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Laboratory test methods for vanadium flow battery electrolyte: towards the development of standards for vanadium electrolyte

Procedure for standard development (ISO/IEC Directive Part 1)

1. **NP Proposal** – to start a new project
2. **WD Preparatory** – expert consensus within working group (TC21/JWG 7)
3. **CD Committee** – committee consensus (IEC TC21)
4. **DIS Enquiry** – national consensus
5. **FDIS Approval** – YES or NO vote
6. **Publication** – International Standard

Review – IS is reviewed and/or revised

With-drawal – IS can be withdrawn

- Joint project: StaVENo- Standardization of vanadium electrolyte solutions for flow batteries: "Analytical methods for vanadium electrolytes and standardization work“

Electrolyte = vanadium V^{n+} + sulphates + sulphuric acid (free acid, H^+) + phosphoric acid + impurities

C_V (vanadium V^{n+}) C_S (sulphates + sulphuric acid (free acid, H^+)) C_P (phosphoric acid)

- Common requirements for commercial $V^{3.5+}$ electrolyte samples (6 suppliers from USA, Europe, China):
  - $V^{3.5+}$ electrolyte based on sulfuric acid (not other acids or mixture as a matrix)
  - C_V ~ 1.5 - 1.8M, C_S ~ 3.7 – 4.5M, V3+/4+ mol. ratio ~ 1:1 (it means +3.5)
  - No exact presets for inorganic impurities

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on the basis of a decision by the German Bundestag

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Overview of key electrolyte metrics and measurement techniques

as a commercial product

$V^{3.5+}$

as a VFB component

Electrolyte metrics	$V^{3.}$ SOC „-50%“	(-) $V^{3+/2+}$ SOC 10-90%	(+) $V^{5+/4+}$ SOC 10-90%	Methods
• Concentrations of the main components (C_V , C_S , C_P)	C_V , C_S , C_P	C_V *, C_S**	C_V *, C_S**	Potentiom. titration, ICP-MS, ICP-OES, IC, gravimetry, therm. titration
• Concentrations of inorganic impurities ($C_{impur.}$)	C_{impur}	C_{impur}**	C_{impur}**	ICP-MS
• Concentration of sulfur (IV) impurities (SO_2)	*?*	gas (ppm range)	-	Semi-quantitative gas tube sensors
• Concentrations of organic impurities (TOC)	*failed*	-	-	TOC-analyzer
• Insoluble residues	particles	?	?	Filtration using fine porosity filter
• Physical properties: conductivity, density, viscosity (σ, d, ν)	σ, d, ν	σ, d, ν	σ, d, ν	Conductometry, density measurement, viscosimetry (Ubbelohde)
• Chemical stability at high SOC/high T°C (V_2O_5)	-	-	solid phase	Visual inspection, potentiom.titration
• Chemical stability at high SOC/high T°C (H_2)	-	gas (ppm range)	-	Online headspace MS
• Chemical stability at high SOC/low T°C	-	solid phase	-	Visual inspection, potentiom. titration
• Cell/VFB test performance	cell test			Charge-discharge test in a lab. cell

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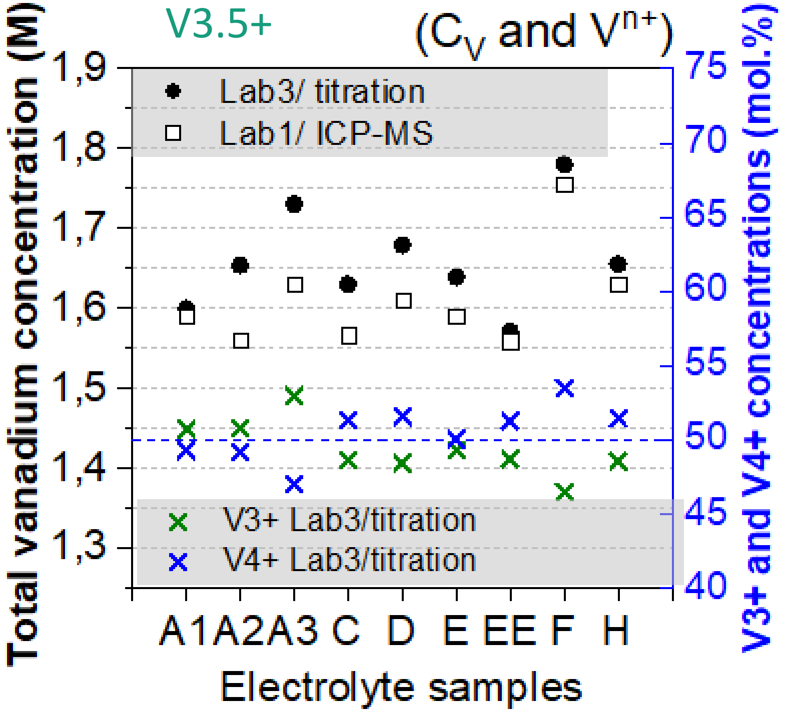
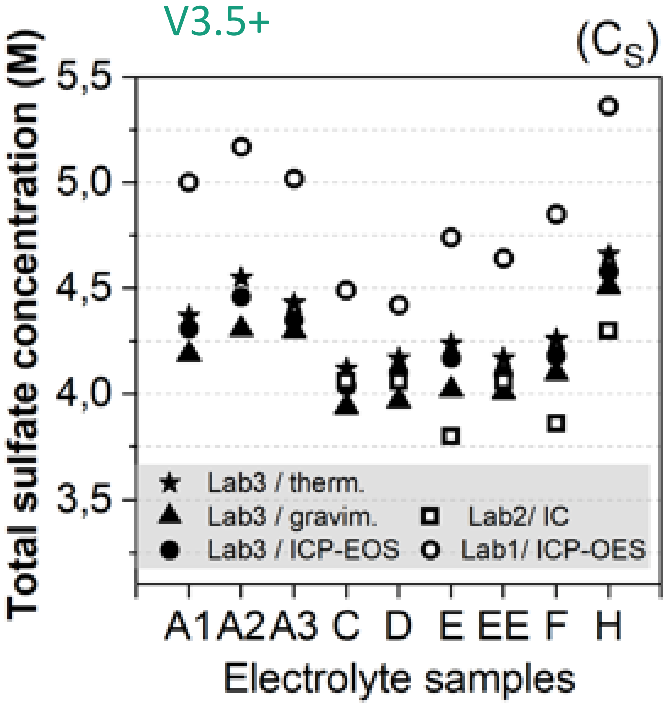
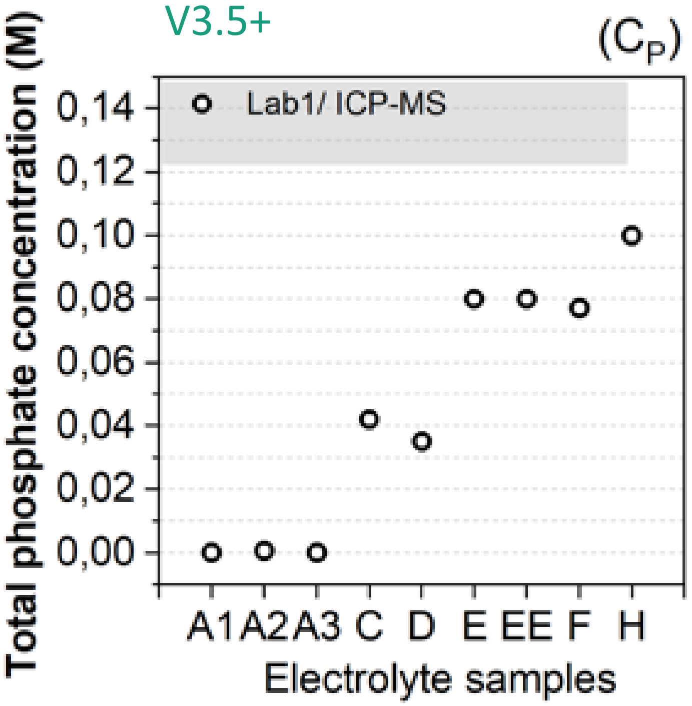
* are assumed to be the same as in $V^{3.5+}$, or not considered, ** not enough data available

Concentrations of the main components







- Discrepancy between titration and ICP-MS results for C_V in case of several samples
- Discrepancy between results for C_S from various laboratories, deviation up to 5% of C_S value within one lab and various methods
- C_P level is still a subject of investigations

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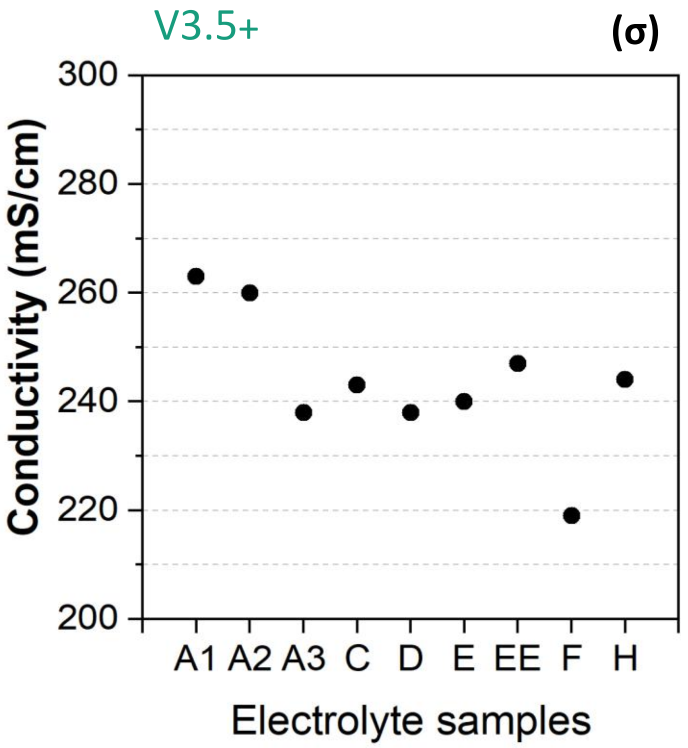
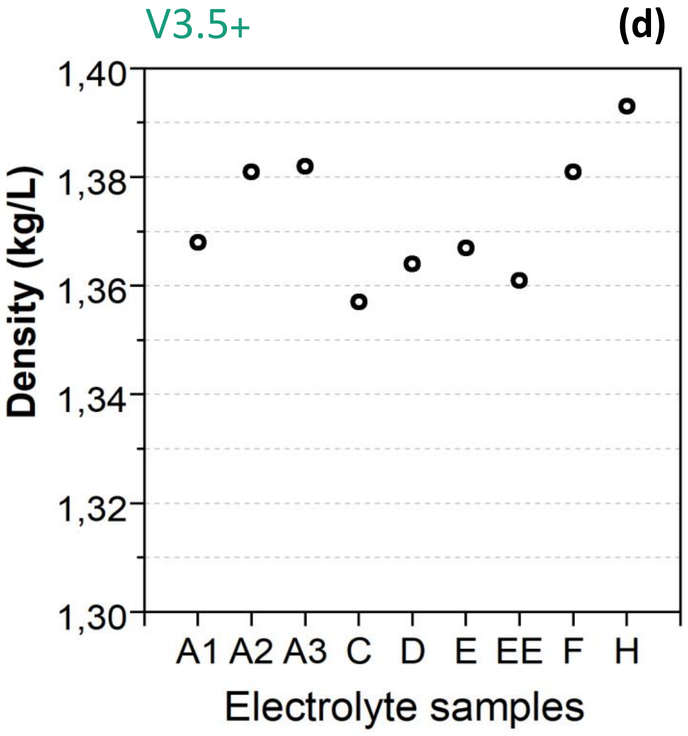
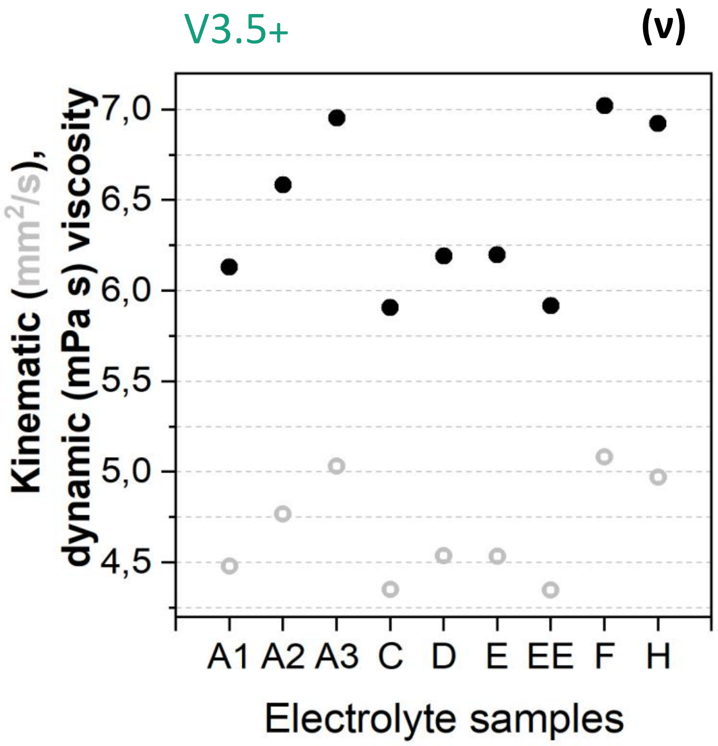
Physical properties: conductivity, density, viscosity

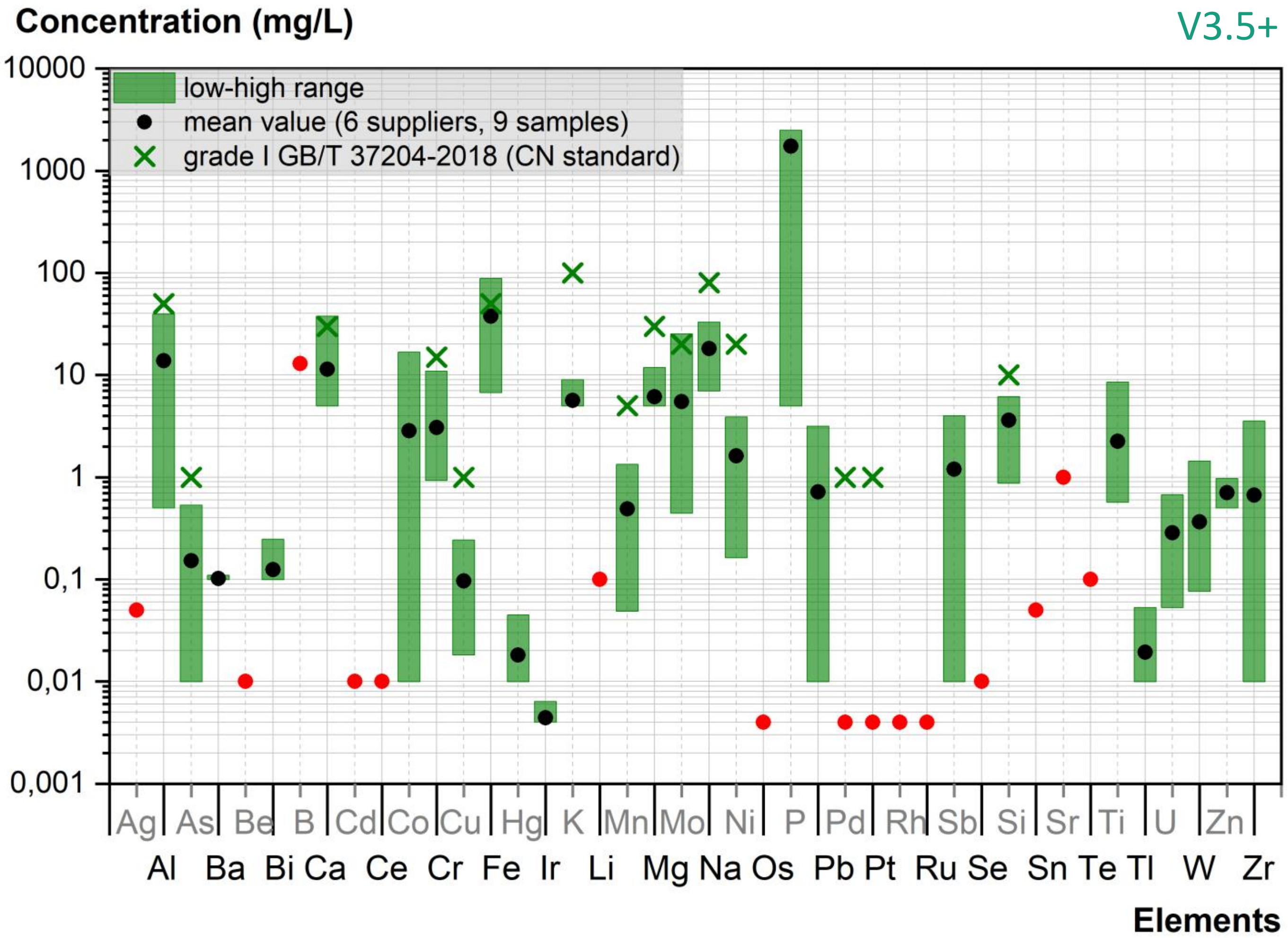






- Density and viscosity values correlate with C_V and C_S
- Conductivity reflects both of C_S , C_V values and amount of free acid (protons)

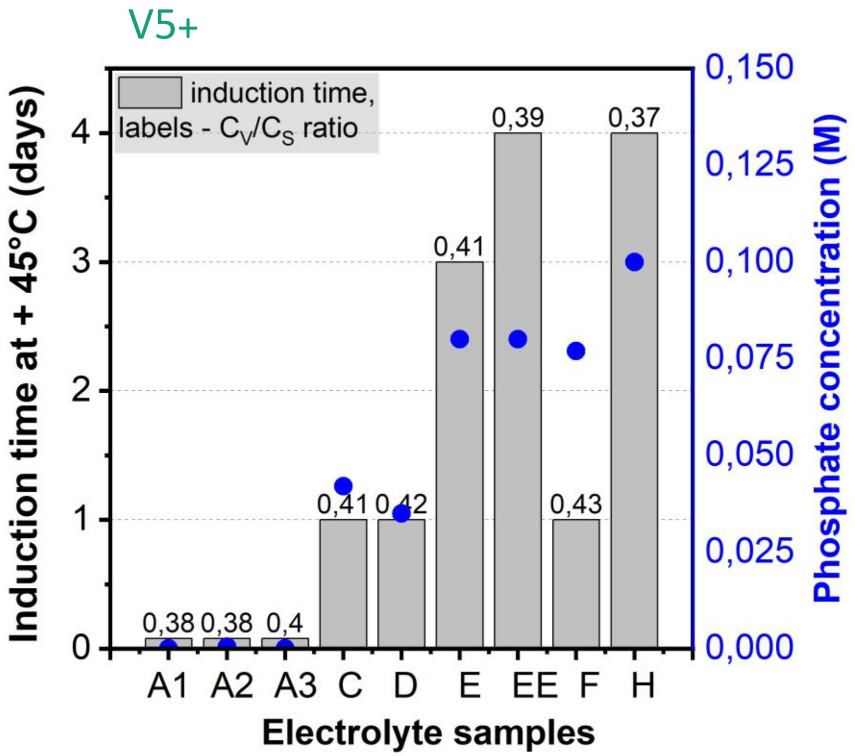
Concentrations of inorganic impurities

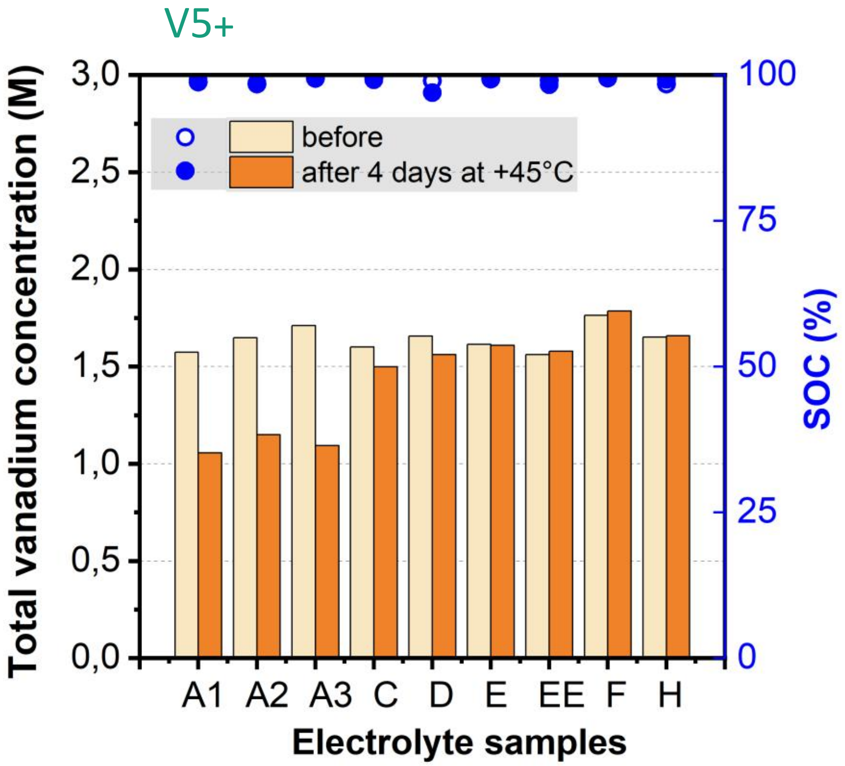


- Impurities level is a subject of negotiation within TC21/JWG 7 experts
- Current trend:
  - consider upper limit
  - to classify by grade (I and II)

Impurities levels in commercial electrolytes detected by ICP-MS technique (Red labels - the values below the limit of quantification).

Chemical stability at high SOC/high T°C (V5+)





- Correlation of V5+ thermal stability to C_P values and (?) to C_V /C_S ratio
- C_V /C_S ratio and conductivity seems to be useful metrics of V3.5+ electrolyte to predict its thermal stability in VFB

(left) Schematic representation of an ex-situ thermal ageing test of electrolyte samples. (right) Titration results for V5+ samples kept at +45°C for 4 days

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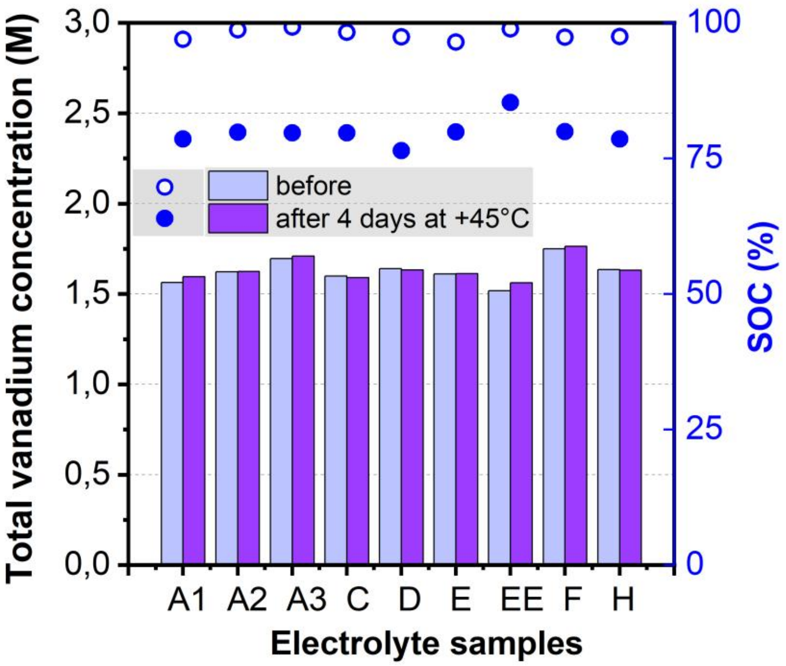
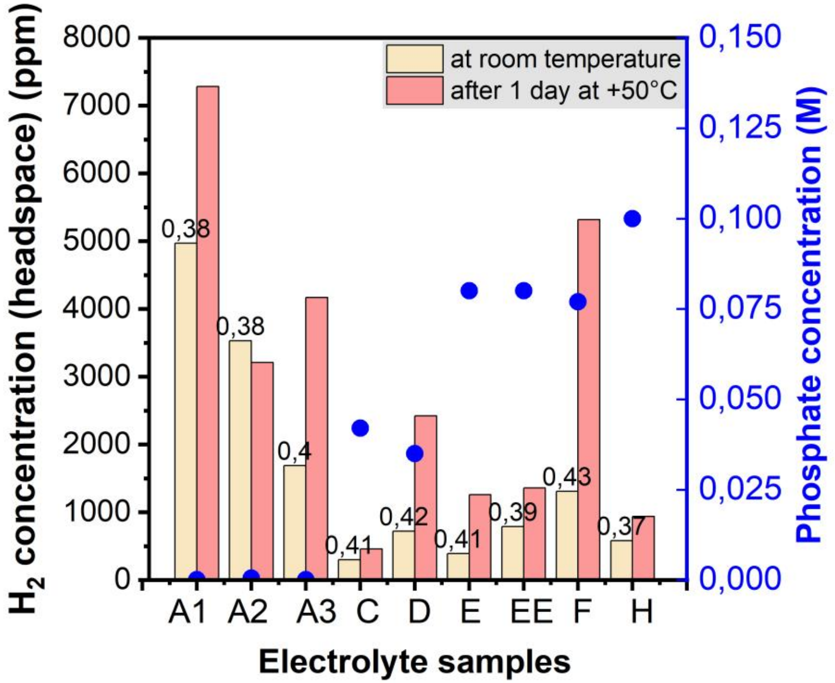
Chemical stability at high SOC/high T°C (V2+)

V2+



V2+



- V2+ stability is hardly to link either to C_V /C_S ratio or to other metrics
- More deep investigation of V2+ stability is still needed

(left) Titration results for V2+ samples kept at +45°C for 4 days and (right) amount of hydrogen detected by online mass-spectrometry in the headspace of vials with V2+ after keeping at RT and at +50°C for one day.

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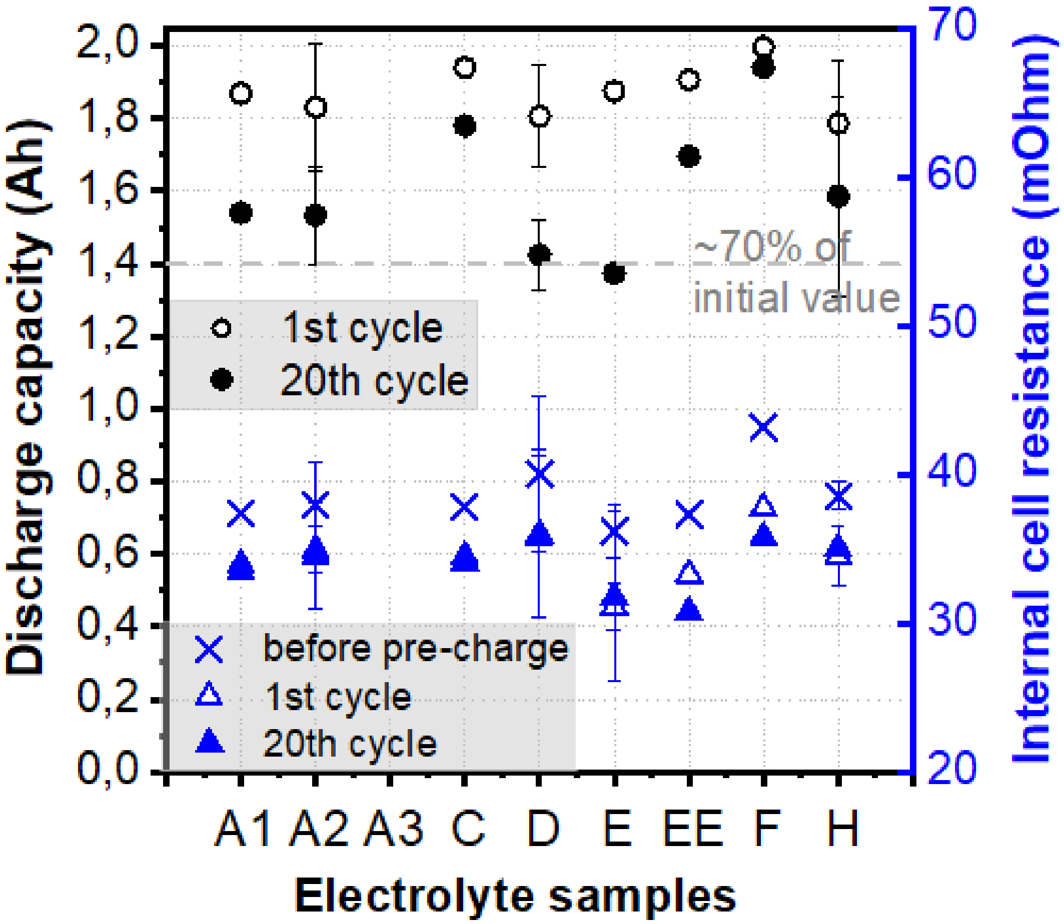
Cell test of $V^{3.5+}$ electrolytes and summary



- Energy efficiency of 80-83% and ca. 70% of discharge capacity retained after 20 cycles for all the samples

- VFB cell performance is less sensitive to the differences in $V^{3.5+}$ metrics (at least) in the range C_V ~ 1.55 - 1.75M, C_S ~ 4 – 4.5M, C_P ~ 0 – 0.1M than chemical stability of electrolytes at high SOC and elevated temperature

- Comprehensive statistics is still required to access the accuracy and applicability of measurement procedures

Charge-discharge test in a 40cm2 cell with 60:60 ml electrolyte samples: internal cell resistance, discharge capacity at 75 mA/cm2.

Kontakt

Thank you for attention!

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