



**1** Laboratory glass cell for electrochemical investigations in 2- or 3-electrode set-up with separation of compartments by a membrane.

**2 & 4** Routine laboratory work in the electrochemistry lab.

**3** Stability tests on material samples stored in electrolyte solutions at different state-of-charge in a temperature chamber.

## ELECTROLYTE FORMULATION AND SPECIFICATION FOR FLOW BATTERIES

Various redox-active couples in acidic or neutral aqueous solutions can be evaluated at Fraunhofer ICT to develop new electrolyte formulations or novel RFB chemistries. The institute has long-standing practical experience in all-vanadium acidic electrolyte chemistry.

Since the flow battery half-cell reactions take place at the interface between the electrode and the electrolyte, the electron transfer kinetics and electrolyte conductivity have a strong impact on the battery performance (kinetic and ohmic losses). To select the redox couples for new electrolyte formulations it is necessary to evaluate:

- Redox potentials of half-cell reactions which thermodynamically enable a high cell voltage, but at the same time at least kinetically prevent secondary reactions
- Stability and solubility of the species in the oxidation states involved
- Kinetics of electrode reactions, which should be rapid and reversible
- Availability of source materials and their environmental acceptability

### Specifications for vanadium electrolytes

For all-vanadium redox-flow battery (VRFB) electrolytes, which consist of dissolved vanadium salts, the operating temperature range is limited to 0 to 35 °C. This is due to the complex chemistry of the pentavalent vanadium, which tends to condense irreversibly to vanadium pentoxide at around 40 °C. To extend the operating temperature range and therefore improve the efficiency and performance, the following solutions are under investigation:

- Use of additives which stabilize pentavalent vanadium solutions and prevent flocculation of vanadium oxides from the concentrated electrolyte solutions
- Use of other acids or mixtures with sulfuric acid

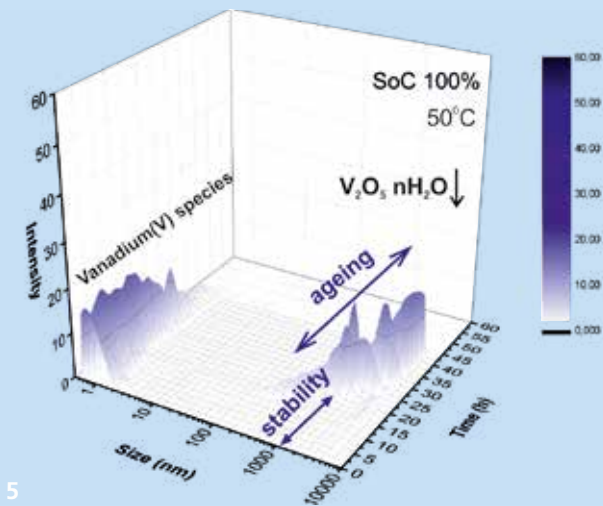
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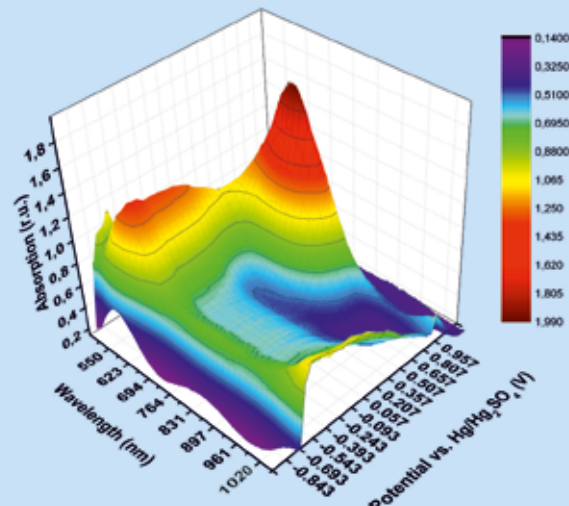
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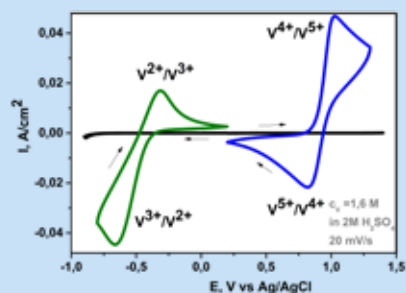
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Impurities in sulfuric acid electrolytes for vanadium flow batteries can affect battery performance by:

- influencing electrode kinetics of battery reactions
- decreasing temperature stability of electrolytes
- influencing chemical stability of metastable oxidation states of vanadium
- causing chemical or electrochemical side-reactions
- decreasing membrane conductivity

With the help of model electrolytes, Fraunhofer ICT has developed specifications for vanadium electrolytes and also the related quality control. In order to evaluate additives and to characterize the coagulation behavior of pentavalent vanadium at elevated temperatures, several analytical techniques are applied, e.g. dynamic light scattering and nuclear magnetic resonance (NMR).

### Cyclic voltammograms of redox conversions of VRFB anolyte and catholyte at glassy carbon electrode.



### Vanadium electrolyte archive

The screening of electrolyte probes for impurities which might have an impact on technical electrolytes, is a routine laboratory procedure at Fraunhofer ICT. Since 2011 industrial as well as laboratory samples of sulfuric-acid-based vanadium electrolyte have been collected from various suppliers world-wide and analyzed according to standardized procedures. With the help of this electrolyte archive, Fraunhofer ICT can help electrolyte manufacturers to optimize their product. The extensive electrolyte data is also useful for flow battery manufacturers in selecting their best choice of electrolyte supplier.

### Chemical stability test of materials

When exposed to VRFB electrolyte, some polymeric or elastomeric materials are prone to destruction in the acidic oxidative and reductive chemical environment that can occur during long-term battery operation. To investigate corrosion damage, Fraunhofer ICT has developed a procedure to measure the chemical aging of polymeric and elastomeric materials based on DIN-standards for chemical stability.

### Our services

For RFB electrolytes:

- Voltammetric investigations at stationary or rotating disk electrode (kinetics of redox conversions, electrochemical stability, side reactions)
- Evaluation of electrolyte compatibility with cell materials
- Techno-economic and feasibility analysis

For all-vanadium RFB:

- Wet chemical or instrumental analytics (potentiometric titration to determine total vanadium concentration and state-of-charge, gravimetric determination of total sulfate content, UV-vis characterization, dynamic light scattering for the monitoring of particle formation)
- Ex-situ thermal stability test (visual observation, dynamic light scattering)
- Validation of sensors for the state-of-charge control, thermal aging, detection of electrolyte imbalances
- Electrolyte formulation, investigations into additives
- Synthesis and production procedure of solid vanadium (II) sulfate hydrate or vanadium (II) sulfate hydrate for model electrolyte samples

5 Evolution of particle size distribution curves derived from dynamic light scattering measurements in VRFB catholyte at 50 °C.

6 3D surface plot representing changes of absorption spectra in the VIS/NIR range for diluted vanadium electrolyte solution with linear sweep of working electrode potential.