Status and perspectives of current flow battery technologies

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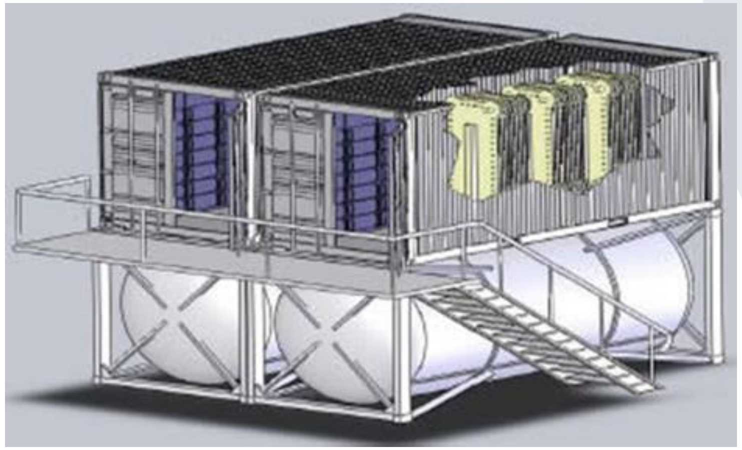
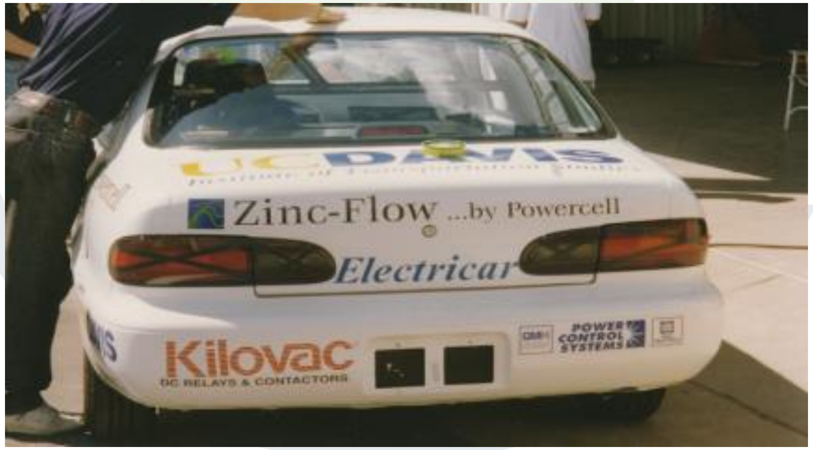
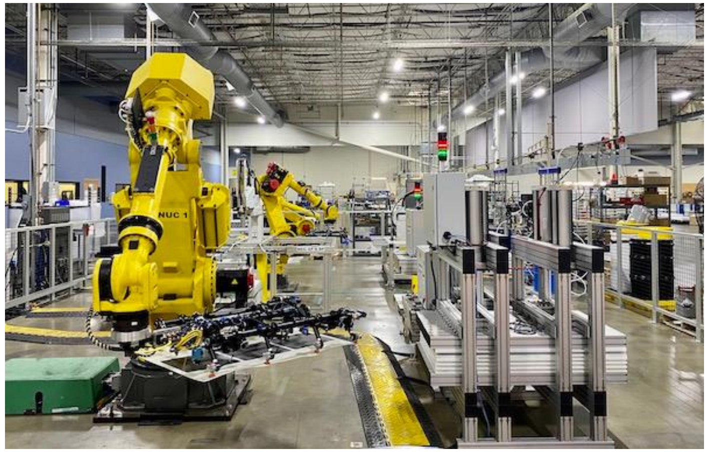
6. Herbstworkshop Energiespeicher, TU-Dresden, Germany, 2022







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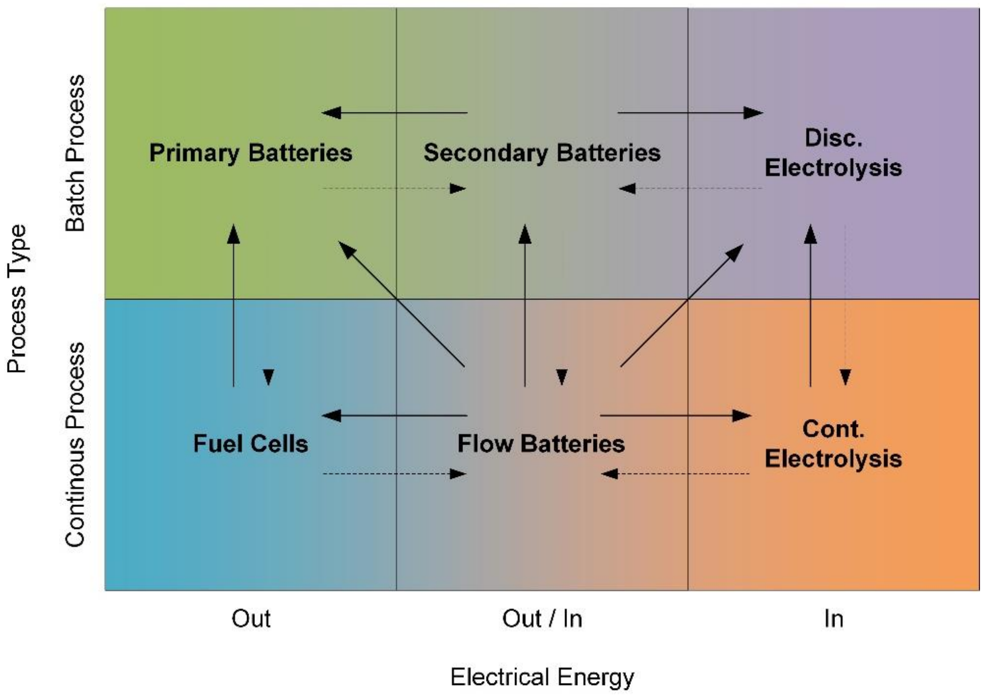
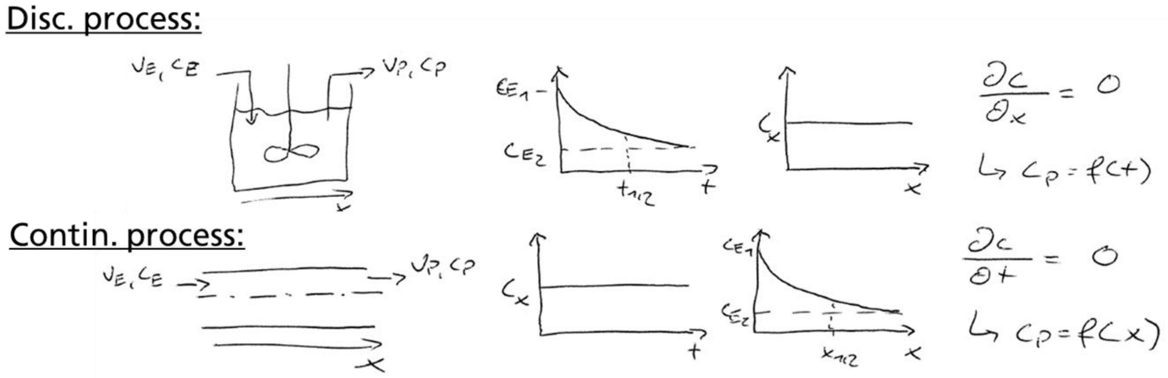
What is a flow battery?





IEC TC21/TC105 JWG7:

"„Flow batteries are all electrochemical energy converters that use flowing media as or with active materials and where the electrochemical reactions can be reversed."

- Fluid-fluid is Flow Batteries
- Solid-fluid is Hybrid Flow Batteries

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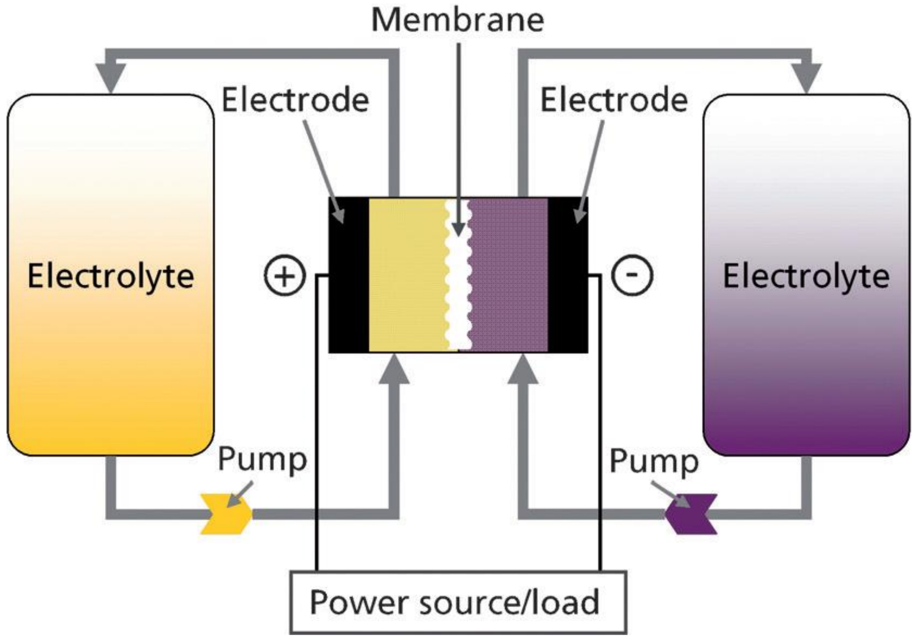
Overview of inorganic flow battery chemistries



Anode: $$A^{x} \rightleftharpoons A^{x+z} + ze^{-}$$

Cathode: $$C^{y} + ze^{-} \rightleftharpoons C^{y-z}$$

Cell: $$A^{x} + C^{y} \rightleftharpoons A^{x+z} + C^{y-z}$$

Anode \ Cathode	E^0,V	Mn_2O_3/MnO_2	$Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$	Cu/Cu^+	I^-/I_3^-	Fe^{2+}/Fe^{3+}	VO^{2+}/VO_2^+	$Br^-/ClBr_2^-$	Br^-/Br_2^*	NpO_2^{2+}/NpO_2^+	I_2/IO_3^-	O^{2-}/O_2	$Cr^{3+}/HCrO_4^-$	Cl^-/Cl_2	Pb^{2+}/PbO_2	Mn^{2+}/Mn^{3+}	Ce^{3+}/Ce^{4+}	Co^{2+}/Co^{3+}
		0.15	0.36	0.52	0.54	0.77	0.99	1.04	1.09	1.14	1.2	1.23	1.35	1.36	1.46	1.54	1.72	1.82
$Al/Al(OH)_4^-$	-2.31											B						
$Zn/Zn(OH)_4^{-2}$	-1.22	B	B															
Zn/Zn^{2+}	-0.76				B	B	B	B	C					B			B	
Fe/Fe^{2+}	-0.45					B												
S_2^{2-}/S	-0.43		B						C			B						
Cr^{2+}/Cr^{3+}	-0.41					C			A				B					
Cd/Cd^{2+}	-0.40					B												
V^{2+}/V^{3+}	-0.26					B	C	B				B				B	B	B
Pb/Pb^{2+}	-0.13														B			
Sn/Sn^{2+}	-0.14								B									
H_2/H^+	0.00					B	B		B					B				
Ti^{3+}/TiO^{2+}	0.04					A		A						A		B		
Cu^+/Cu^{2+}	0.15			B											B			
Np^{3+}/Np^{4+}	0.15									B								
Sn^{2+}/Sn^{4+}	0.15					B			B									
Cu/Cu^{2+}	0.34														B			
I^-/I_2	0.54										A							
Fe^{2+}/Fe^{3+}	0.77															B		

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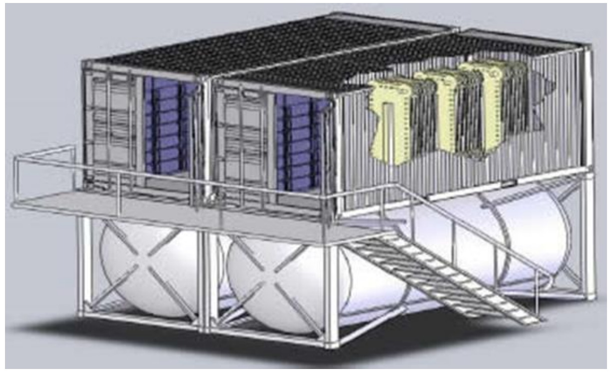
Iron/Chromium redox flow batteries (Fe/Cr RFB)



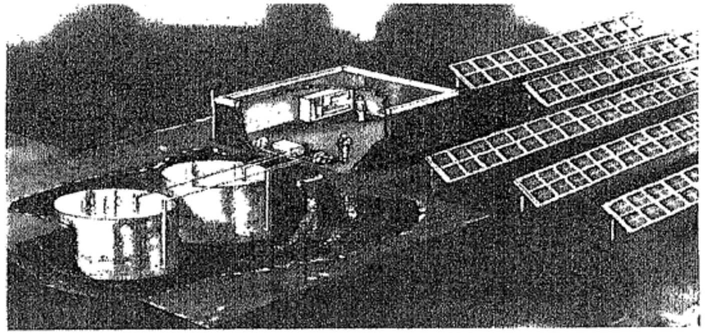


Fig. 3- NASA Redox Installation for Photovoltaic Energy Storage

Turlock 250 kW / 1 MWh Fe/Cr RFB © EnerVault

Anode: $Cr^{3+} + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Cr^{2+} \qquad \varphi^{0,+} = -0.42\ V$

Cathode: $Fe^{2+} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Fe^{3+} + e^- \qquad \varphi^{0,+} = +0.77\ V$

Cell: $Cr^{3+} + Fe^{2+} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Cr^{2+} + Fe^{3+} \qquad U_{cell} = 1.19\ V$

Advantages

- Low cost of materials
- Very simple reactions
- Low positive potentials (corrosion)

Disadvantages

- Catalysts/inhibitors required for anode
- Low energy and power density
- H_2 Formation at the anode
- Energy losses through heating

- Last commercialisation by Enervault, California, USA (~2016)
- Only very few publications since 2000s
- Increasing commercialisation interest in 2022

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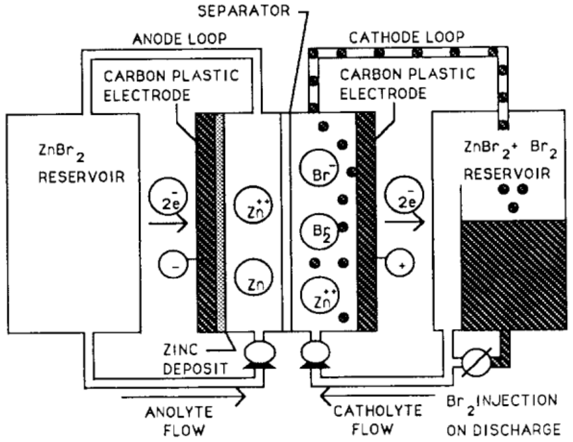
Zinc/Bromine redox flow batteries

$$\text{Anode:}\quad Zn^{2+} + 2e^{-} \xrightleftharpoons[\text{discharge}]{\text{charge}} Zn \qquad \varphi^{0,-} = -0.762\ \text{V}$$

$$\text{Cathode:}\quad 3Br^{-} \xrightleftharpoons[\text{discharge}]{\text{charge}} Br_3^{-} + 2e^{-} \qquad \varphi^{0,+} = +1.06\ \text{V}$$

$$\text{Cell:}\quad Zn^{2+} + 3Br^{-} \xrightleftharpoons[\text{discharge}]{\text{charge}} Zn + Br_3^{-} \qquad U_{cell} = 1.82\ \text{V}$$

- Zinc deposition on negative electrode (hybrid RFB)
- Two electron transition of Zn (energy density)
- Bromine/Bromide on positive electrode
- High solubility of bromine



Lex, P. J.; Matthews, J. F. Recent Developments in Zinc/Bromine Battery Technology at Johnson Controls. In *IEEE 35th International Power Sources Symposium*; IEEE: Cherry Hill, NJ, USA, 1992; pp 88–92. https://doi.org/10.1109/IPSS.1992.282047.

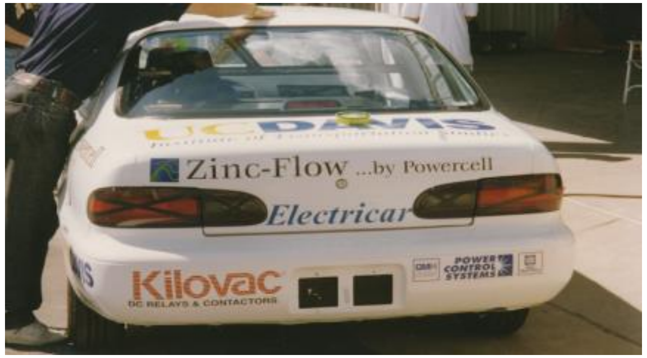
https://www.youtube.com/watch?v=FbBnoTMfYvs
US-President Obama @ ZBB Energy 2010

Advantages

- Low cost of materials
- High energy density ~80 Wh/L
- Uses microporous separators
- High cell voltage ~1,8 V

Disadvantages

- Zn deposition can have dendrites (stripping)
- Bromine is toxic (complexing agents)
- Complexing agents are expensive
- Bromine is aggressive (material stability)
- Moderate cycle life (~3000)
- Moderate current densities ~25 mA/cm²



35 kWh Zn/Br race car ~1994 © Gerd Tomazic
Roth, Noack, Skyllas-Kazacos, Flow Batteries, Wiley-VCH 2022

- Only Redflow Australia is selling Zn/Br RFBs 2022

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Zinc/Bromine redox flow battery
Redflow Australia

3 kW / 10 kWh ZBM3

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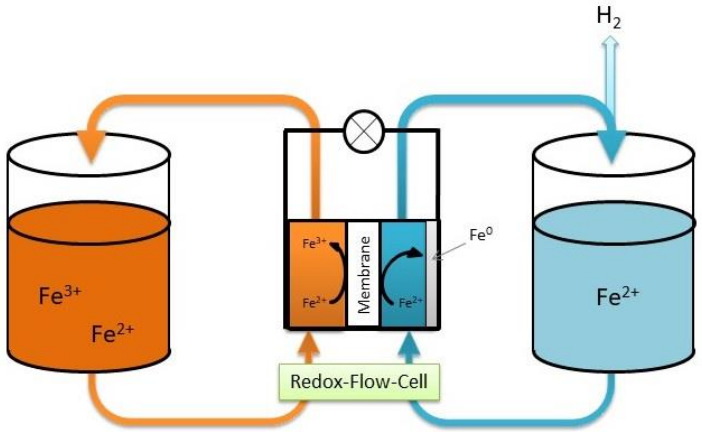
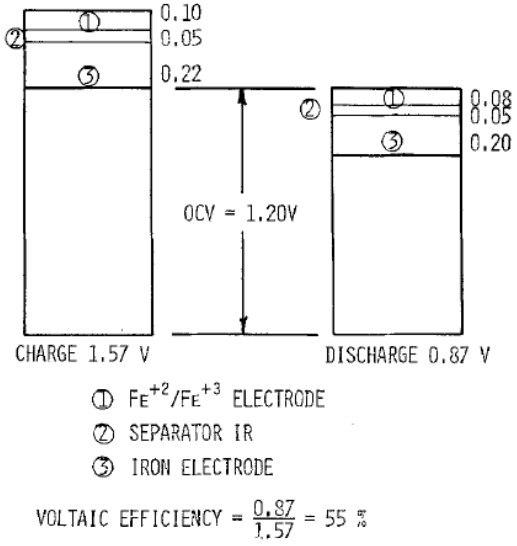
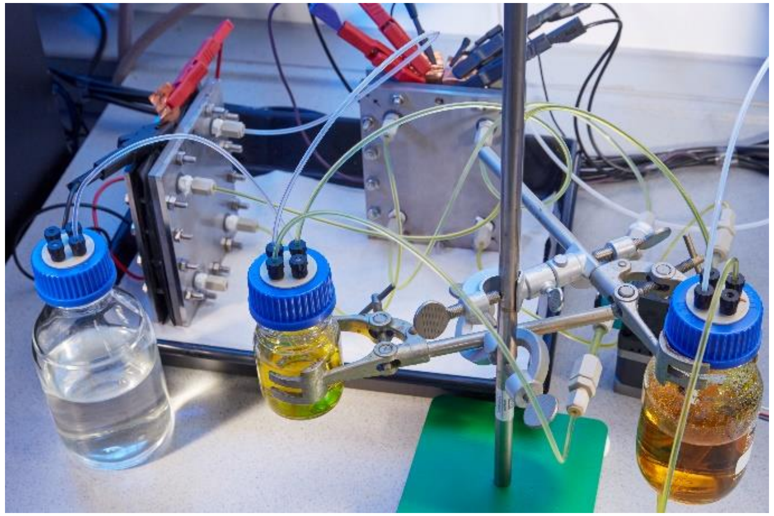
Iron/Iron redox flow batteries

Anode:	$Fe^{2+} + 2e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Fe$	$\varphi^{0,-} = -0.44$ V
Cathode:	$Fe^{2+} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Fe^{3+} + e^-$	$\varphi^{0,+} = +0.77$ V
Cell:	$2Fe^{2+} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Fe + Fe^{3+}$	$U_{cell} = 1.21$ V





Hruska, L. W. Investigation of Factors Affecting Performance of the Iron-Redox Battery. J. Electrochem. Soc. 1981, 128 (1), 18. https://doi.org/10.1149/1.2127366.



Fe/Fe RFB @ Fraunhofer ICT

- Very cheap active material ($FeCl_2$)
- Deposition of Fe on negative electrode ($2e^-$)
- Hydrogen evolution as side reaction
  - Results in an increase of pH
  - Precipitation of $Fe(OH)_2$
- Slow Fe/Fe^{2+} reactions
- Only one company (ESS Inc. USA)

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Iron/Iron redox flow battery
ESS inc. USA

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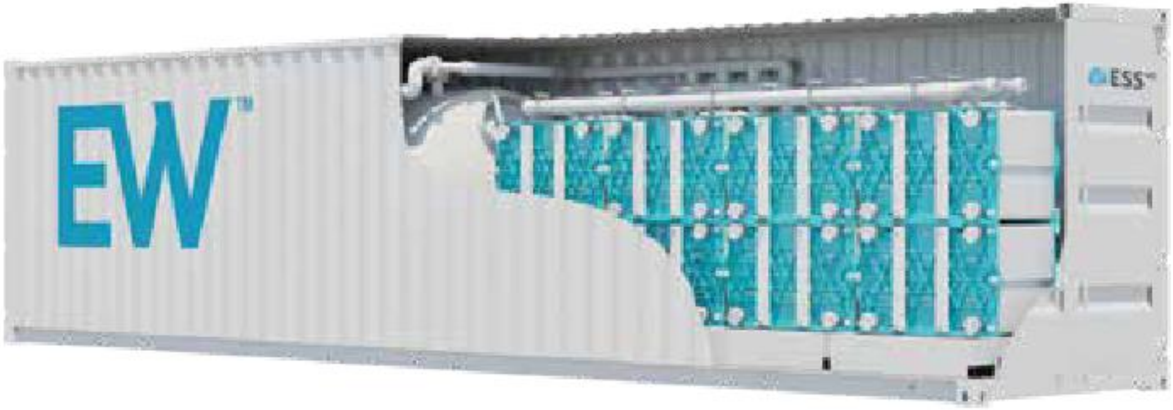

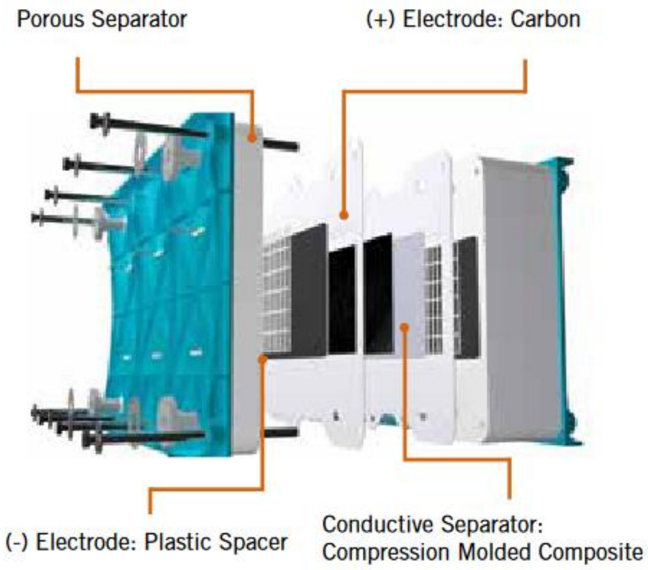

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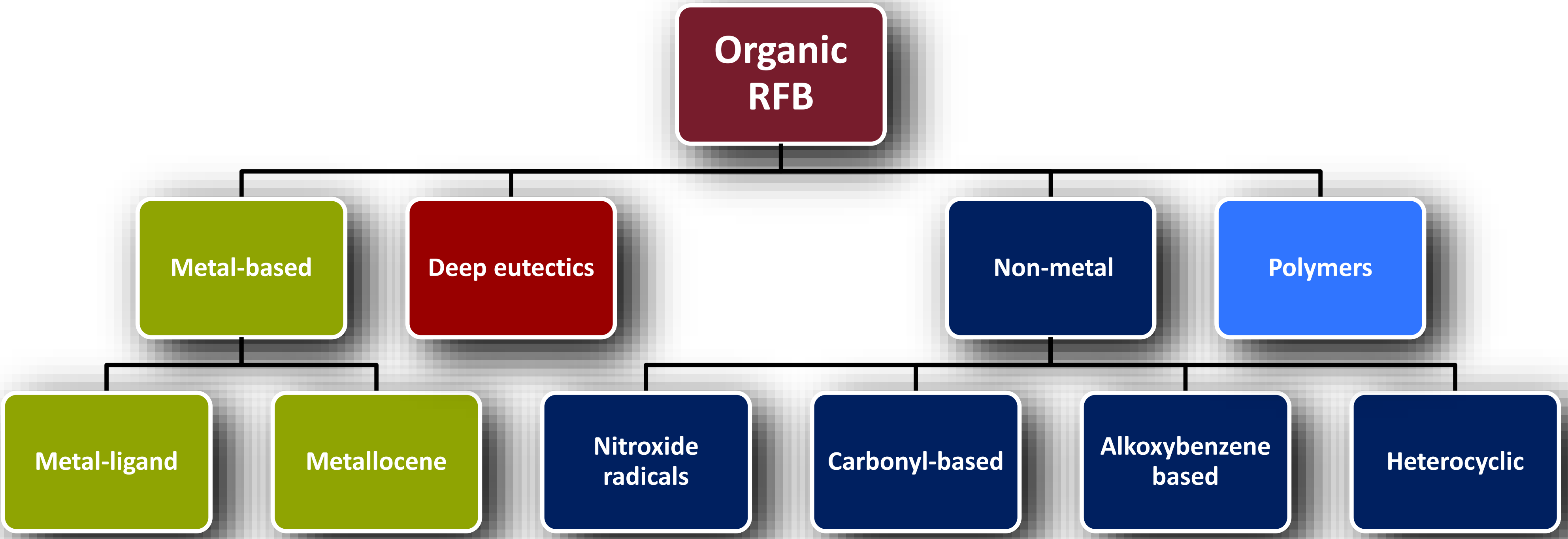
Overview of organic flow battery chemistries



- Very young R&D area (~2015!)
- Focus of many research groups worldwide, a few companies (Jena Batteries, Kemiwatt, CMblue, Lockhead Martin,...)
- Often separation between aqueous / non-aqueous

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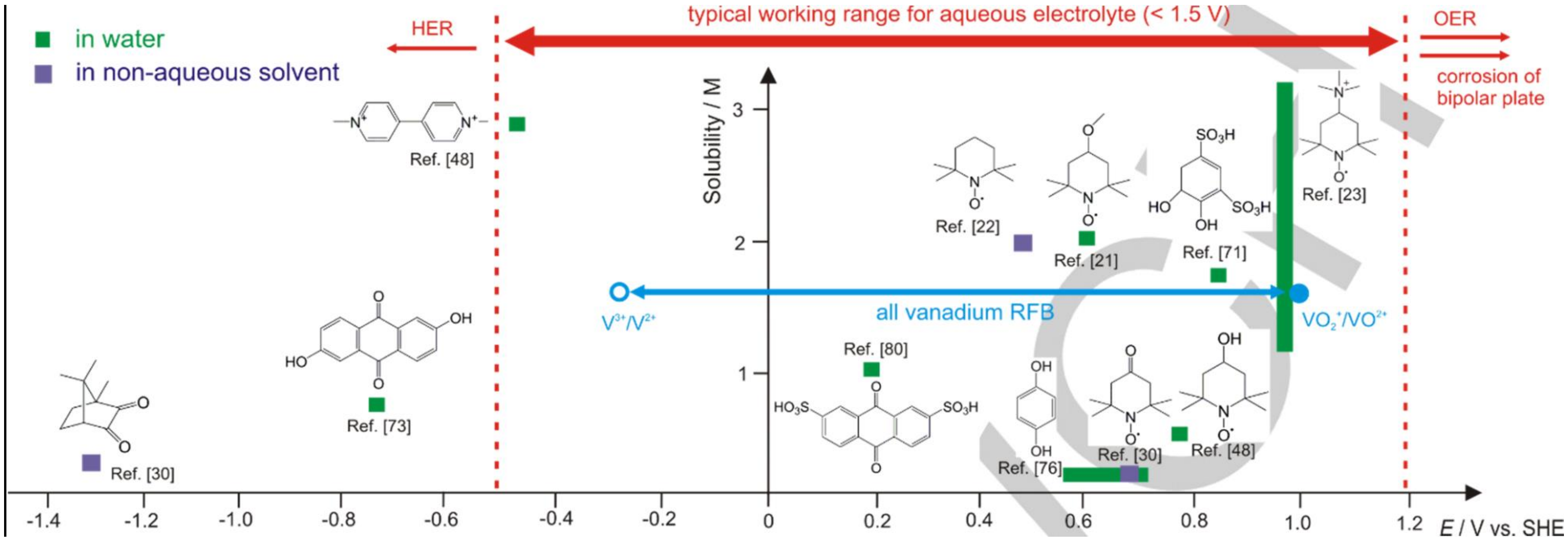
Overview of organic flow battery chemistries



Chen, R., ChemElectroChem 2019, 6 (3), 603–612. https://doi.org/10.1002/celc.201801505.

Reasons for organic redox flow batteries:

- Huge number of different active materials with different properties
- Abundant materials, Safe, non-toxic, Easy re-cycleable
- Non-aqueous RFBs with high voltage - > High energy density possible (e.g. LIB-RFB)
- Aqueous RFBs with high safety and low cost

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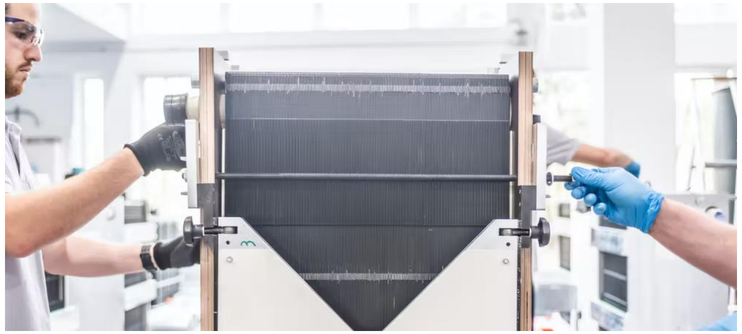
Organic redox flow batteries

© Jena Batteries

© KEMIWATT



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Organic redox flow batteries

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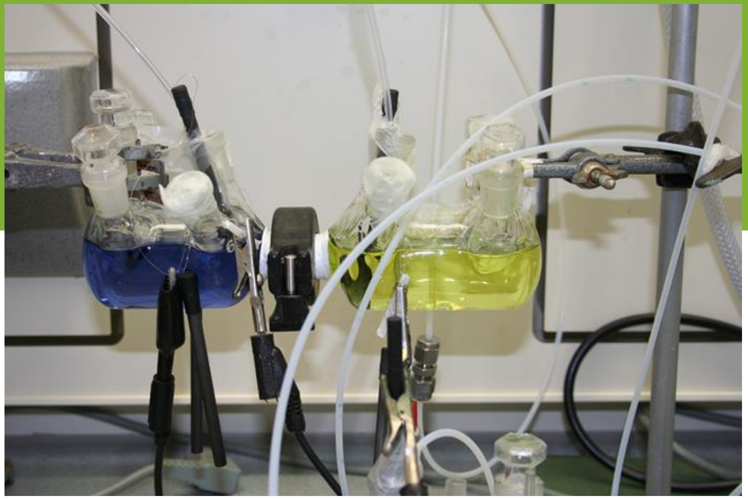
Vanadium redox flow batteries (VRFB)



1st VRFB (non-flow) at Fraunhofer ICT 2008

$$\text{Anode:}\quad V^{3+} + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} V^{2+} \qquad \varphi^{0,-} = -0.255\ \text{V}$$

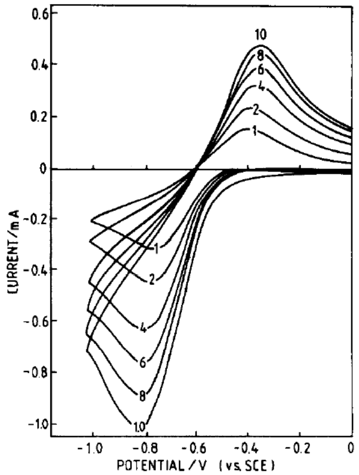
$$\text{Cathode:}\quad VO^{2+} + H_2O \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} VO_2^+ + 2H^+ + e^- \qquad \varphi^{0,+} = +1.00\ \text{V}$$

$$\text{Cell:}\quad VO^{2+} + V^{3+} + H_2O \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} VO_2^+ + V^{2+} + 2H^+ \qquad U_{cell} = 1.25\ \text{V}$$

- Invented 1985 by Maria Skyllas-Kazacos and co-workers at UNSW
- Uses only Vanadium as active material
- Moderate till high current densities up to several 100s mW/cm²
- Best studied RFB
- Most installed RFB
- Several companies with commercialisation worldwide

Advantages
- Relatively simple
- Very high cycle life (>10.000)
- High power density possible
- Flexible design
- Recycling of Vanadium electrolyte
- No self-discharge (pumps off)
- High energy efficiency > 75 %

Disadvantages
- Redox couple potentials in the borders of solvent stability
- VO_2^+ solutions are strong oxidizing agents
- Balancing of electrolyte necessary
- High fluctuations of Vanadium price



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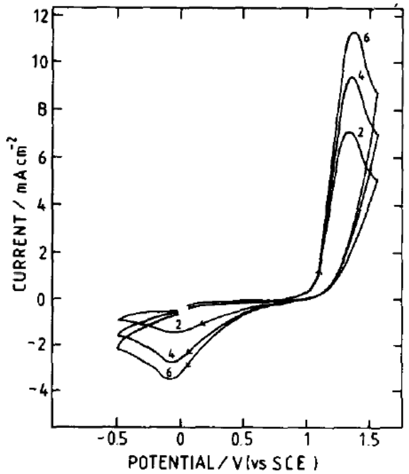

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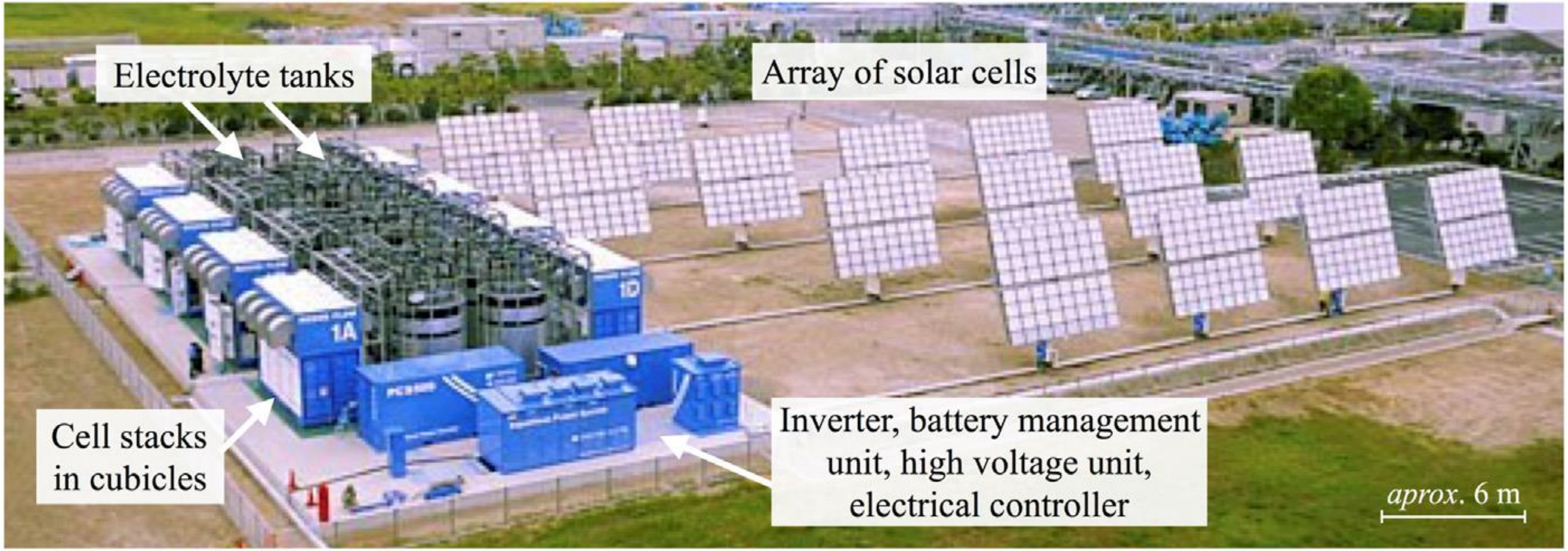
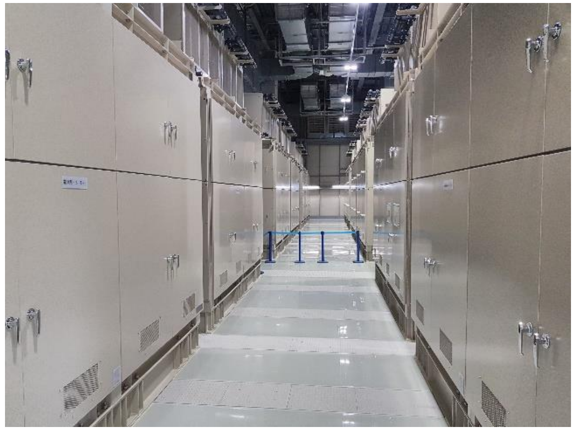
Vanadium redox flow batteries (VRFB)
Sumitomo 5 MWh VRFB Yokohama / Japan 2012



Arenas, L. F.; Ponce de León, C.; Walsh, F. C. Engineering Aspects of the Design, Construction and Performance of Modular Redox Flow Batteries for Energy Storage. *Journal of Energy Storage* **2017**, *11*, 119–153. https://doi.org/10.1016/j.est.2017.02.007.

Vanadium redox flow batteries (VRFB)
Sumitomo 15 MW / 60 MWh VRFB Hokkaido / Japan 2012



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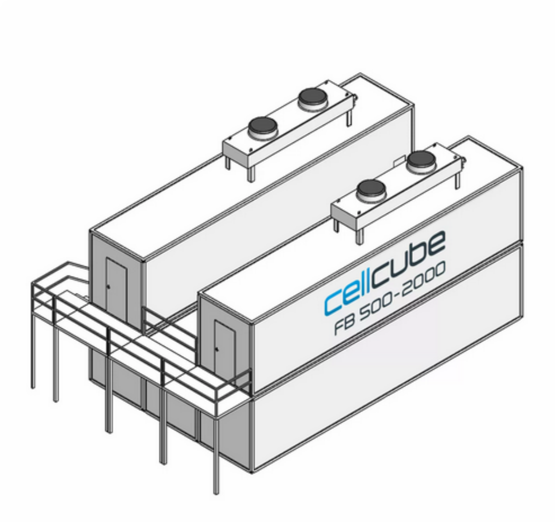
Vanadium redox flow batteries (VRFB)
Cellcube containerised solutions

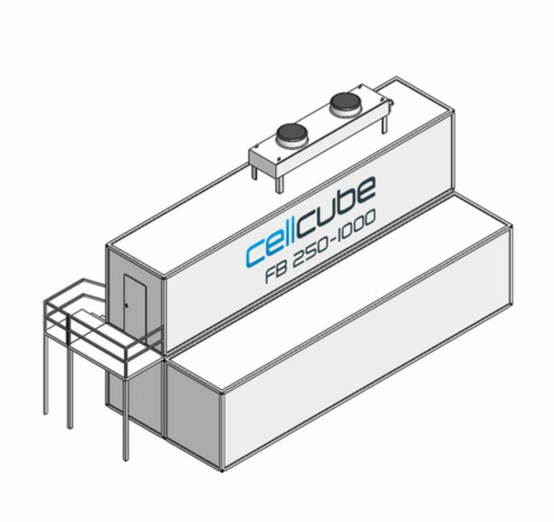
FB 250 / FB 500 SERIE, RELEASE 4.00



CELLCUBE FB 500-2.000

Der große Energiespeicher mit drei Energie- und zwei Leistungseinheiten. Ideal für den Aufbau industrieller Speicherlösungen.

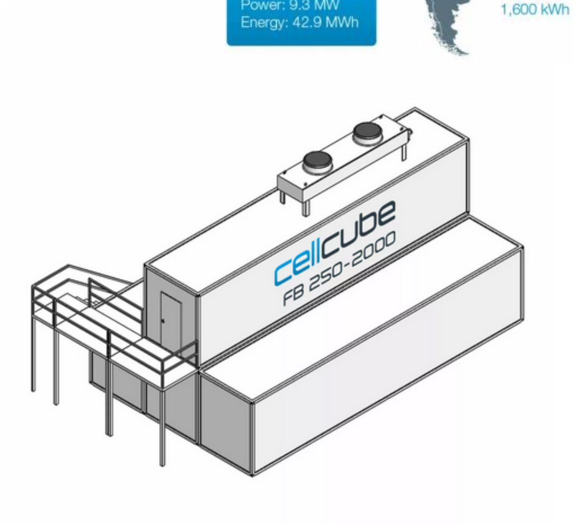
Nennleistung = 500 kW
P max, Ladung = 1.000 kW



CELLCUBE FB 250-1.000

Die kleine Speicherlösung mit zwei Energieeinheiten und einer Leistungseinheit, ideal für den Microgrid-Einstieg.

Nennleistung = 250 kW
P max, Ladung = 500 kW
P max, Entladung = 375 kW



CELLCUBE FB 250-2.000

Der Energiespeicher mit langem Atem mit drei Energieeinheiten und einer Leistungseinheit. Ideal, um die Nacht durchzumachen.

Nennleistung = 250 kW
P max, Ladung = 500 kW

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Vanadium redox flow batteries (VRFB)
Rongke Power 200 MW / 800 MWh VRFB

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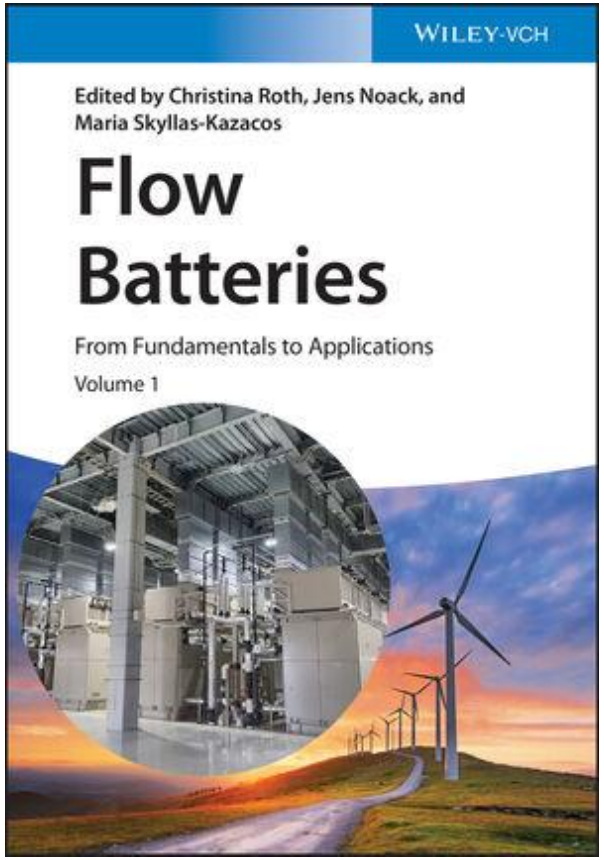

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