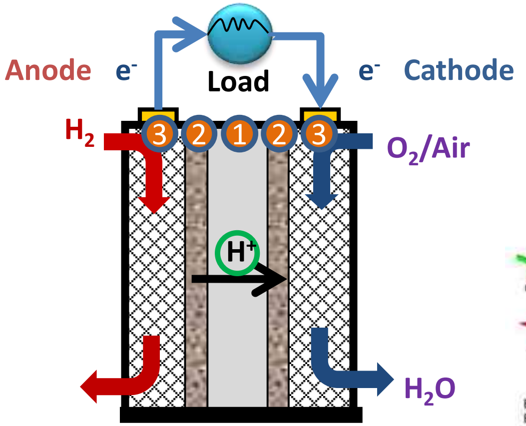
Education:

- Ph.D. in Materials Science and Engineering, National Tsing Hua University, Taiwan
- Ms. & Bs. in Chemical Engineering, National Taiwan University, Taiwan

Electrochemical Conversion —Fuel cell

Polymer Electrolyte Fuel Cell

Membrane-Electrode-Assembly: MEA

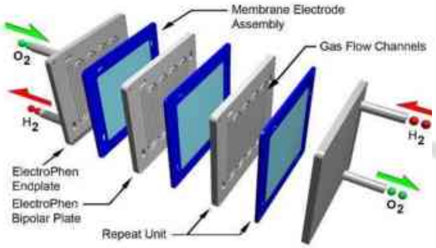


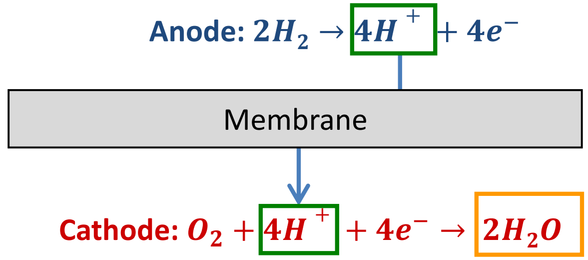
Chemical energy → Electrical energy

① Electrolyte: Nafion®

② Catalyst layer: Pt/C

③ Gas diffusion layer: porous carbon cloth or carbon paper





Anode: $2H_2 \rightarrow \boxed{4H^+} + 4e^-$

Membrane

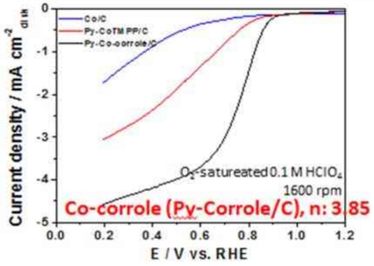
Cathode: $O_2 + \boxed{4H^+} + 4e^- \rightarrow \boxed{2H_2O}$

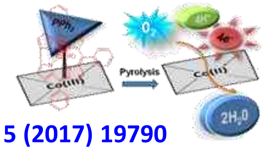
Overall: $2H_2 + O_2 \rightarrow 2H2O$

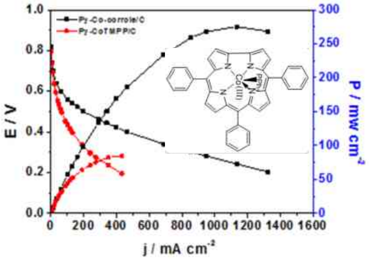
One “full” reaction MUST include:

1. Species: Fuel and oxidants
2. Electrons
3. Protons

Non-precious Metal Catalysts

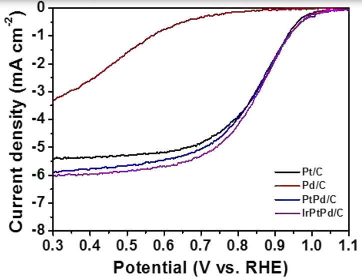


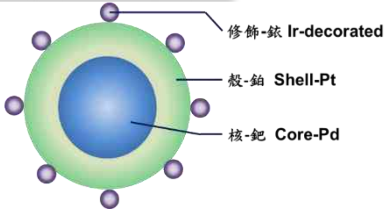




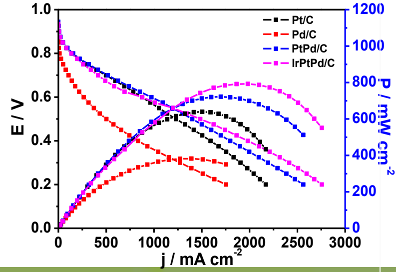
- ✓ J. Mat. Chem. A, 5 (2017) 19790
- ✓ ACS Sus. Chem. & Eng., 5 (2017) 2897
- ✓ Electrochim. Acta, 211 (2016) 933
- ✓ Green Chem., 18 (2016) 2819
- ✓ J. Power Sources, 277 (2015) 147
- ✓ RSC Adv., 4 (2014) 4207
- ✓ Int. J. Hydro. Energy, 39 (2014) 934
- ✓ J. Mat. Chem. A, 1 (2013) 14692
- ✓ RSC Adv., 3 (2013) 15375
- ✓ Adv. Funct. Mat., 22 (2012) 3500
- ✓ Int. J. Hydro. Energy, 37 (2012) 13755
- ✓ Energy & Environ. Sci., 5 (2012) 5305
- ✓ Diamond & Relat. Mater., 20 (2011) 322
- ✓ J. Mat. Chem., 20 (2010) 7551

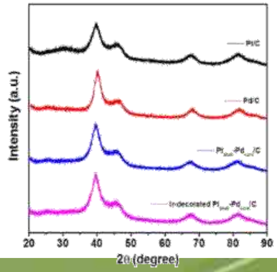
Pt-based Core-Shell Structure Catalysts





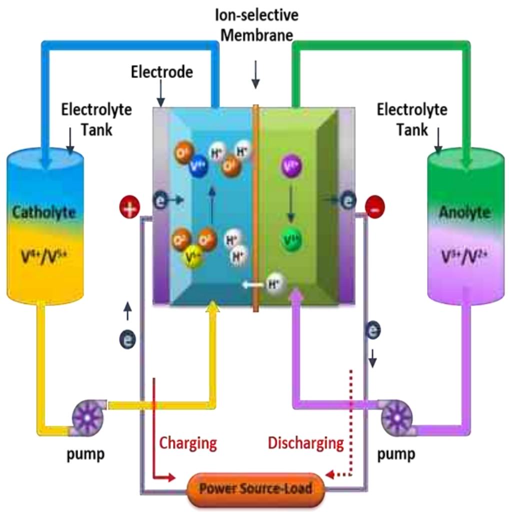
- ✓ Int. J. Hydro. Energy, 42 (2017) 11771
- ✓ J. Colloid & Interface Sci., 427 (2014) 91





Electrochemical Conversion and Storage

Vanadium Redox Flow Battery



Positive electrode (Charge mode)

$$VO^{2+} + H_2O \rightarrow VO_2^{+} + 2H^{+} + e^{-} \rightarrow E^0 = 1.00\ V$$

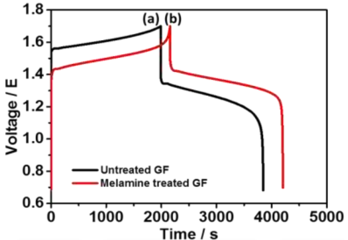
Negative electrode (Charge mode)

$$V^{3+} + e^{-} \rightarrow V^{2+} \quad E^0 = -0.255\ V$$

Net reaction (Charge Mode)

$$VO^{2+} + H_2O + V^{3+} \rightarrow VO^{2+} + 2H^{+} + V^{2+} \quad E^0 = 1.255\ V$$

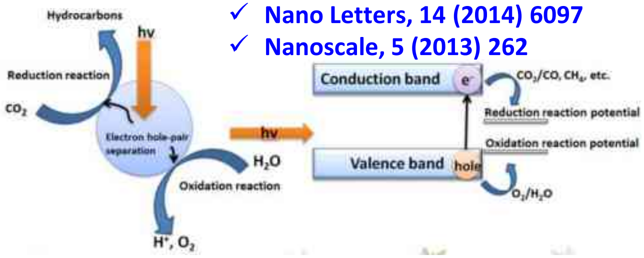
- ✓ ACS Sus. Chem. & Eng., 6 (2018) 3019–3028.
- ✓ RSC Adv., 8 (2018) 8537
- ✓ Sustainable Energy & Fuels 1 (2017) 2091
- ✓ J. Power Sources, 341 (2017) 270
- ✓ J. Power Sources, 364 (2017) 1
- ✓ RSC Adv., 6 (2016) 102068
- ✓ J. Mat. Chem. A, 4 (2016) 11472

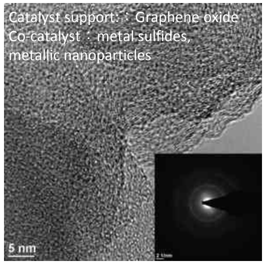


- Decoupling capacity from power
- Modular design facilitates different applications
- Fast response time
- Efficiency >75 % possible
- Long calendar life, cycle stability (> 10,000)

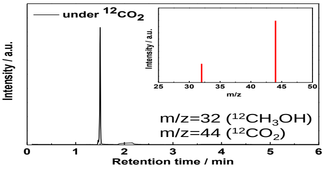
Photocatalyst

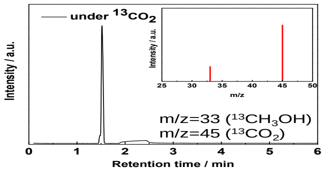
- ✓ Nano Letters, 14 (2014) 6097
- ✓ Nanoscale, 5 (2013) 262

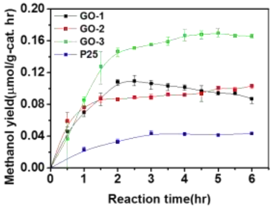




Catalyst support : Graphene oxide
Co-catalyst : metal sulfides, metallic nanoparticles





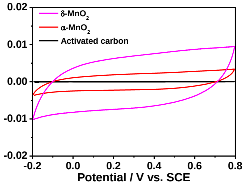


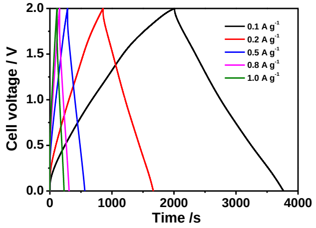
$$^{12}CO_2 + 2H_2O \xrightarrow{h\nu} {}^{12}CH_3OH + \frac{3}{2}O_2 \quad {}^{13}CO_2 + 2H_2O \xrightarrow{h\nu} {}^{13}CH_3OH + \frac{3}{2}O_2$$

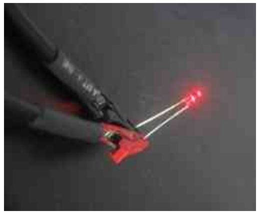
Supercapacitor

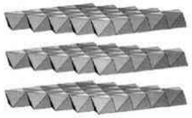
Coin cell
0.5 M Na_2SO_4

- ✓ J. Mat. Chem. A, 5 (2017) 12569
- ✓ Adv. Powder Tech., 27 (2016) 1387
- ✓ J. Phys. & Chem. Solids, 85 (2015) 62
- ✓ J. Power Sources, 249 (2014) 1
- ✓ Diamond & Relat. Mater., 25 (2012) 176









Many thanks to all PhD and graduated students in Energy Materials Laboratory.

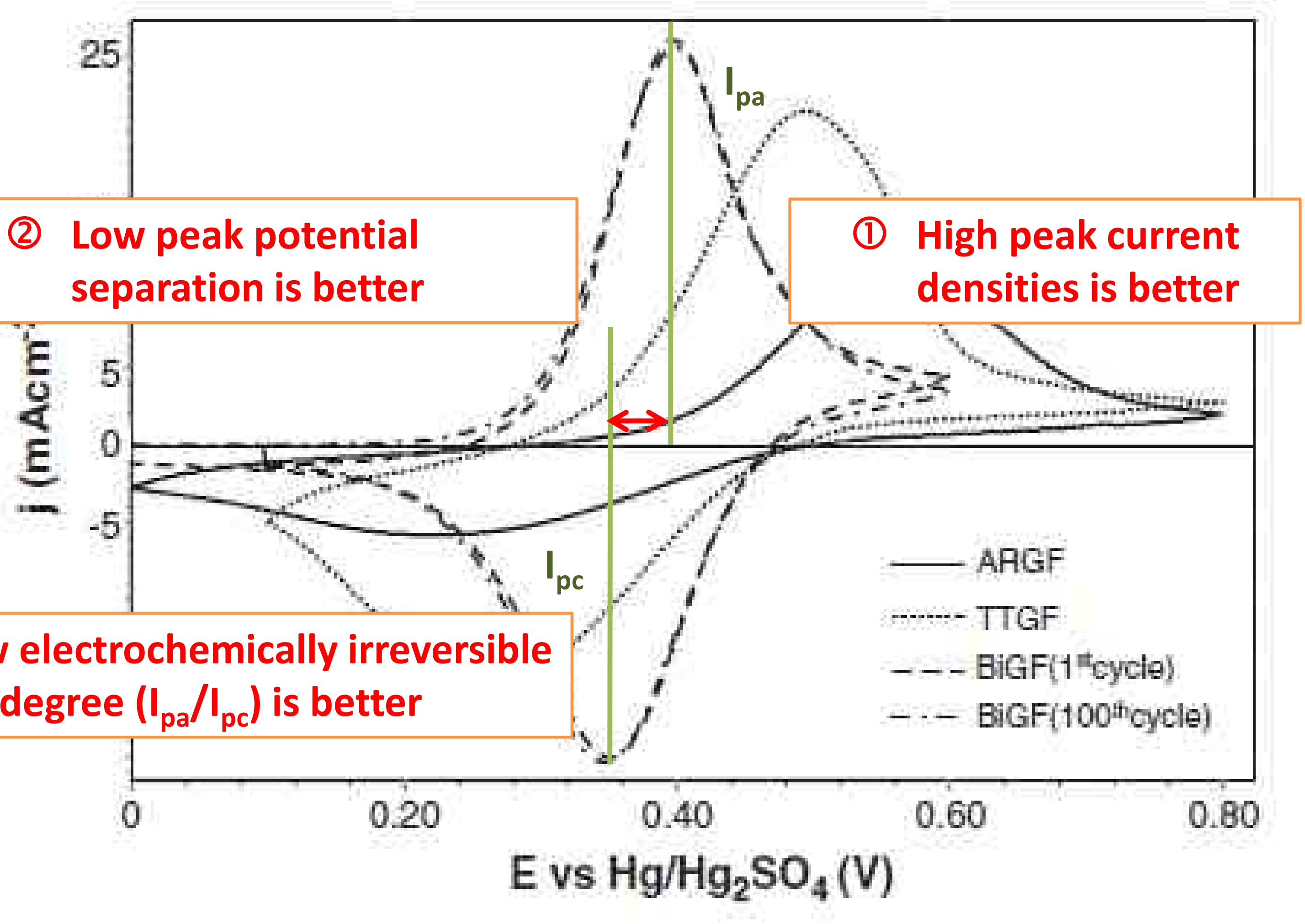
Overpotentials in VRFB

- **Cell potential can be expressed as the equilibrium (open circuit) value minus potential losses:**

$$E_{cell} = E_{cell}^{eq} - \sum |\eta| - \sum iR$$

- **Potential losses are caused by**
  - ***η*, overpotential**: Electrodes, slow kinetics.
  - ***R*, internal resistance**: Electrolytes, membrane, and electrodes

Statement for High-Performance Electrode in CV analysis



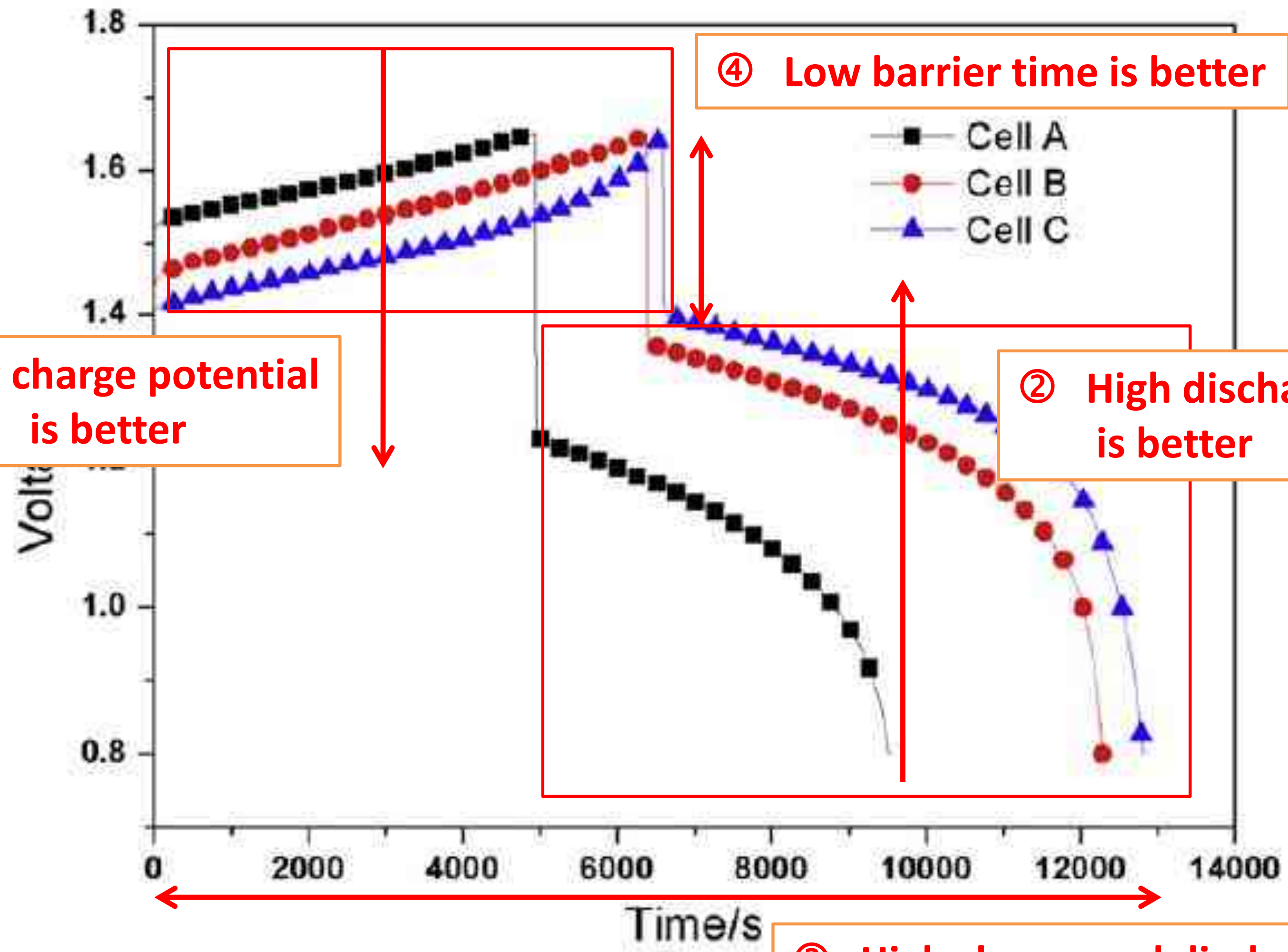
② Low peak potential separation is better

① High peak current densities is better

③ Low electrochemically irreversible degree (I_{pa}/I_{pc}) is better

Z. González *et al.*, Electrochemistry Communications, 13 (2011) 1379-1382.

Criteria for High Performance of VRFB



① **Low charge potential is better**

② **High discharge potential is better**

③ **High charge and discharge time is better**

④ **Low barrier time is better**

C. Yao *et al*., Journal of Power Sources, 218 (2012) 455-461.

Challenges of Carbon-based Electrode

- **Low electrochemical activity**
  - High inner resistance, poor hydrophilicity…
- **Chemical stability**
  - Corrosion, passivation, hydride formation…
- **Mechanical stability**
  - High stresses, poor adhesion of coating
- **Poisoning**
  - Irreversible adsorption and film formation
- **Time dependent performance**
  - All of above!

Calculations of Three Efficiencies

The definitions of columbic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) are:

$$CE\ (\%) = \left(\frac{\text{Discharging capacity}}{\text{Charging capacity}}\right) \times 100\% = \left(\frac{\int_0^{t_d} I_d dt}{\int_0^{t_c} I_c dt}\right) \times 100\%$$

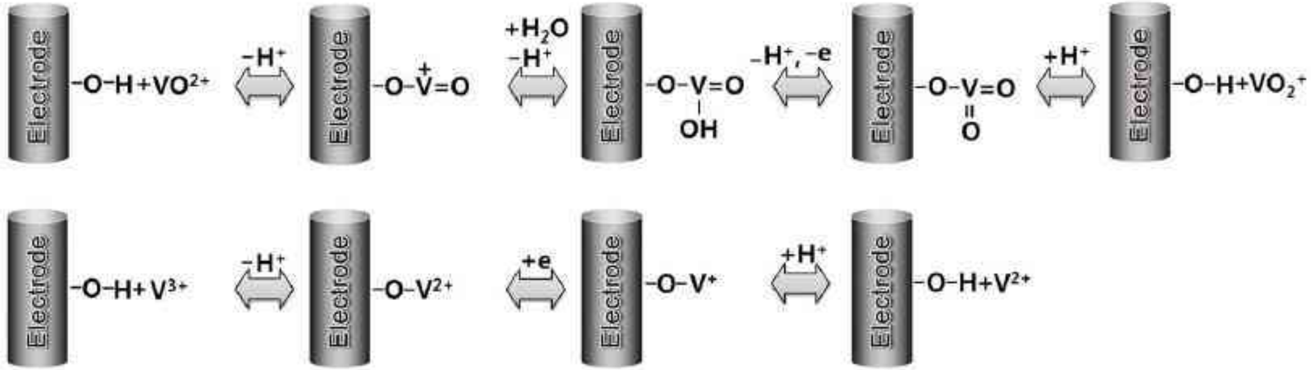
$$EE\ (\%) = \left(\frac{\text{Discharging energy}}{\text{Charging energy}}\right) \times 100\% = \left(\frac{\int_0^{t_d} I_d V_d dt}{\int_0^{t_c} I_c V_c dt}\right) \times 100\%$$

$$VE\ (\%) = \frac{EE(\%)}{CE(\%)} \times\ 100\%$$

I_d is the discharge current, I_c is the charge current, t_d is the discharge time, t_c is the charge time, V_d is the discharge voltage, and V_c is the charge voltage. V_d and V_c are functions of time.

Other Proposed Mechanism

L. Yue, W. Li, F. Sun, L. Zhao, L. Xing, Carbon, 48 (2010) 3079-3090.



X.W. Wu, T. Yamamura, S. Ohta, Q.X. Zhang, F.C. Lv, C.M. Liu, K. Shirasaki, I. Satoh, T. Shikama, D. Lu, S.Q. Liu, J. Appl. Electrochem., 41 (2011) 1183-1190.

W. Zhang, J. Xi, Z. Li, H. Zhou, L. Liu, Z. Wu, X. Qiu, Electrochim. Acta, 89 (2013) 429-435.

Conclusions and Perspective of VRFB Electrode

- **Surface treatments for carbon materials increase the reactivity and the wettability of the electrodes**
- **The incorporation of nitrogen species in the electrode play the effective active sites.**
- **Hybrid electrode by using 1D (CNT) and 2D (Graphene, carbon nanowall) in the electrode can not only enlarge the specific surface area but also increase the catalytic activity.**
- **The low-cost and high-activity metal oxide-based catalysts embedded in the electrode can strongly enhance the performance.**
- **Future research will focus on the use of high electrical conductivity carbon materials for a-high-power-density VRFB stack.**