



ParisTech



ENERGIE
RS2E

Institut de recherche
de Chimie Paris



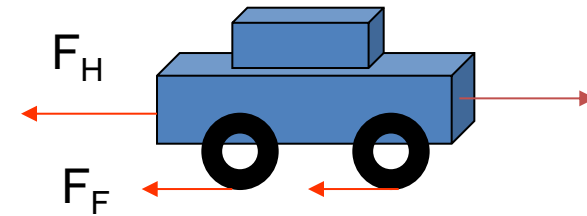
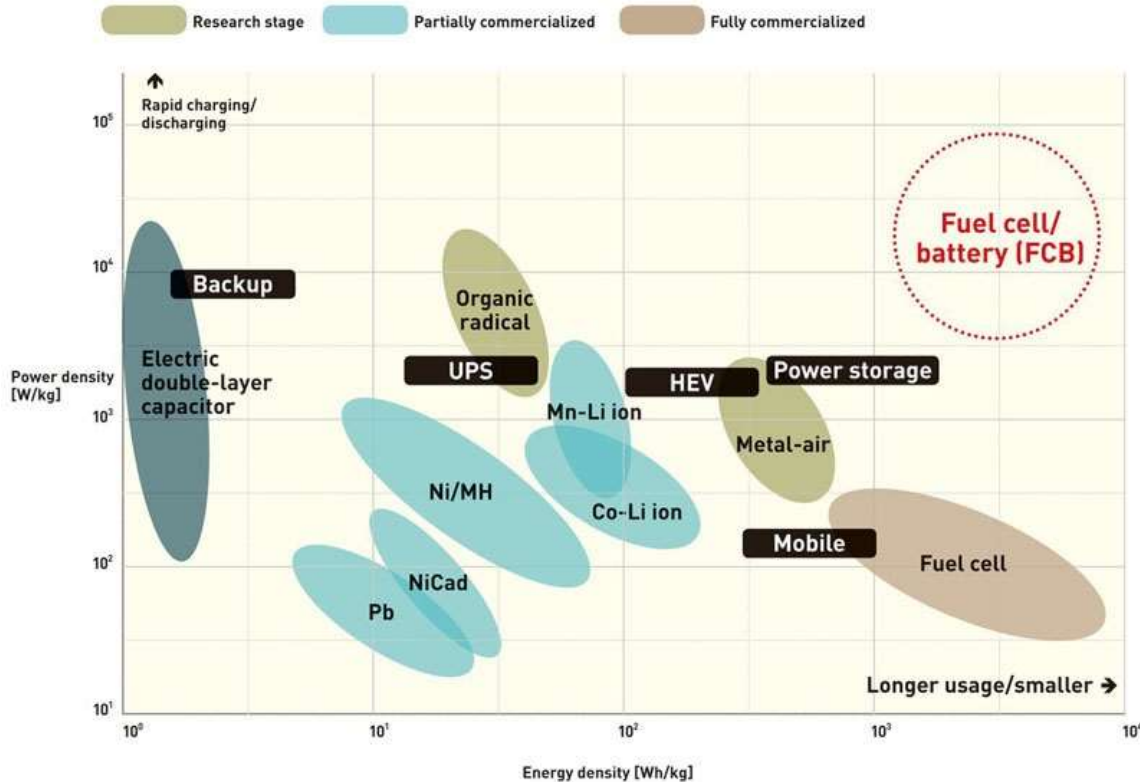
Des nouvelles batteries au-delà des matériaux d'intercalation entre transport et stationnaire

Philippe Barboux

Institut de Recherche de Chimie Paris- CNRS

philippe.barboux@chimie-paristech.fr

au delà du lithium -ion



10 kW à 100 km/h
50 kW acceleration

1 km \approx 100 Wh
 \approx 1 kg de LiB



pour adresser le problème de l'autonomie
un objectif de 260 Wh/L (150 Wh/kg) au prix de 175 €/kWh
mais cela ne resoud pas le problème de la recharge (\approx 6 h)

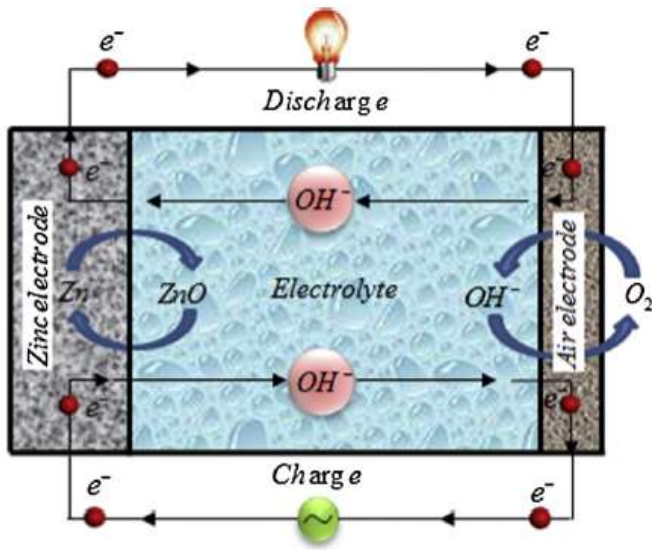
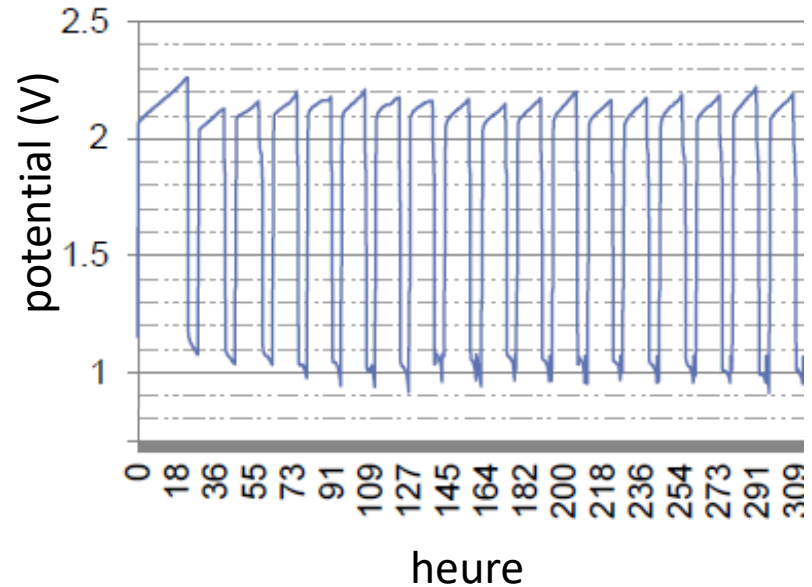


Fig. 4. Schematic view of zinc-air battery based on bi-electrodes.

Zinc-air batteries

- $\text{Zn} + 4 \text{OH}^- \rightarrow \text{Zn}(\text{OH})_4^{2-} + 2 \text{e}^- -1.2 \text{ V vs NHE}$
- $\frac{1}{2} \text{O}_2 + 2\text{e}^- + \text{H}_2\text{O} \rightarrow 2 \text{OH}^- 0.44 \text{ V vs NHE}$
- Théorie $\text{Zn} + \frac{1}{2} \text{O}_2 \rightarrow \text{ZnO} 1.65 \text{ V}$

- Avantages
 - densité d'énergie
 - bas prix 30 E/kWh
 - pas de toxicité
 - Sécurité (aqueux, ?)
- Défaut
 - faible puissance (C/3) cathode
 - faible rendement (60%)
 - peu de cycles (200 cycles)



batteries métal –air

Metal (M)	V vs O ₂	Wh/kg	/on the basis	Wh claimed
Li	2,4	4893	Li ₂ O ₂	13000
Al	1,6	1626	KAl(OH) ₄	8100
Fe	1,2	642	KFe(OH) ₄	1200
Zn	1,3	405	K ₂ Zn(OH) ₄	1300
		1053	ZnO	

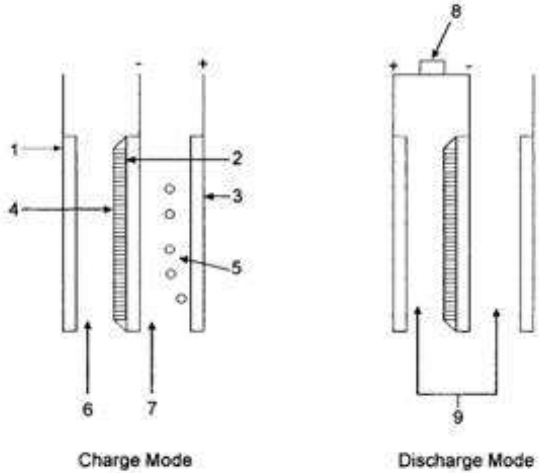


batterie Zinc-air
Sony 1971



1,000-Mile Aluminum Air
Range-Extended Electric Vehicle
Phinergy 2014

l'électrode à air

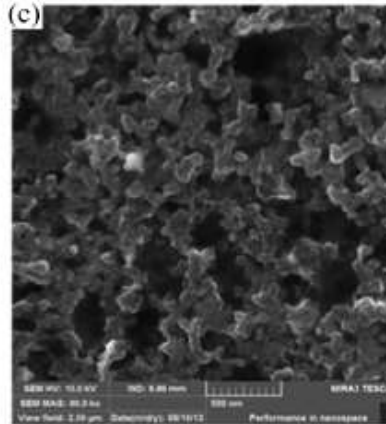
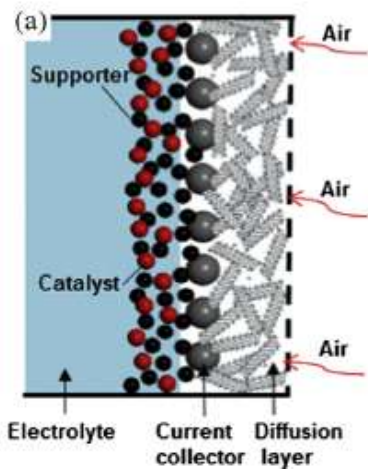


Catalyseurs bons pour ORR et OER
 systèmes Tri-electrodes complexes
 Limitent carbon corrosion

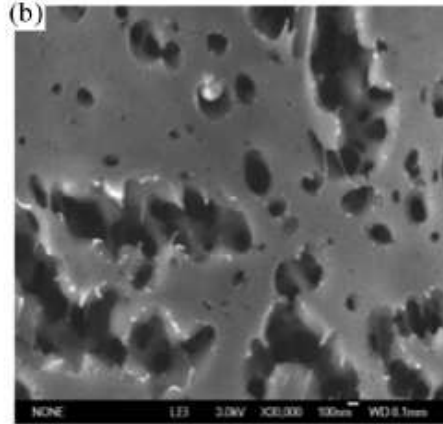
clogging
 oxydation du carbone
 mechanical breakdown
 carbonatation

Bi-electrode more compact
 Catalysts:

(La,Sr)MO₃, MnO₂ ...
 (NiFe)OHCO₃ LDH
 N-doped CNT
 20 up to 50 mA/cm²

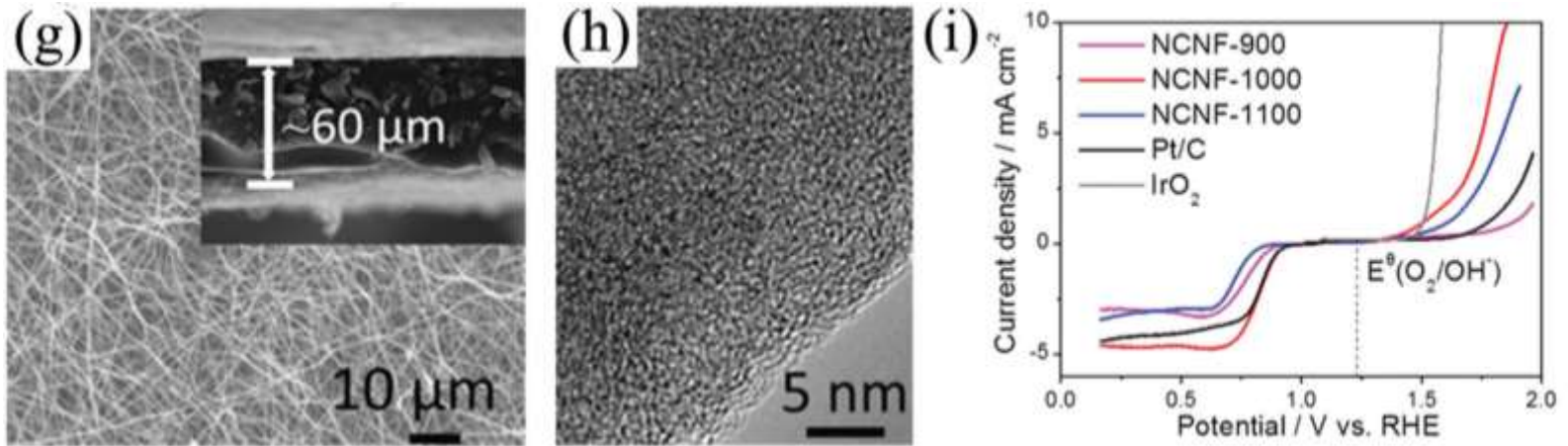


Catalytic side



Gas diffusion layer

catalysts



C-CoPAN900 mat based Zn–air battery

new carbons

Bi-Catalysts: spinels / perovskites

MnO_2 – Ni G.

CoMn_2O_4 – RGO

Co_3O_4 – SS

$(\text{La,Ca})\text{CoO}_3$

$(\text{NiFe})\text{OHCO}_3$

Current capacity 20 up to $50\ \text{mA/cm}^2$ 200 cycles

J. Pang et al. Adv. Sci. 2018, 1700691

Q. Liu, et al., Adv. Mater. 2016, 28, 3000

Toussaint ECS trans 28 (2010) 25

M. Prabu, Electrochem Comm. 41 (2014) 59

Lee Du et al. Advanced energy materials

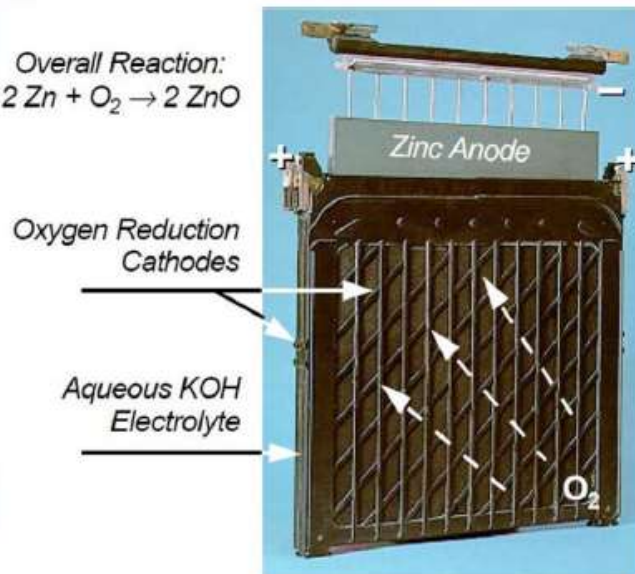
S. Muller, Electrochimica acta 39 (1994) 1661

LDH/CNT Y. Li Nat. Comm 4 (2013) 1805

électrodes mécaniquement rechargeables

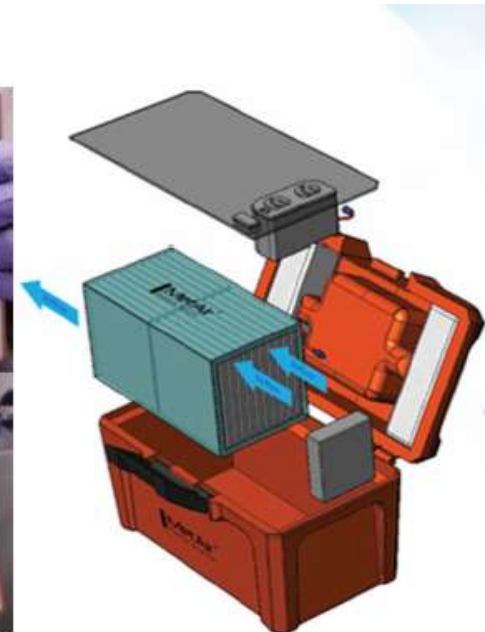
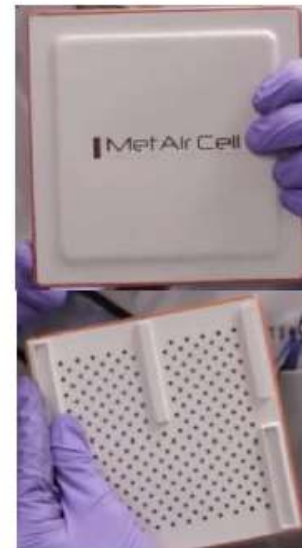
Zinc replacement

Overall Reaction:
 $2 \text{Zn} + \text{O}_2 \rightarrow 2 \text{ZnO}$



Mechanically rechargeable Zn-air battery

K. Kim., et al., *J. Korean Electrochem. Soc.*, 2013, 16



Commercialized Zn-air battery of Met-air

<http://www.metair.co.za>

from presentation of J. Cho Unist Korea 2015

Mechanically rechargeable electrodes

J.F. Cooper, R. Krueger, USA DOE 2006

Alternatives techniques for Zn and electrolytes regenerations

dendrites de zinc /Flow batteries

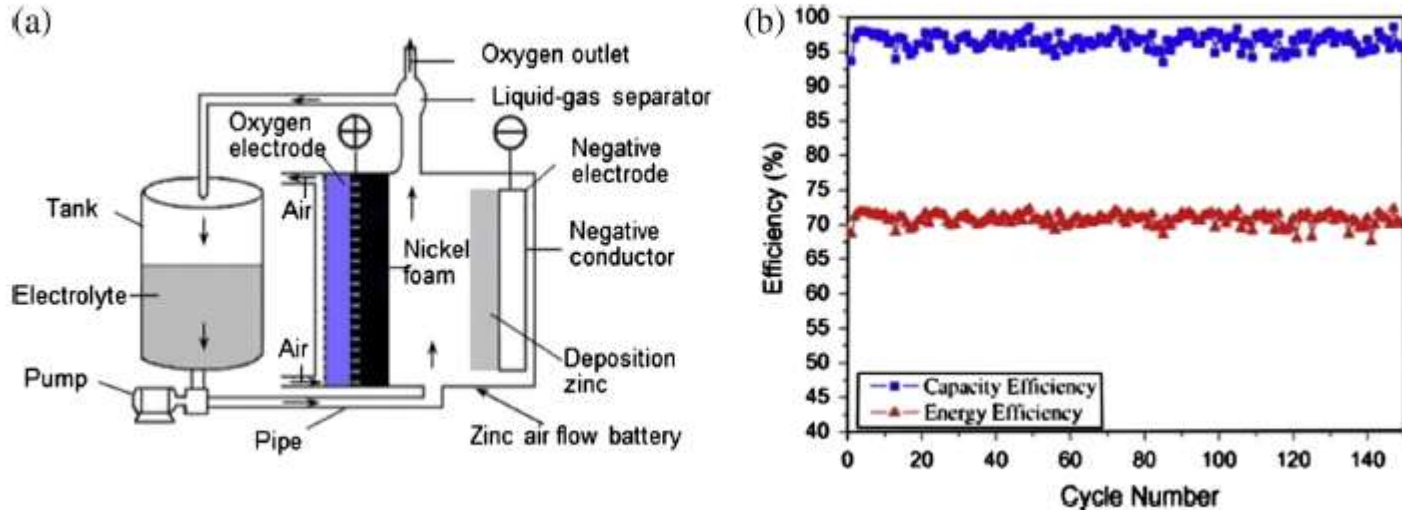


Fig. 8. (a) Schematic view of the flow zinc-air battery, and (b) coulombic efficiency and energy efficiency in 150 cycles [97].

électrolytes circulant:
gère les bulles d'oxygène
égalise les concentrations d'électrolyte
empêche la croissance dendritique de Zn
dissipe la chaleur

Start – ups mastering Zn or air electrode separately



ZAF batteries NiZn → Zn/NiOOH

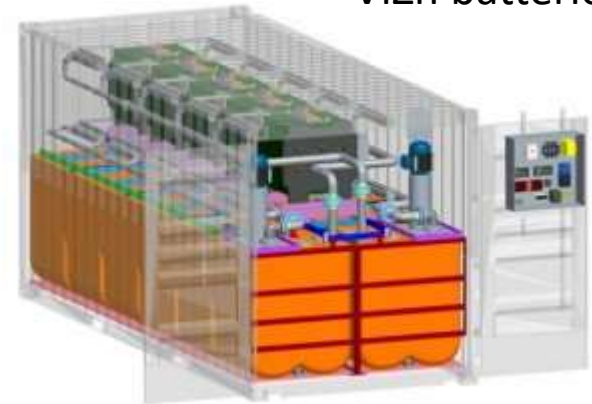
1,65 V

2x the Energy, 2x the Power and 2x the life of lead acid batteries

65 à 80 Wh/kg or 120 à 140 Wh/dm³

aging Zn electrode

ViZn batteries



Fluidic Zn-air batteries

hybrid flow batteries



Phinergy has patented a "nano-porous silver-based catalyst", which allows oxygen into the electrode and the cell while at the same time blocking carbon dioxide

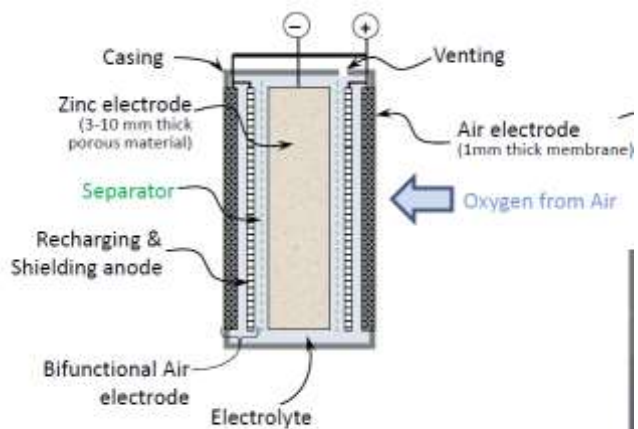




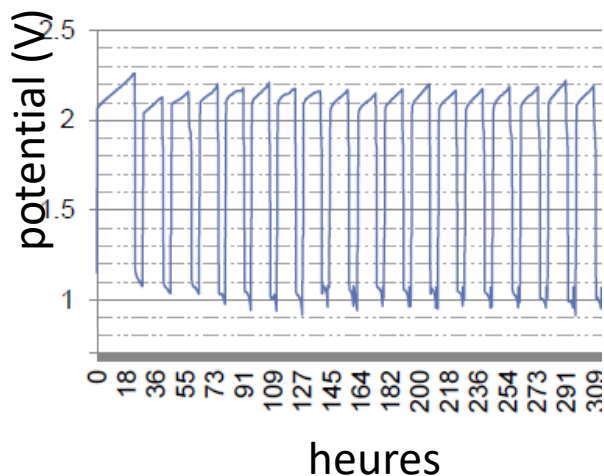
Zinc-Air

Cheap and Safe Batteries
for Electrical Vehicles
& Stationary Electricity Storage

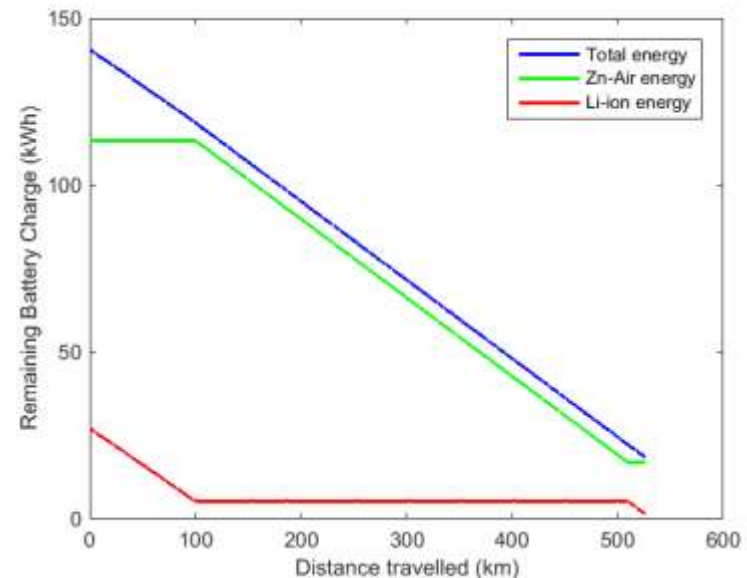
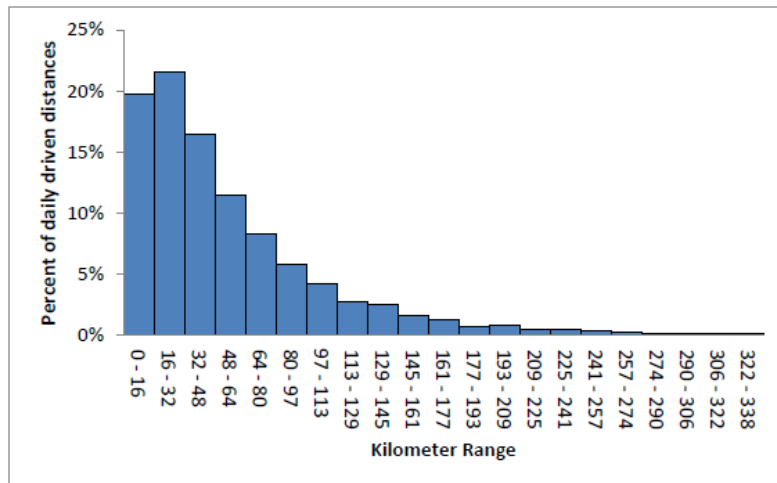
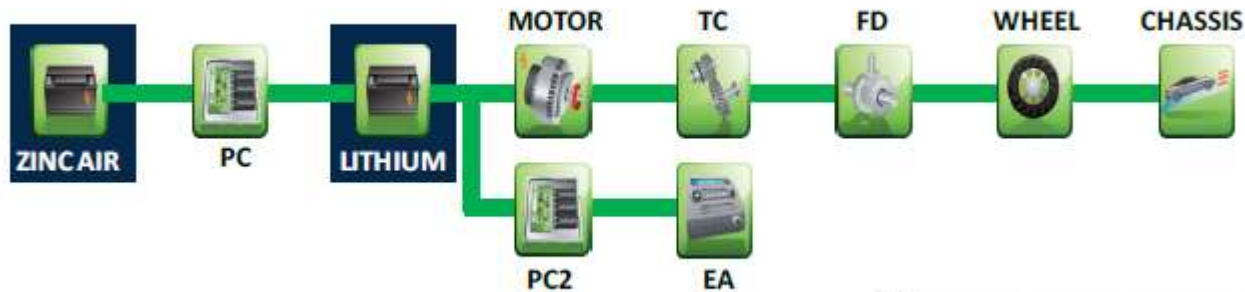
D. Guillonnet
J.F. Fauvarque



100 Wh/kg 200 cycles 25 mA/cm²
durée de vie de l'électrode à air 2500 h
séparateur antidendrite
circulation d'électrolyte
demo packs scooter



dual Energy storage system



Dual energy storage system dual ESS

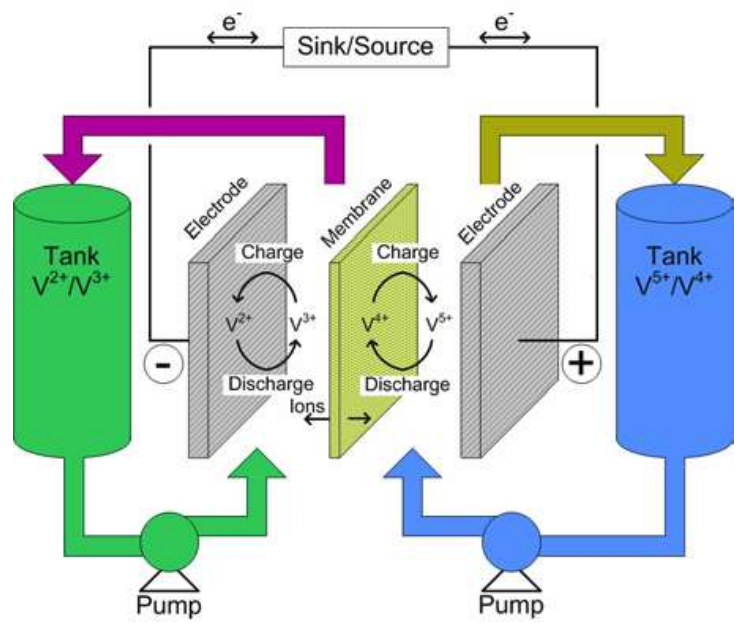
Range-extending Zinc-air battery for electric vehicle

Steven B. Sherman, Zachary P. Cano, Michael Fowler* and Zhongwei Chen

AIMS Energy 2018 6 121



redox flow vanadium



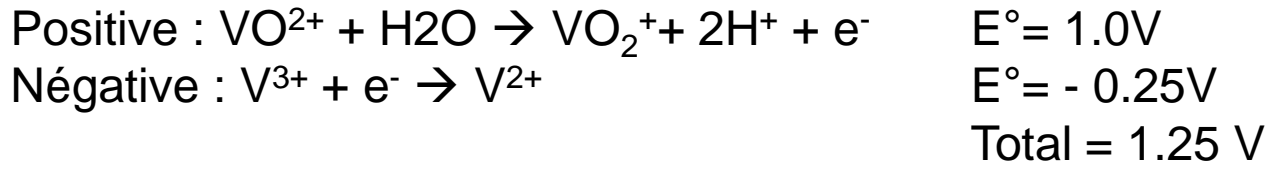
Electrolyte: 1.5–2M V/H₂SO₄

Couple Négatif V³⁺/V²⁺

Couple Positif V(IV)/V(V)

Energie spécifique (energy kg⁻¹) **15–25Wh.kg⁻¹**

Densité d'énergie (energy l⁻¹) 20–33Wh.l⁻¹



Bonne réversibilité
Bon rendement

Coût de la membrane (nafion)
Faible solubilité (1,7 mol/L → 25 Wh/l)
Dégagements gazeux

Vanadium Redox flow

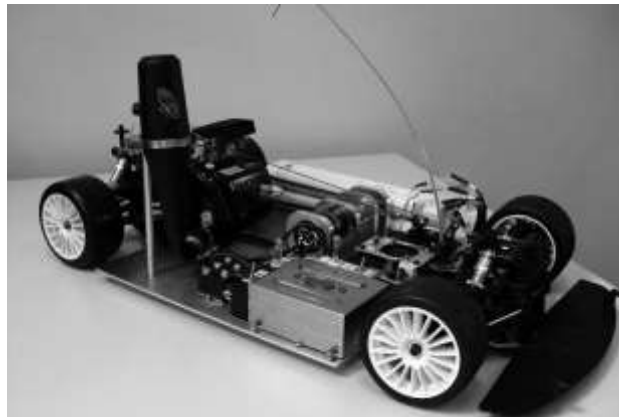


stack 1 kW ?

Fraunhofer Institute für chemical technology
Laboratoire Umsicht Oberhausen



up to 80 kW



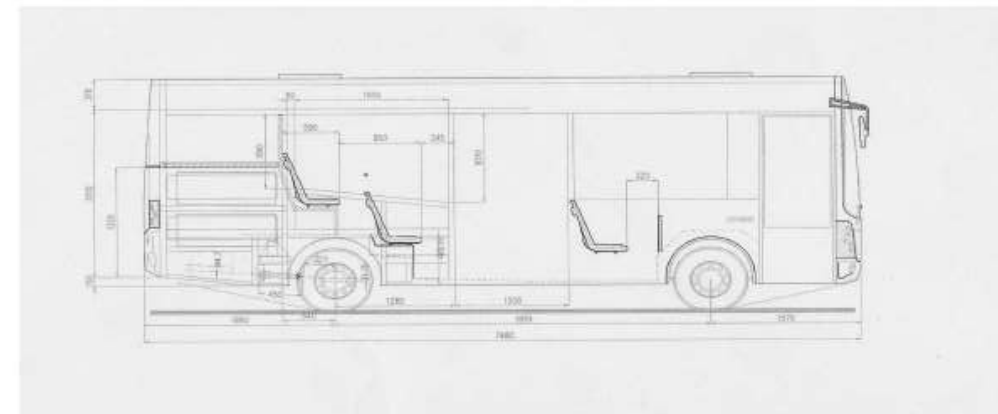
autonomie estimée
25 km (1/5 ?)



M. Skillas Kazacos



redtenery.com



The Ecobus is a lead-acid battery backed up with a VRB
40 kWh RFB +
2x600 L → 40 kWh RFP + 70 kW PbA buffer
→ 30 km autonomie
recharge 5-10 mn
24 h/j

Ar Van Tregan



= bateau électrique en breton

catamaran électrique sans batteries qui mesure 22,1 mètres sur 7,2 mètres et peut accueillir 113 personnes, dont 3 à mobilité réduite, ainsi que 10 vélos.

8x16 = 128 Condensateurs / Pack de 400 V poids de 6 t !?

supercondensateurs carbone

puissance 2 kW/kg

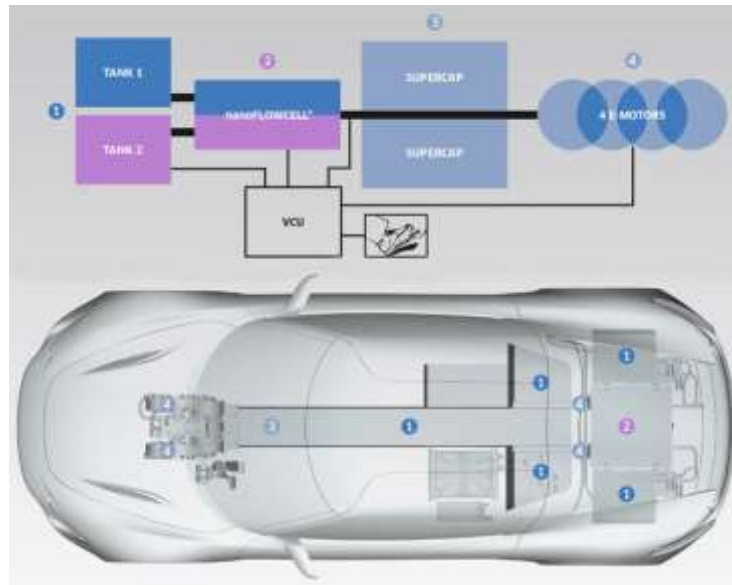
puissance 5 Wh/ kg

(Lorient, Juillet 2013)



Quant e-Sport limousine

2x200L



5,25 m
2300 kg
0-100 km/h 2.8s

Batterie puissance de 30 kW
120 kilowatt-hour flow-cell/2x200 L
densité 300 Wh/L (mieux qu'un solide)

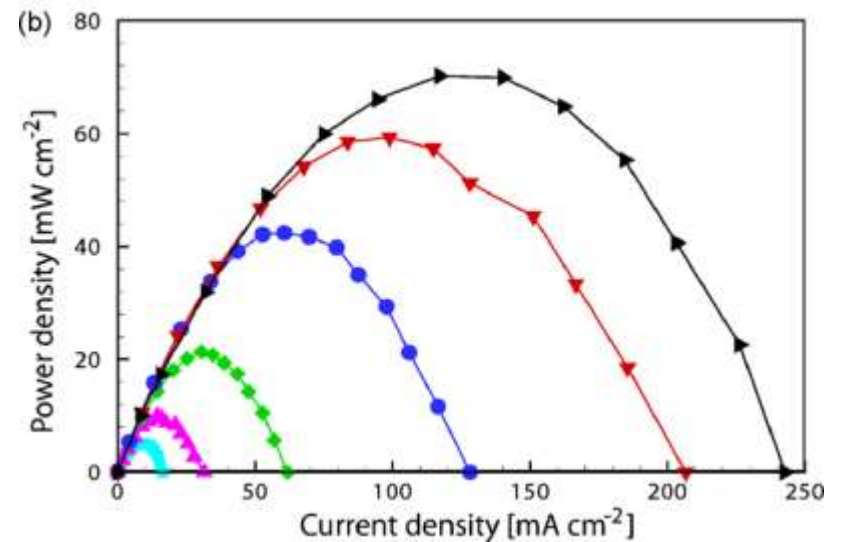
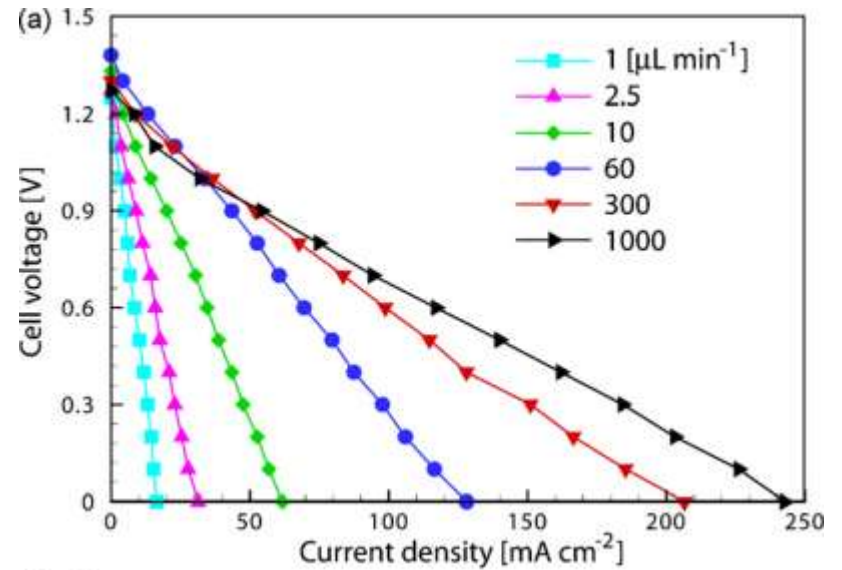
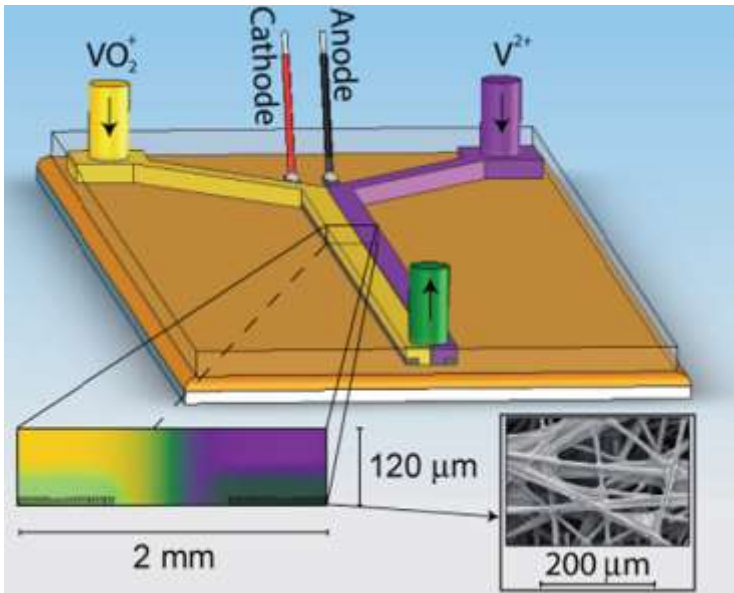
Bi-ion = ionized nanoparticles (???)

Nunzio LaVecchia <http://www.nanoflowcell.com/en/nanoflowcell> mars 2014

2017: 12 kWh par 100 km dans un test mixte

Microfluidic VRB cell

2M vanadium in 2M H₂SO₄



Erik Kjeang et al.
Electrochimica Acta 52 (2007) 4942–4946

Amélioration: Brevet du M.I.T.

(19) **United States**

(12) **Patent Application Publication**

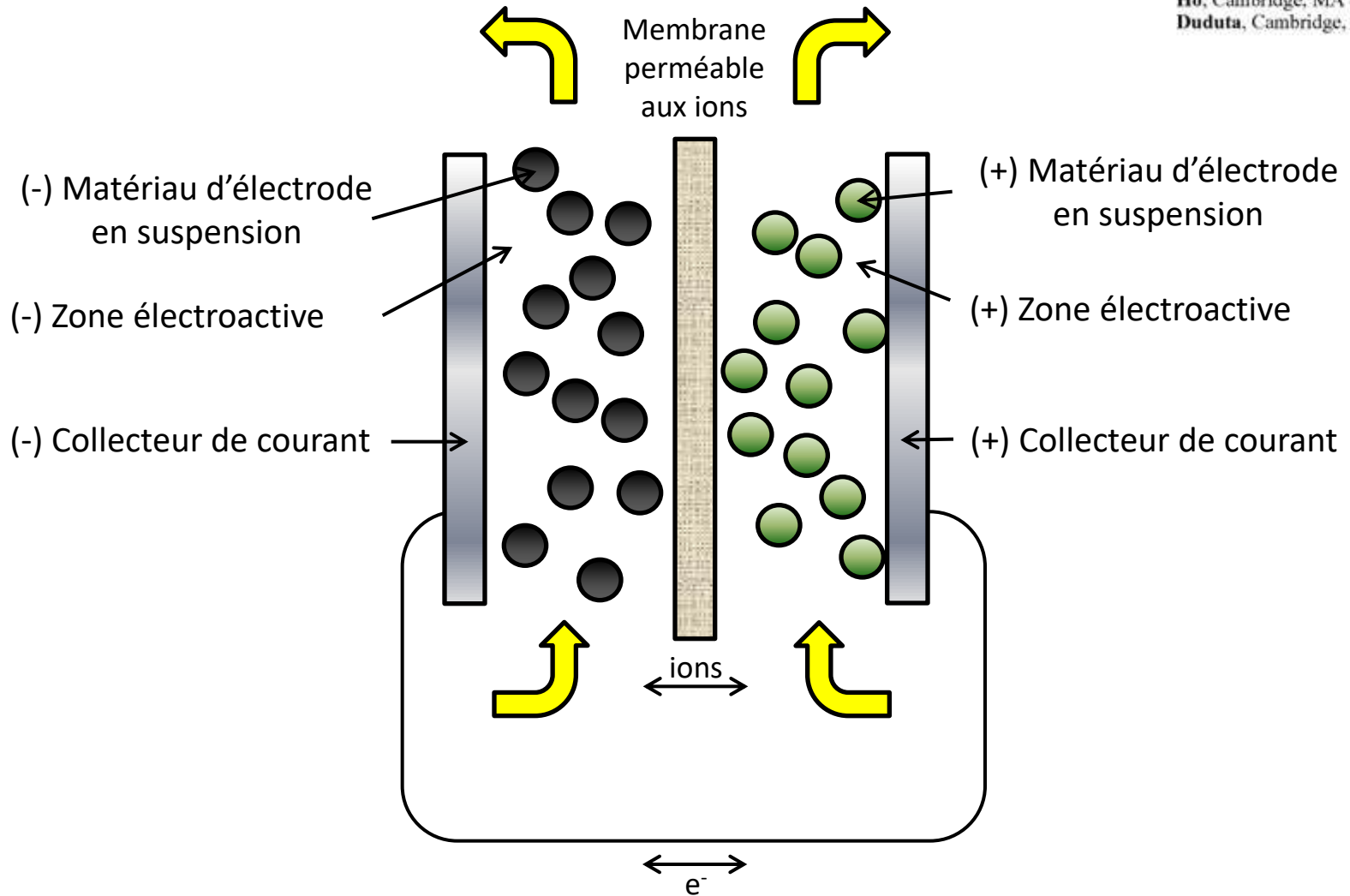
Chiang et al.

(10) Pub. No.: **US 2010/0047671 A1**

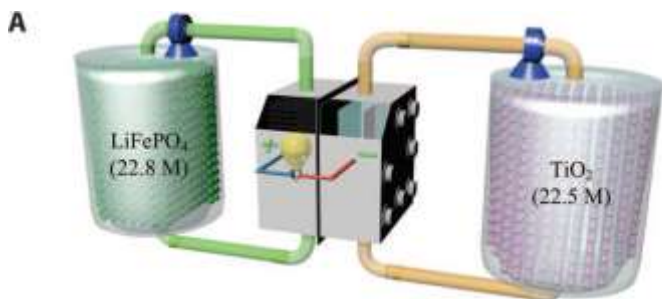
(43) Pub. Date: **Feb. 25, 2010**

(54) **HIGH ENERGY DENSITY REDOX FLOW DEVICE**

(75) Inventors: **Yet-Ming Chiang**, Framingham, MA (US); **W. Craig Carter**, Jamaica Plain, MA (US); **Bryan H. Ho**, Cambridge, MA (US); **Mihai Duduta**, Cambridge, MA (US)

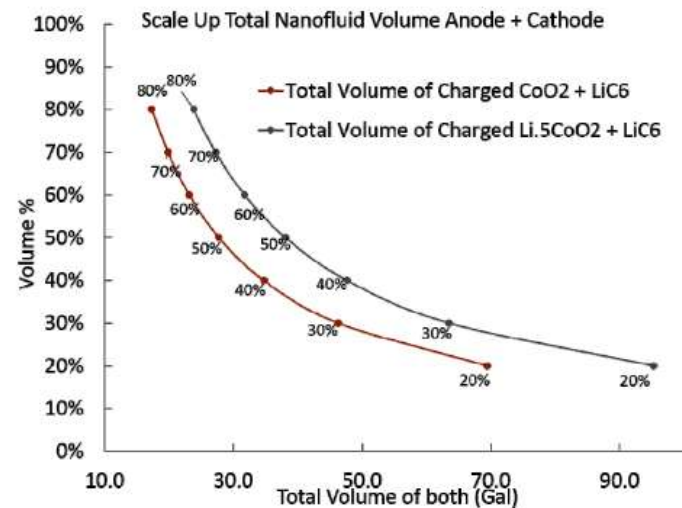
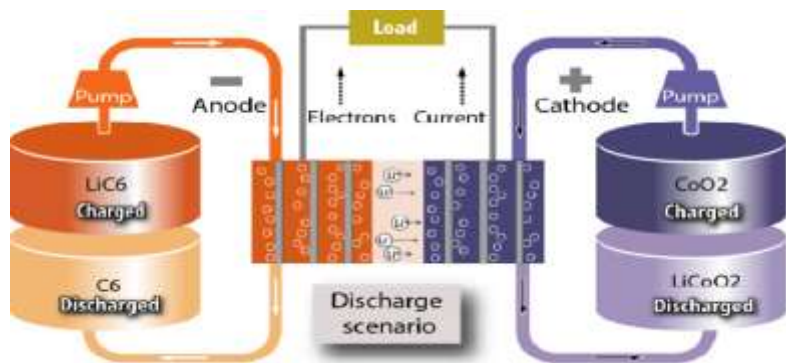


batteries à suspensions



claim
800 Wh/l

Jia et al. Sci. Adv. 2015;1:e1500886



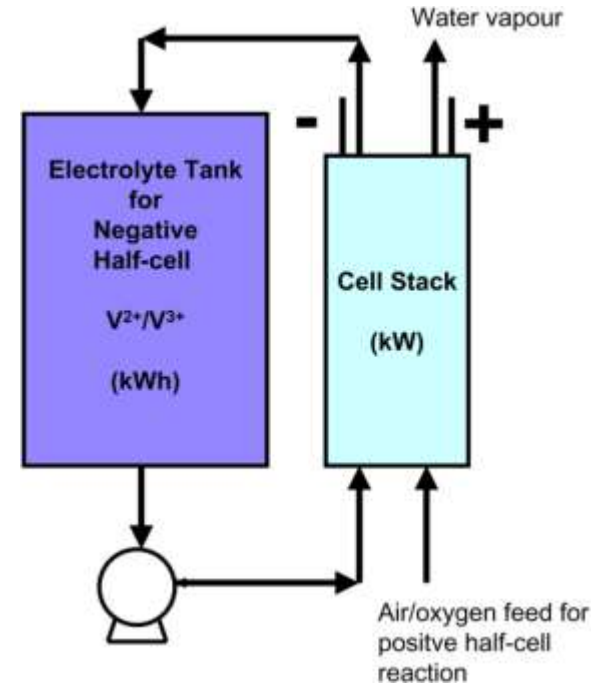
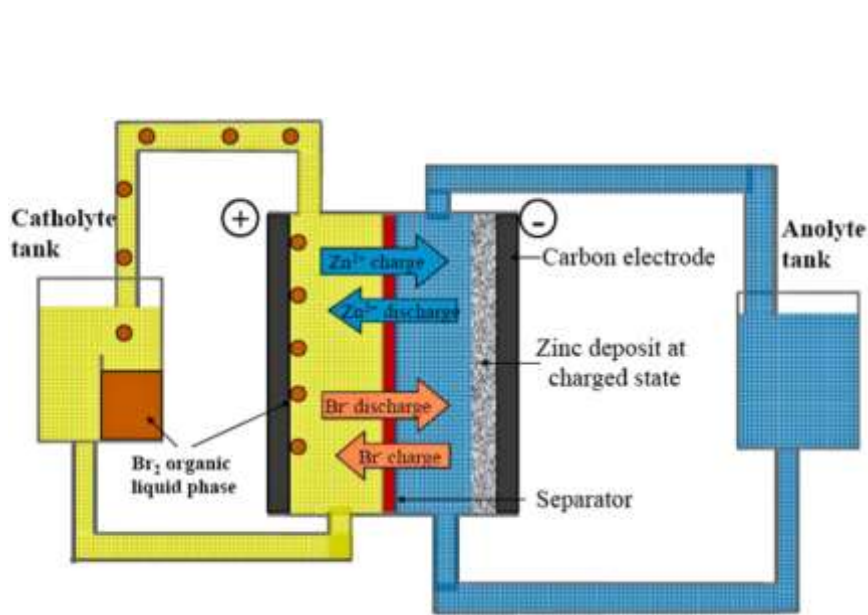
volume necessary to obtain 100 kWh

Integration of Flow Batteries into Electric Vehicles: Feasibility and the Future

J. P. Katsoudas, E. V. Timofeeva, C. U. Segre, D. Singh

NSTI-Nanotech 2014, www.nsti.org, ISBN 978-1-4822-5830-1 Vol. 3, 2014

flow batteries hybrides



Zn/Br₂

efficacité énergétique 85%

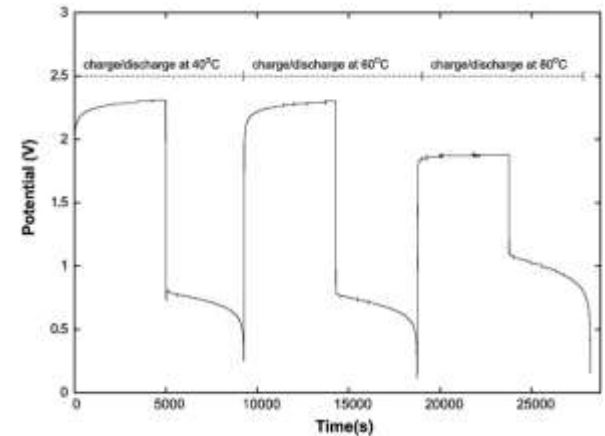
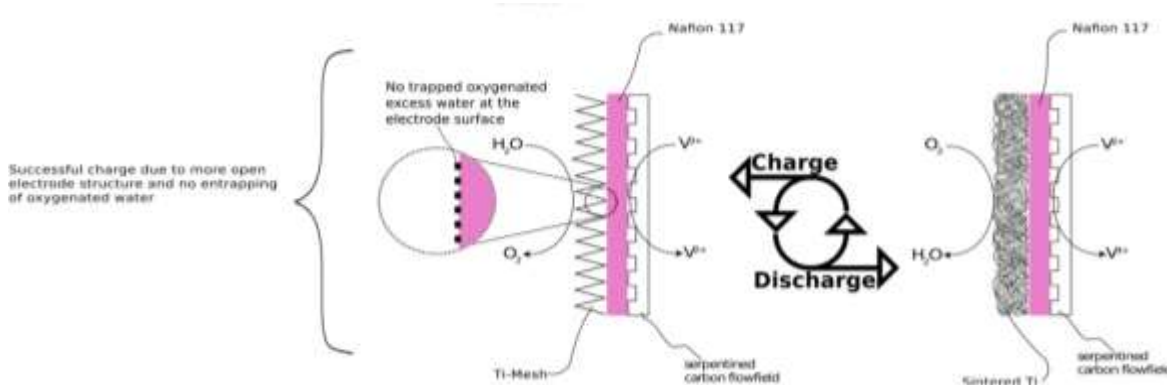
densité d'énergie 85 Wh/kg

80°C → 4 M/L de V ds H₂SO₄
pas de précipitation de V⁵⁺

Progress in Flow Battery Research and Development

M. Skyllas-Kazacos,^{a,*},^z M. H. Chakrabarti,^b S. A. Hajimolana,^b F. S. Mjalli,^c
and M. Saleem Journal of The Electrochemical Society, 158 (8) R55-R79 (2011)

vanadium –oxygen redox fuel cell



2 M V^{2+}/V^{3+} in 3 M H_2SO_4
 charge ($E_{th} = 1,49$ V)
 $4H_2O \rightarrow 4H^+ + O_2 + 4 e^-$ (1,23 V)
 $V^{3+} + e^- \rightarrow V^{2+}$ (-0.26 V)

efficacité énergétique 46 %
 densité d'énergie 40 Wh/kg

x 2 à 80°C

Conclusion

les batteries métal –air sont une alternative crédible en stationnaire

elles peuvent le devenir sous condition d'améliorer les cycles ou la recharge mécanique

les batteries à flux permettraient des recharges rapides

le travail sur des électrodes à air réversible est un enjeu majeur