Sustainable, Safe and Scalable Stationary Energy Storage

Organic redox-flow batteries for stationary energy storage

EFRE
EUROPE FOR THURINGIA
EUROPEAN REGIONAL DEVELOPMENT FUND

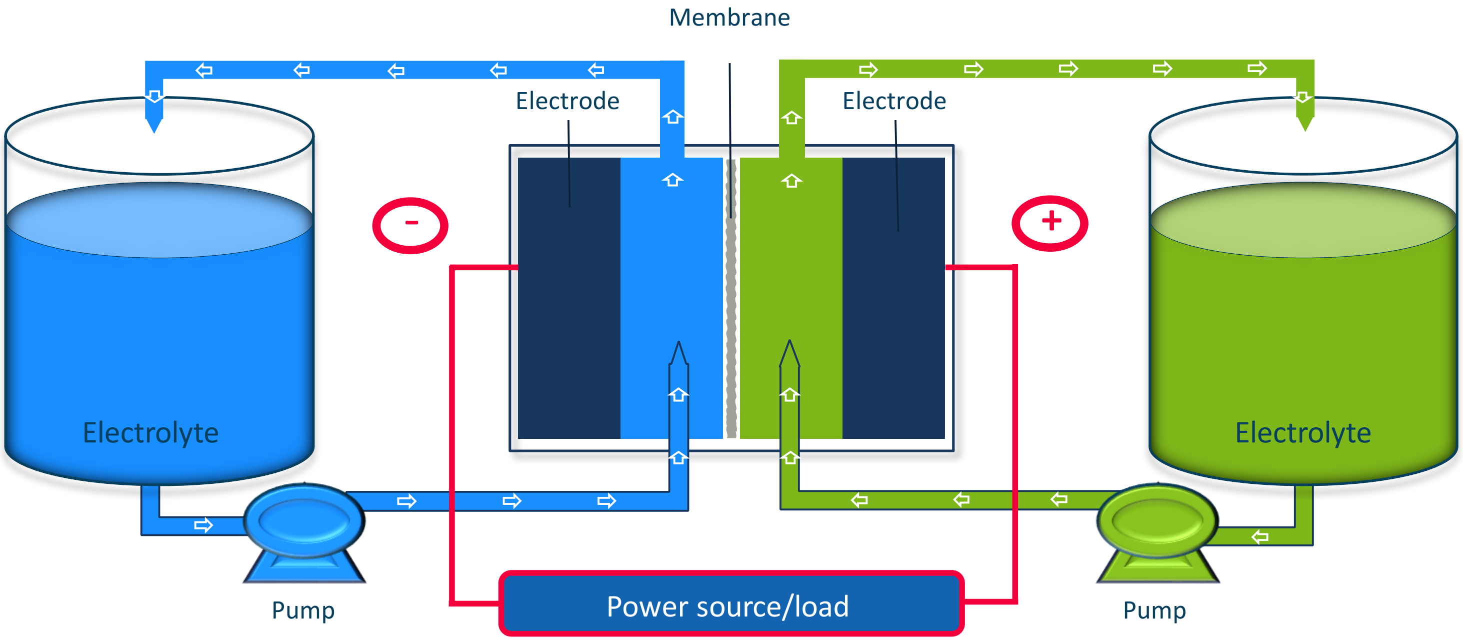
Federal Ministry
for Economic Affairs
and Energy
on the basis of a decision
by the German Bundestag

Federal Ministry
of Education
and Research

ZIM
Zentrales
Innovationsprogramm
Mittelstand

Thüringer Aufbaubank

Conventional redox flow batteries – a solid mature foundation



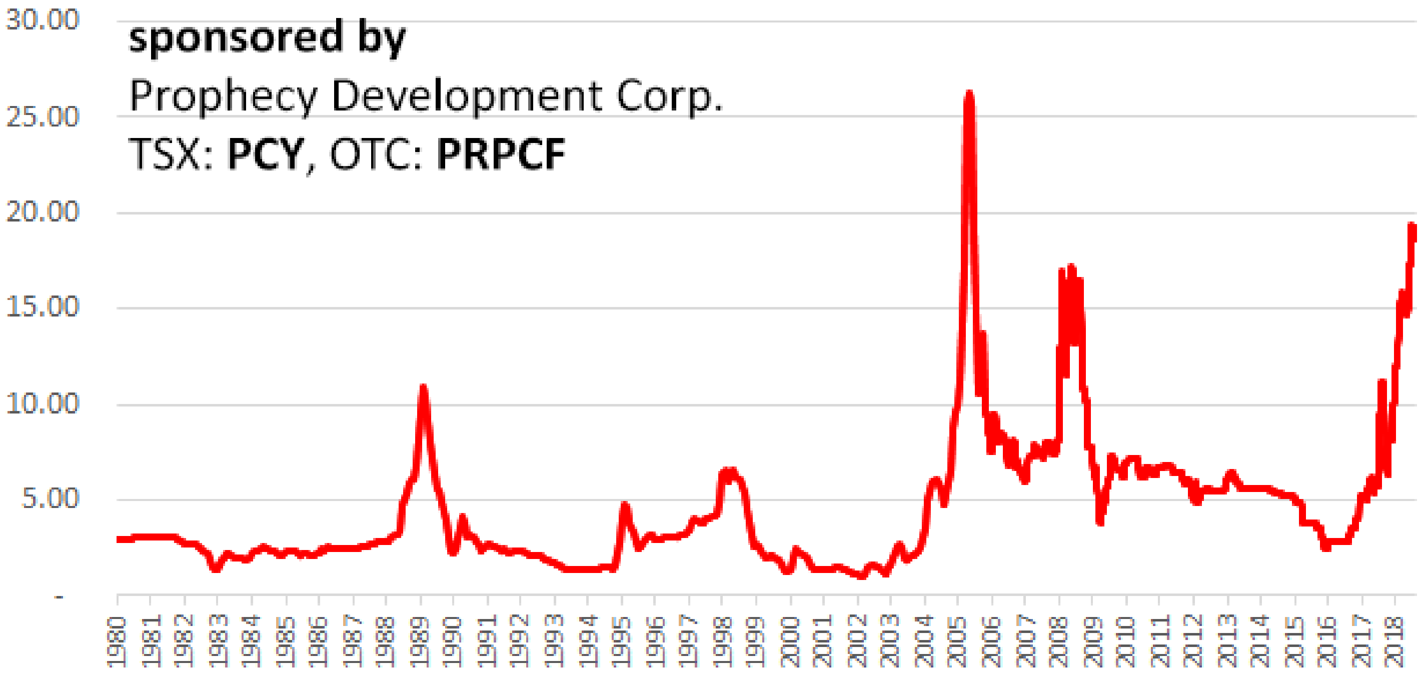
Chemical energy

Converter

Electrical energy

Vanadium, iron, chromium, bromine, …

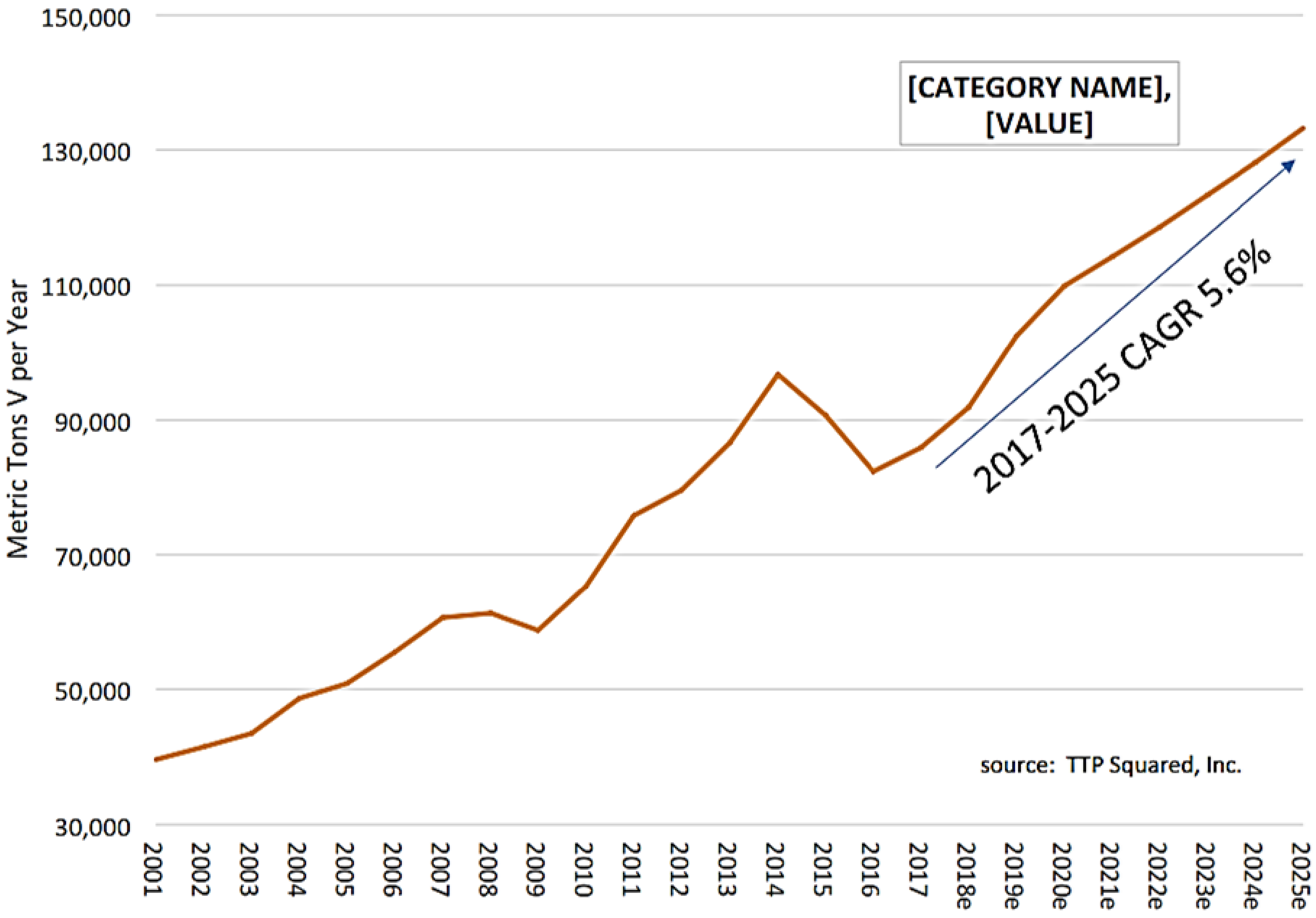
Vanadium-RFB: An unpredictably expensive system



- Demand exceeds supply (80,000 t vs. 75,000 t, 2016)
- China and South Africa are closing down polluting mines
- China introduces stricter standards for structural steel (higher V share) from November 2018
- High cost of extraction as by-product from coal, …

https://www.vanadiumprice.com/

Vanadium demand in competitive markets is on the rise



source: TTP Squared, Inc.

IFBF, 2018.

Li-ion batteries

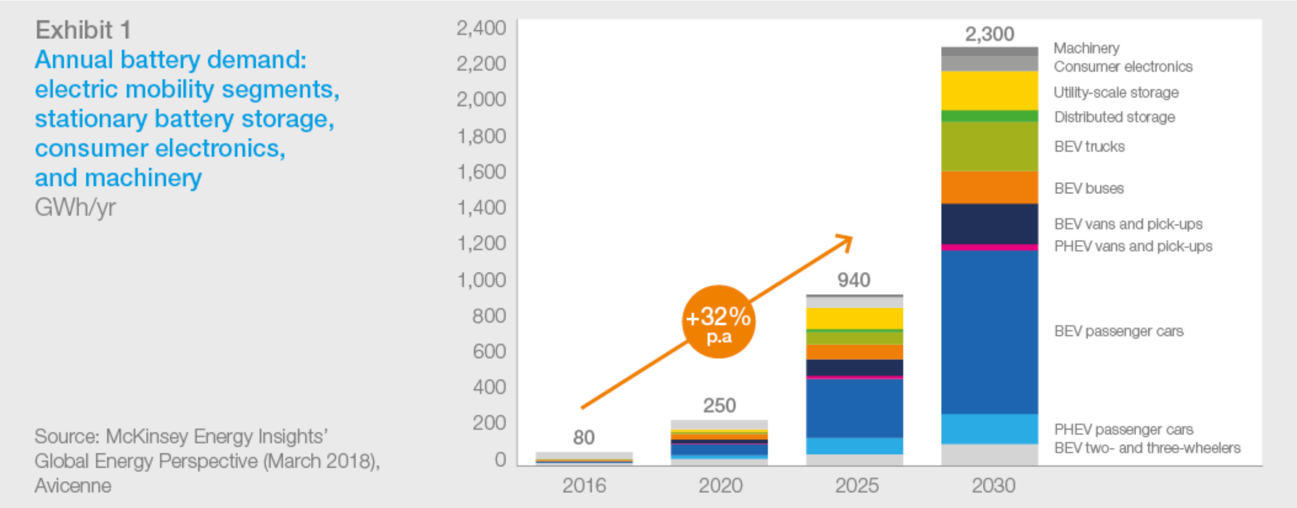


Exhibit 1

Annual battery demand: electric mobility segments, stationary battery storage, consumer electronics, and machinery

GWh/yr

Source: McKinsey Energy Insights' Global Energy Perspective (March 2018), Avicenne

Cobalt from Congo and substitute **nickel**: A bottleneck

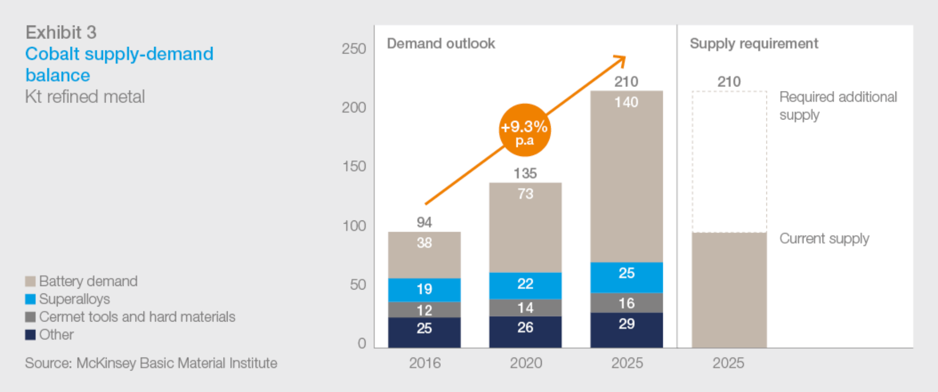


Exhibit 3

Cobalt supply-demand balance

Kt refined metal

Source: McKinsey Basic Material Institute

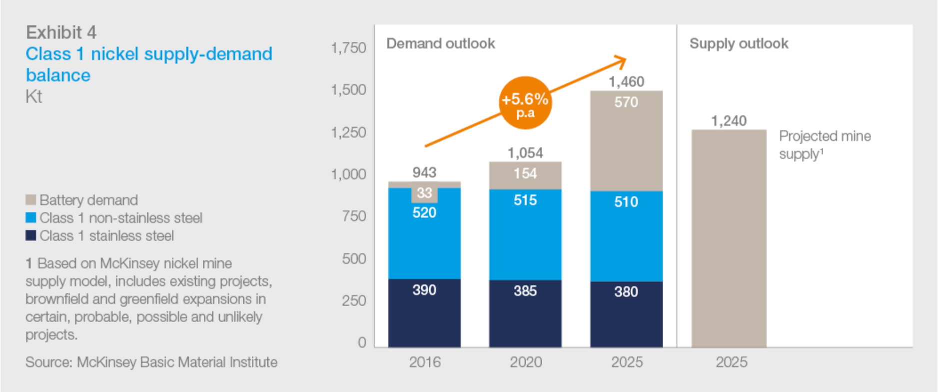


Exhibit 4

Class 1 nickel supply-demand balance

Kt

1 Based on McKinsey nickel mine supply model, includes existing projects, brownfield and greenfield expansions in certain, probable, possible and unlikely projects.

Source: McKinsey Basic Material Institute

McKinsey, 2018.

About JenaBatteries GmbH

- Founded in 2012, JB holds global patents for organic redox-flow batteries.
- In August 2016 we welcomed two new investors with outstanding expertise in R&D, Engineering and Business Development. This speeds up the transformation towards an economically successful company.
- JB is an innovative company that produces and develops large-scale energy storage systems from 40 kWh upwards.
- We are currently building a global partner network with project developers/technology partners and we are delivering selected pilot plants.
- Our award-winning Batteries avoid heavy metals and aggressive materials like sulphuric acid.
- JB is supported by:

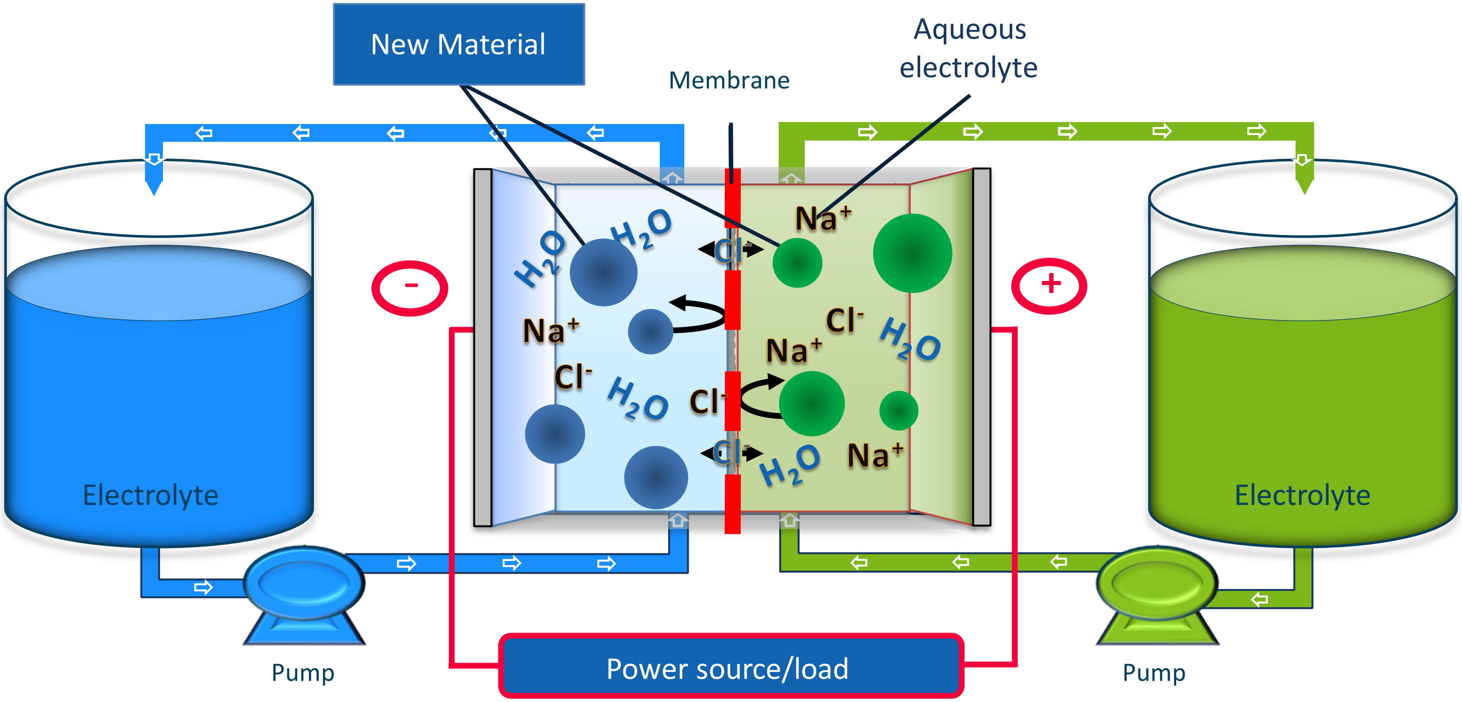
EFRE
EUROPA FÜR THÜRINGEN
EUROPÄISCHER FONDS FÜR REGIONALE ENTWICKLUNG

Federal Ministry
for Economic Affairs
and Energy

on the basis of a decision
by the German Bundestag

- Homepage: www.jenabatteries.com

JenaBatteries' metal free aqueous RFB



Sustainable and easy-to-handle:
A water-based electrolyte replaces
highly corrosive, acidic, vanadium-based electrolytes.

RFB electrolytes

Organic solvents

- Acetonitrile, organic carbonates, …
- High electrolysis stability
- Expensive salts (TBAPF$_6$, NaClO$_4$…)
- Low ion-mobility
- High resistance
- High cost
- Flammable

↓

Simple molecular design

Water

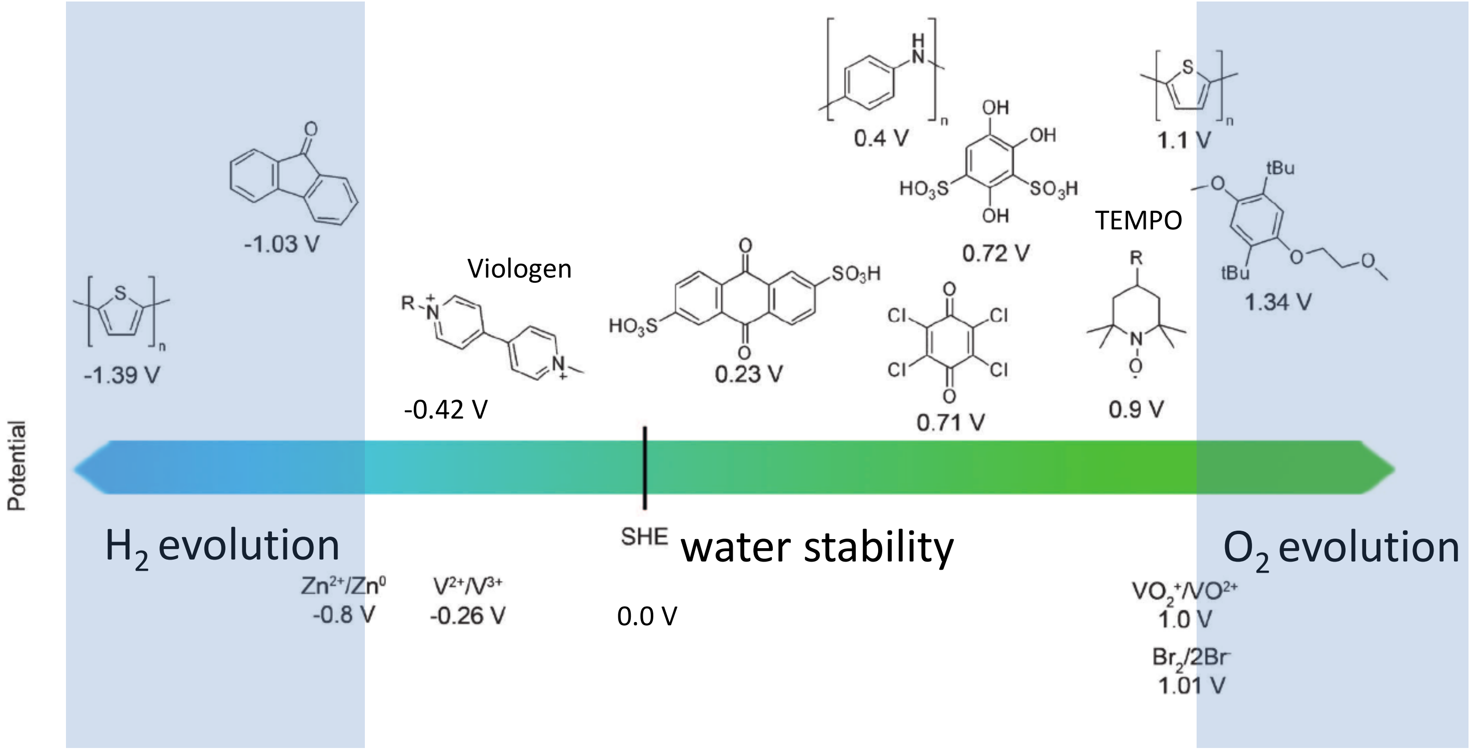
- Limited potential window due to water electrolysis
- Cheap and nontoxic salts (NaCl, …)
- High ion-mobility
- Low resistance
- Low cost
- Safe

↓

Water soluble molecules needed

Angew. Chem. Int. Ed. **2016**, *55*, 14427-14430.

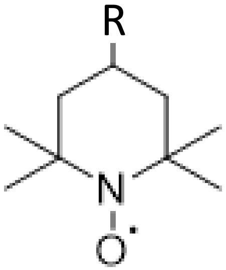
Organic active materials



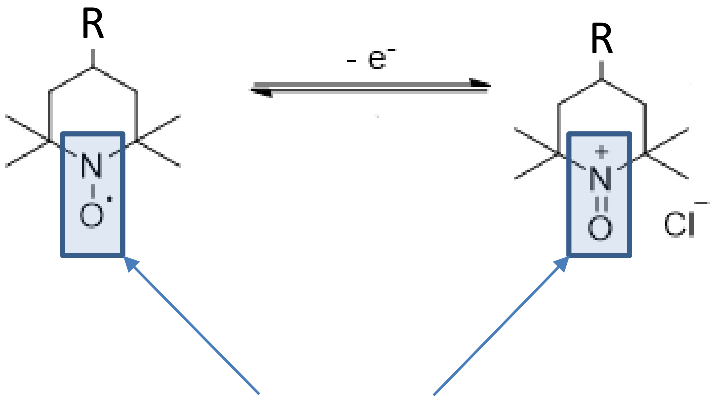
- Aqueous solutions are favored due to cost, safety and conductivity
- TEMPO/viologen-system uses a great part of water stability window

J. Winsberg *et al.*, Angew. Chem. Int. Ed. **2017**, *56*, 686-711.

How to chose organic active materials



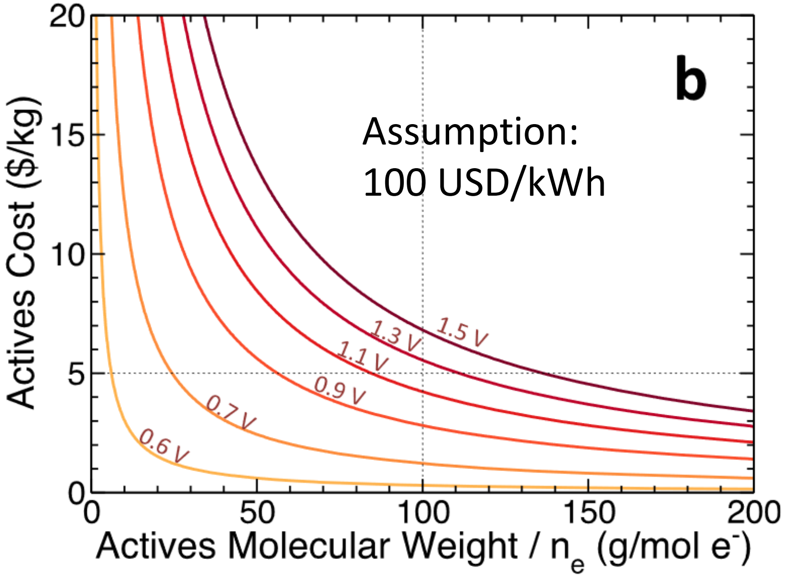
- 2,2,6,6-Tetramethylpiperidinyloxyl (TEMPO) derivatives
- Persistent radicals
- Cheap educts (acetone und ammonia)
- Simple synthesis routs for various R-groups



Active part

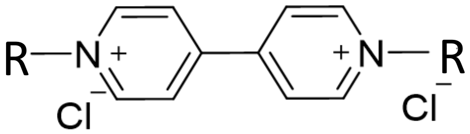
Molar mass N-O: 30 g/mol

Molar mass TEMPO: 156 g/mol

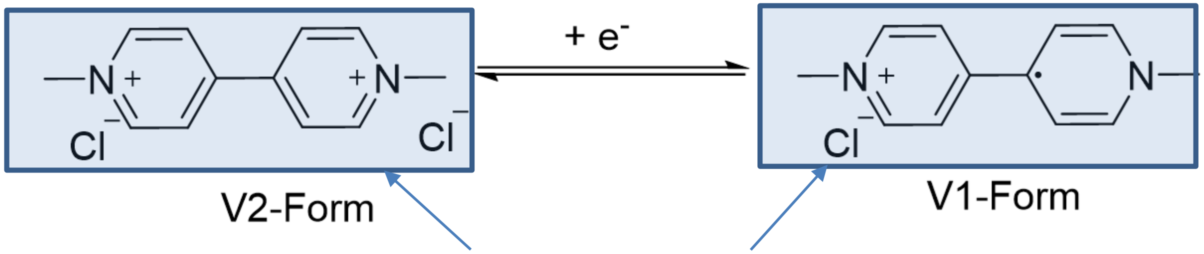


R. Dmello *et al.*, *J. Power Sources* **2016**, *333*, 261-272.

How to chose organic active materials

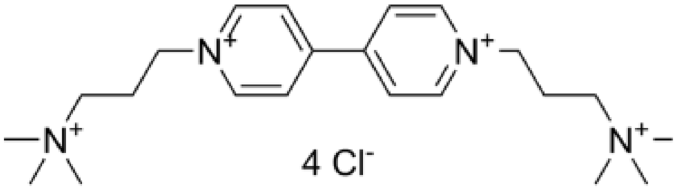


- 4,4‘-Bipyridinium derivative (viologene)
- Rapid redox kinetics
- Some derivative are available on industrial scale



Active part

Molar mass = 257 g/mol

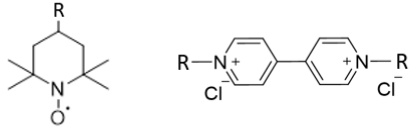


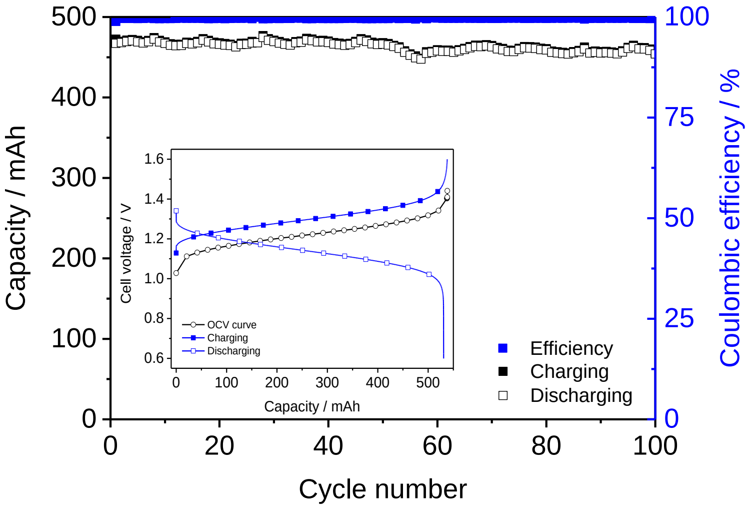
BTMAP-Vi

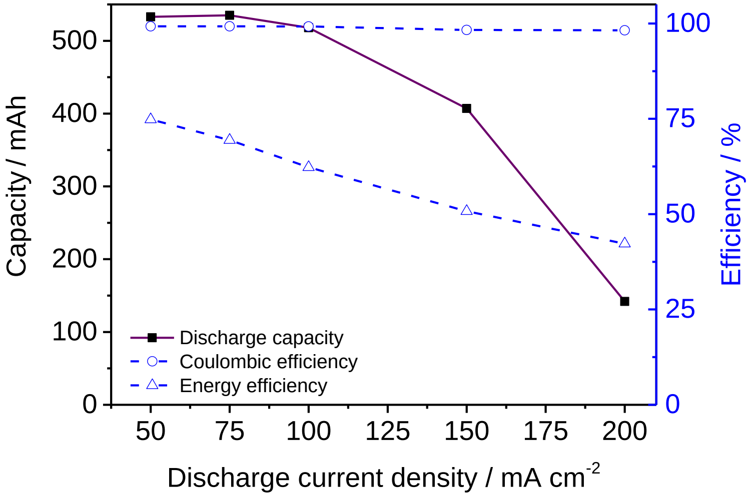
Molar mass = 500 g/mol

E.S. Beh *et al.*, *ACS Energy Lett*. **2017**, 2, 639-644.

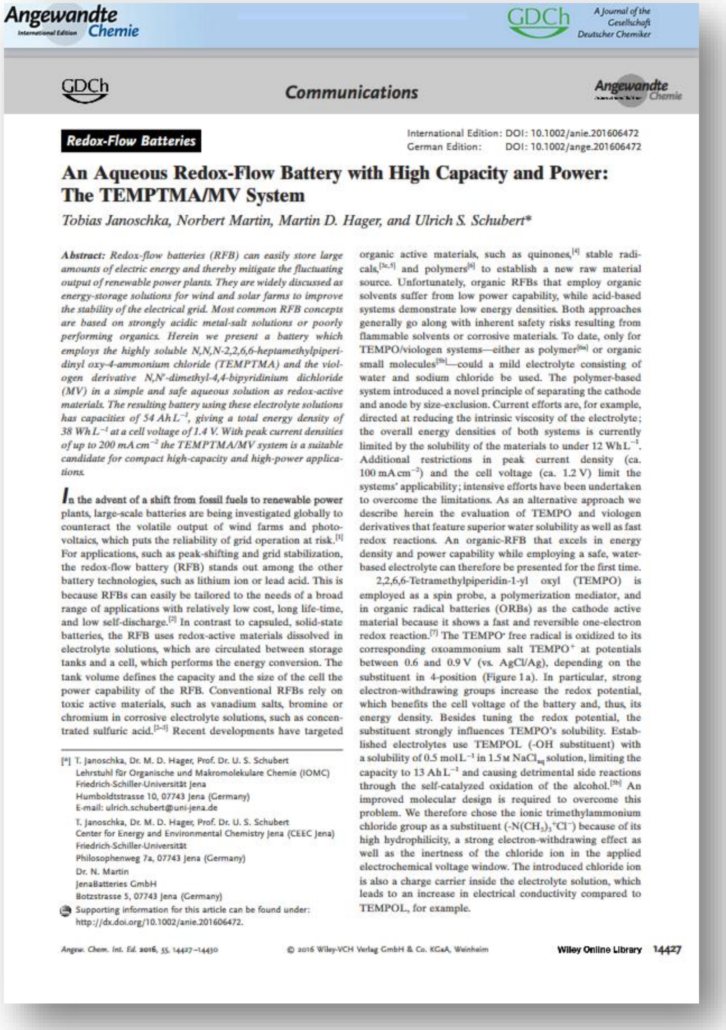
Electrochemical performance







T. Janoschka *et al.*, *Angew. Chem. Int. Ed*. **2016**, *55*, 14427-14430.



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Redox-Flow Batteries

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An Aqueous Redox-Flow Battery with High Capacity and Power: The TEMPTMA/MV System

*Tobias Janoschka, Norbert Martin, Martin D. Hager, and Ulrich S. Schubert**

Abstract: *Redox-flow batteries (RFB) can easily store large amounts of electric energy and thereby mitigate the fluctuating output of renewable power plants. They are widely discussed as energy-storage solutions for wind and solar farms to improve the stability of the electrical grid. Most common RFB concepts are based on strongly acidic metal-salt solutions or poorly performing organics. Herein we present a battery which employs the highly soluble N,N,N-2,2,6,6-heptamethylpiperidinyl oxy-4-ammonium chloride (TEMPTMA) and the viologen derivative N,N'-dimethyl-4,4-bipyridinium dichloride (MV) in a simple and safe aqueous solution as redox-active materials. The resulting battery using these electrolyte solutions has capacities of 54 Ah L^{-1}, giving a total energy density of 38 Wh L^{-1} at a cell voltage of 1.4 V. With peak current densities of up to 200 mA cm^{-2} the TEMPTMA/MV system is a suitable candidate for compact high-capacity and high-power applications.*

In the advent of a shift from fossil fuels to renewable power plants, large-scale batteries are being investigated globally to counteract the volatile output of wind farms and photovoltaics, which puts the reliability of grid operation at risk.[1] For applications, such as peak-shifting and grid stabilization, the redox-flow battery (RFB) stands out among the other battery technologies, such as lithium ion or lead acid. This is because RFBs can easily be tailored to the needs of a broad range of applications with relatively low cost, long life-time, and low self-discharge.[2] In contrast to capsuled, solid-state batteries, the RFB uses redox-active materials dissolved in electrolyte solutions, which are circulated between storage tanks and a cell, which performs the energy conversion. The tank volume defines the capacity and the size of the cell the power capability of the RFB. Conventional RFBs rely on toxic active materials, such as vanadium salts, bromine or chromium in corrosive electrolyte solutions, such as concentrated sulfuric acid.[2–3] Recent developments have targeted organic active materials, such as quinones,[4] stable radicals,[3c–5] and polymers[6] to establish a new raw material source. Unfortunately, organic RFBs that employ organic solvents suffer from low power capability, while acid-based systems demonstrate low energy densities. Both approaches generally go along with inherent safety risks resulting from flammable solvents or corrosive materials. To date, only for TEMPO/viologen systems—either as polymer[6a] or organic small molecules[5b]—could a mild electrolyte consisting of water and sodium chloride be used. The polymer-based system introduced a novel principle of separating the cathode and anode by size-exclusion. Current efforts are, for example, directed at reducing the intrinsic viscosity of the electrolyte; the overall energy densities of both systems is currently limited by the solubility of the materials to under 12 Wh L^{-1}. Additional restrictions in peak current density (ca. 100 mA cm^{-2}) and the cell voltage (ca. 1.2 V) limit the systems' applicability; intensive efforts have been undertaken to overcome the limitations. As an alternative approach we describe herein the evaluation of TEMPO and viologen derivatives that feature superior water solubility as well as fast redox reactions. An organic-RFB that excels in energy density and power capability while employing a safe, water-based electrolyte can therefore be presented for the first time.

2,2,6,6-Tetramethylpiperidin-1-yl oxyl (TEMPO) is employed as a spin probe, a polymerization mediator, and in organic radical batteries (ORBs) as the cathode active material because it shows a fast and reversible one-electron redox reaction.[7] The TEMPO$^{\cdot}$ free radical is oxidized to its corresponding oxoammonium salt TEMPO^{+} at potentials between 0.6 and 0.9 V (vs. AgCl/Ag), depending on the substituent in 4-position (Figure 1a). In particular, strong electron-withdrawing groups increase the redox potential, which benefits the cell voltage of the battery and, thus, its energy density. Besides tuning the redox potential, the substituent strongly influences TEMPO's solubility. Established electrolytes use TEMPOL (-OH substituent) with a solubility of 0.5 mol L^{-1} in 1.5 M $NaCl_{aq}$ solution, limiting the capacity to 13 Ah L^{-1} and causing detrimental side reactions through the self-catalyzed oxidation of the alcohol.[5b] An improved molecular design is required to overcome this problem. We therefore chose the ionic trimethylammonium chloride group as a substituent ($-N(CH_3)_3^{+}Cl^{-}$) because of its high hydrophilicity, a strong electron-withdrawing effect as well as the inertness of the chloride ion in the applied electrochemical voltage window. The introduced chloride ion is also a charge carrier inside the electrolyte solution, which leads to an increase in electrical conductivity compared to TEMPOL, for example.

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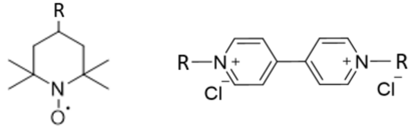
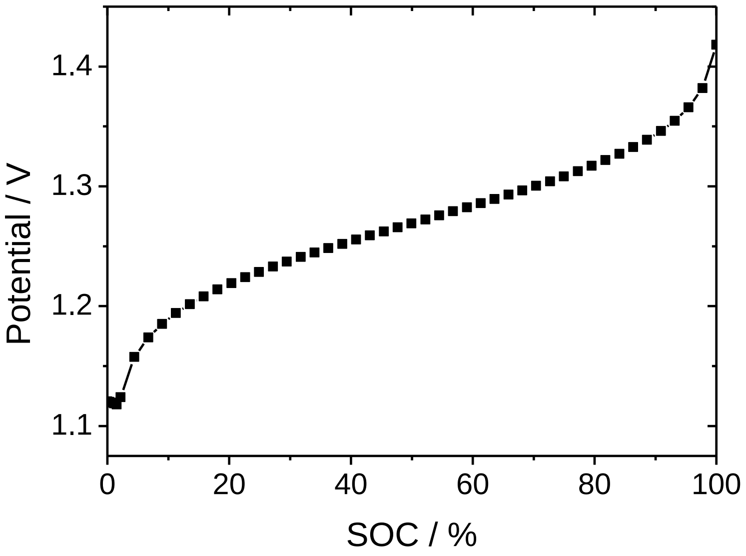
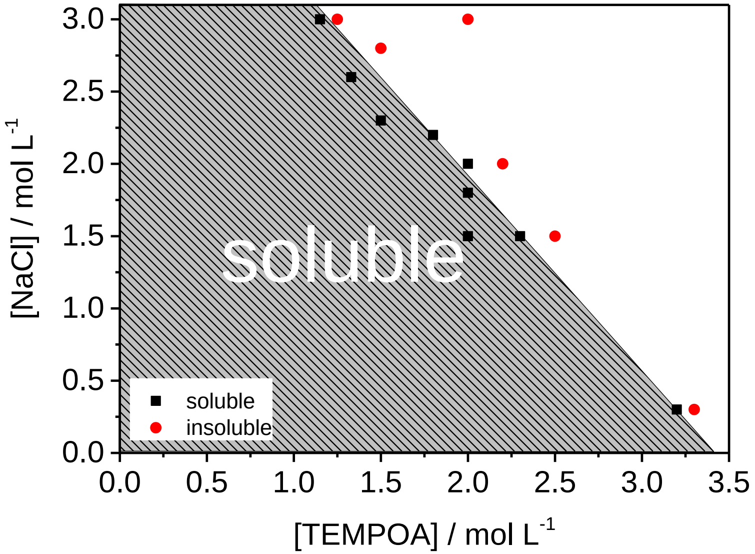
Electrochemical performance



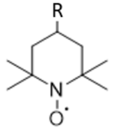


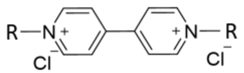


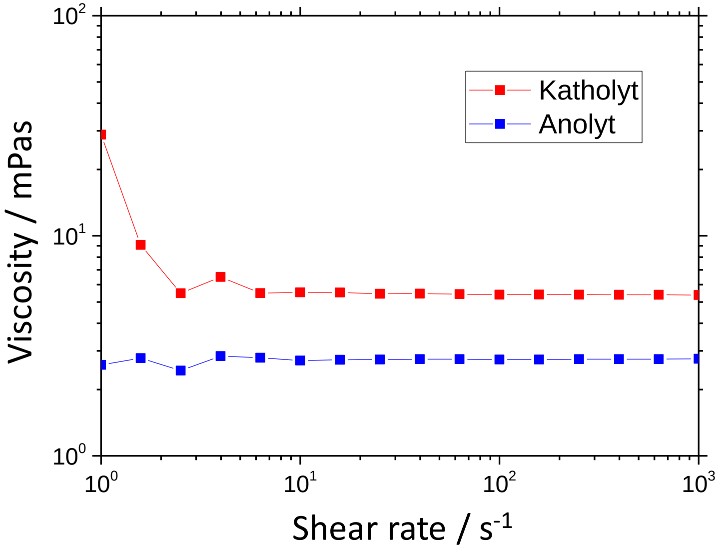
- ▶ Average cell voltage 1.25 V
- ▶ Solubility of organic molecules > 50 %
- ▶ Current energy density at 20 Wh/L (35 Wh/L proved on lab scale)

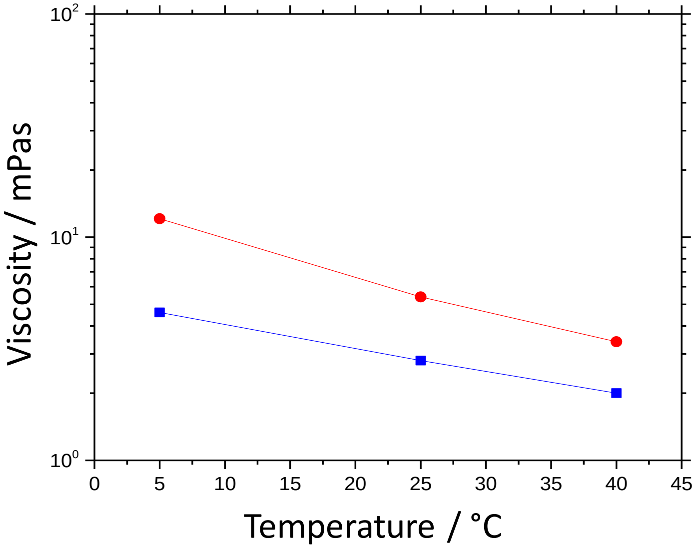
T. Janoschka *et al., Angew. Chem. Int. Ed*. **2016**, *55*, 14427-14430.

Viscosity









- Viscosity at energy density of 20 Wh/L between 3 mPas (anolyte) and 6 mPas (catholyte) at 25 °C

- At 5 °C 5 mPas (anolyte) and 12 mPas (catholyte) are sufficiently low for RFB operation

T. Janoschka *et al., Angew. Chem. Int. Ed*. **2016**, *55*, 14427-14430.

Other organic flow battery technologies

GREEN ENERGY STORAGE

- Country: Italy
- Materials: Bromine + quinones
- Status: First small prototype presented

KEMWATT
Your energy bank

- Country: France
- Materials: Organic
- Status: 10 kW prototype presented

LOCKHEED MARTIN

- Country: USA
- Materials: Metal-organic
- Status: 250 kW/500 kWh prototype presented

Quinenergy
Organic Energy Solutions

- Country: Canada
- Materials: Quinones
- Status: Early stage

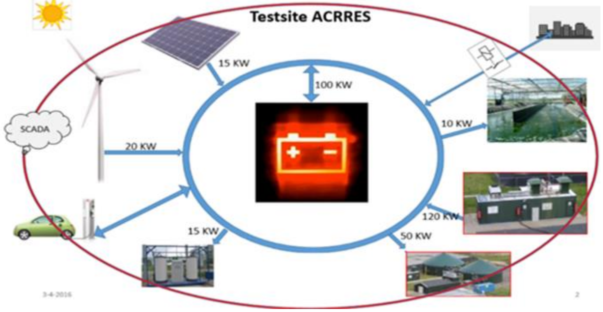
Development

Laboratory and prototype facility:

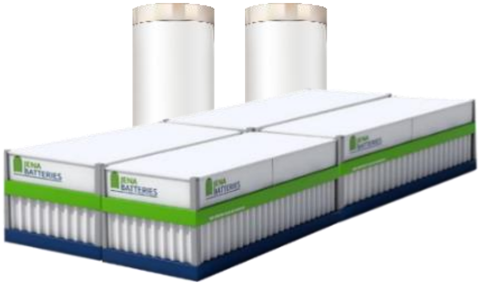
Pilot projects:

PV application

Microgrid



Tailored solutions



EnergyKeeper – Keep the Energy at the right place!

www.energykeeper.eu

This project has received funding from the European Union’s Horizon 2020 research and innovation program under grant agreement No 731239.

EnergyKeeper

Coordinator

ECN

EnergyTeam

JENA BATTERIES

ICM INGENIERIA

Litgrid

PISGA IT Solutions

LEITAT managing technologies

inspiralia

WAGENINGEN UNIVERSITY & RESEARCH

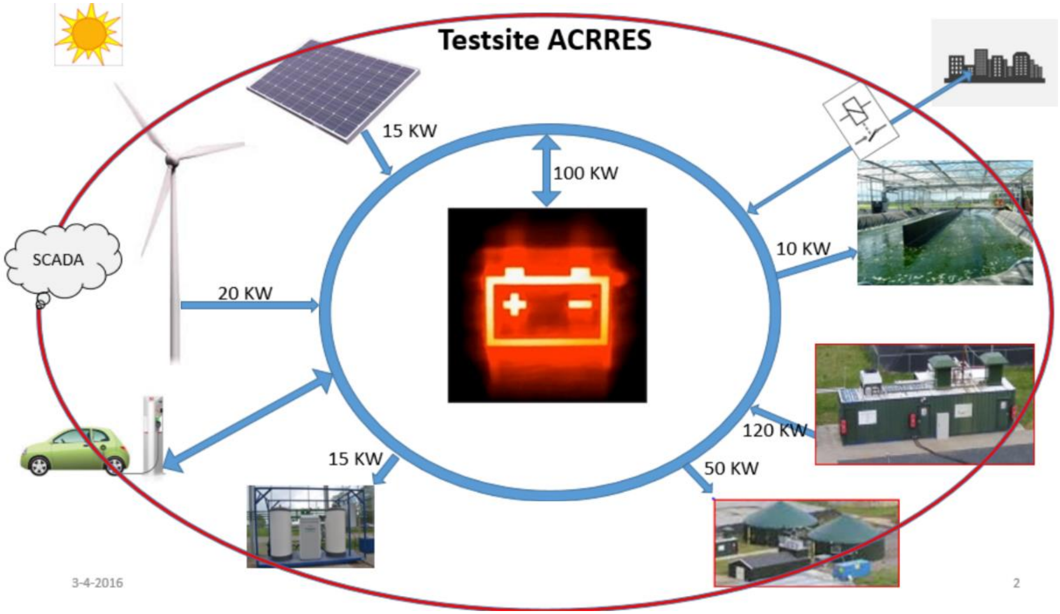
EnergyKeeper

TESTING BATTERY AND BATTERY MANAGEMENT SYSTEM

Intergration with real RES (Renewable Energy Sources), Electric Vehicle chargers and variable power consumption at the ACRRES test site

SMART GRID CONTROL AND COMMUNICATION LAYERS

Communications architecture, grid control and demand side management systems will be designed and implemented

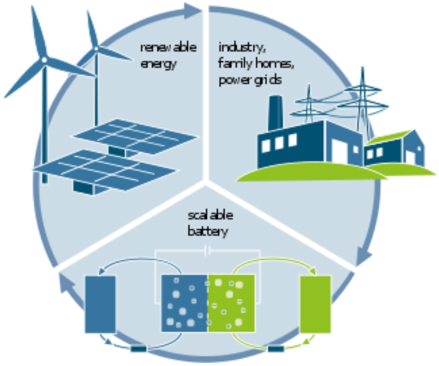


DEVELOPMENT OF SEVERAL PROSUMER BUSINESS MODELS

Prosumer business models oriented to different types of communities

Summary

- Organic molecules provide "unlimited" raw material availability
- Various molecular structures can be used as redox-active materials
- Easy to synthesize, redox potential and low mass per electron are key criteria for selecting redox-active organic molecules
- Water-based systems offer safety advantages
- Stationary energy storage technology (10 kW to >2 MW, 40 kWh to >10 MWh)



Environmentally benign & safe
- simple, water-based electrolyte
- no heavy metals
- noncombustible electrolyte

Low material cost
- cheap active material

Independent scalability
- capacity is "unlimited"
- easy and independent adaption of power and capacity