The Influence of Electrochemical Treatment on Electrode Reactions for Vanadium Redox Flow Batteries

Jens Noack[1,2,3], Nataliya Roznyatovskaya[1,2], Jessica Kunzendorf[1,2], Maria Skyllas-Kazacos[2,3], Chris Menictas[2,3], Jens Tübke[1,2]

[1] Fraunhofer-Institute for Chemical Technology, Joseph-von-Fraunhofer-Str. 7, 76327 Pfinztal, Germany
[2] German-Australian Alliance for Electrochemical Technologies for Storage of Renewable Energy, Mechanical and Manufacturing Engineering, University of New South Wales (UNSW), UNSW Sydney NSW 2052 Australia
[3] University of New South Wales (UNSW), UNSW Sydney NSW 2052 Australia

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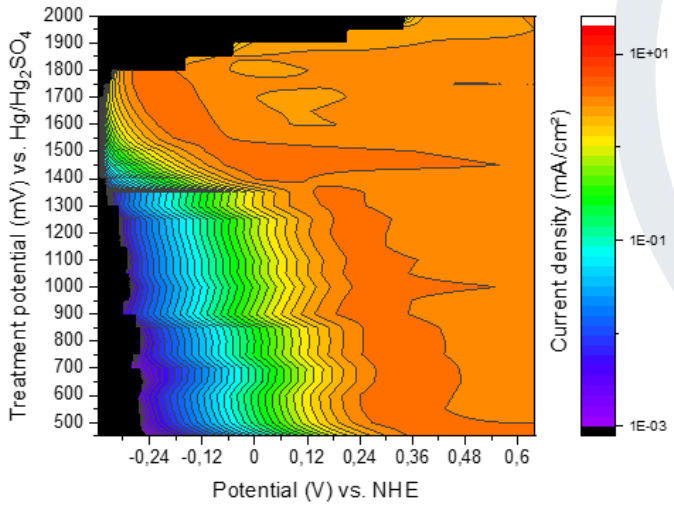

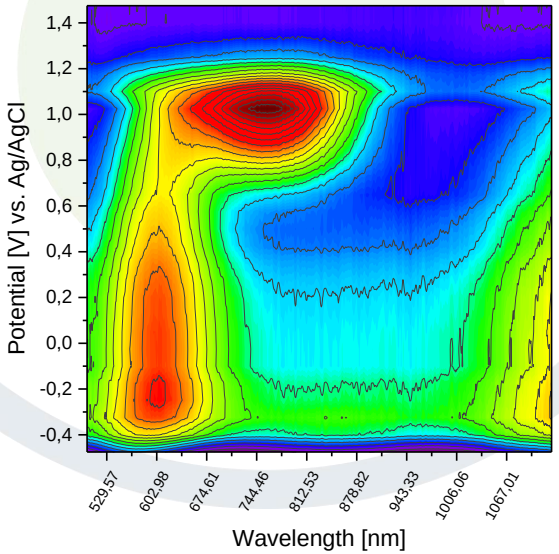

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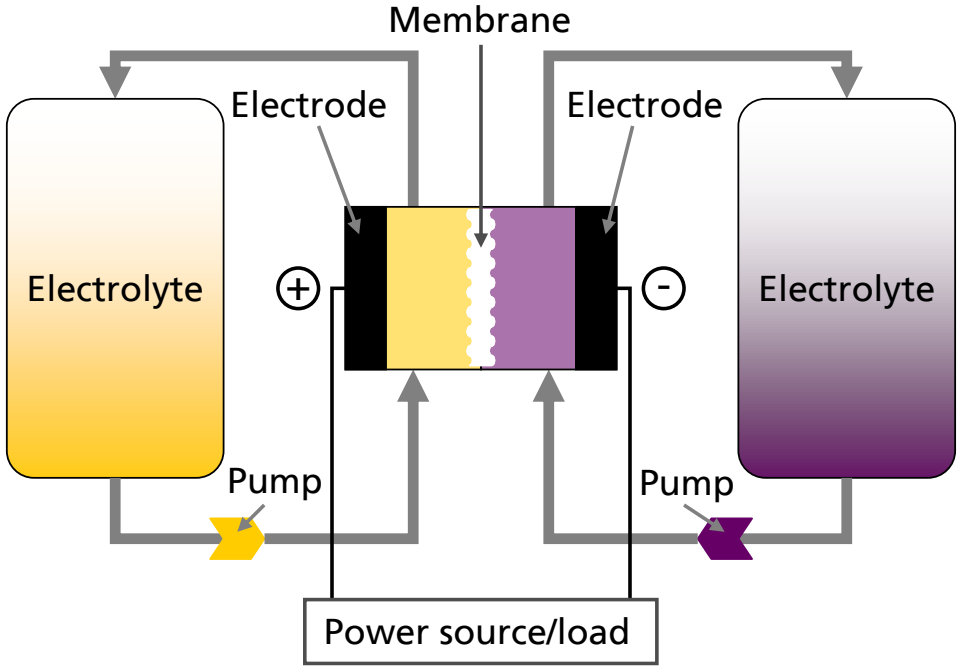
Vanadium redox flow battery - working principle



Neg. el.: $V^{2+} \rightleftharpoons V^{3+} + e^-$ $\varphi^{0,-} = -0.255\ \text{V}$

Pos. el.: $VO^{2+} + e^- \rightleftharpoons VO_2^+$ $\varphi^{0,+} = +1.000\ \text{V}$

$$\varphi_{cell} = \varphi^+ - \varphi^- + \varphi_M \sim 1.4\ \text{V}$$

W. Kangro, „Verfahren zur Speicherung von elektrischer Energie“, German Patent 914264, 1949
W. Kangro, H. Pieper, „Zur Frage der Speicherung von elektrischer Energie in Flüssigkeiten“, Electrochimica Acta Vol. 7, 435 – 448, 1962
M. Skyllas-Kazacos, M. Rychcik, R. G. Robins, A. G. Fane, M. A. Green, Journal of The Electrochemical Society 1986, 133, 1057–1058.

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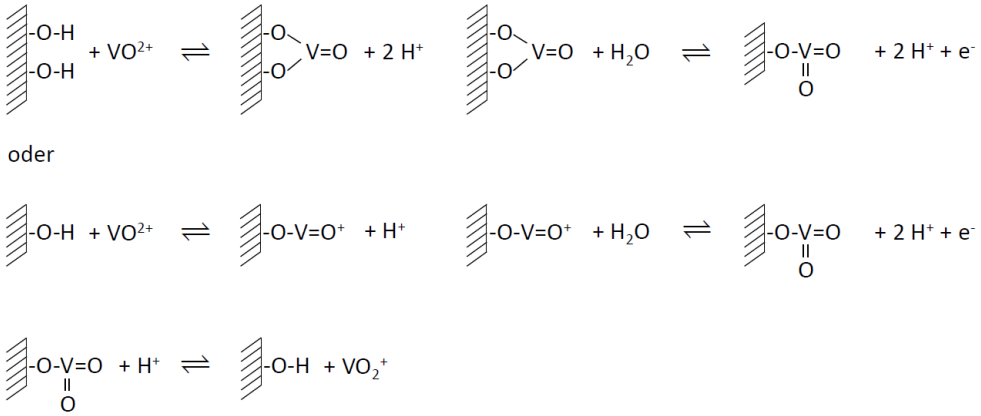
Motivation

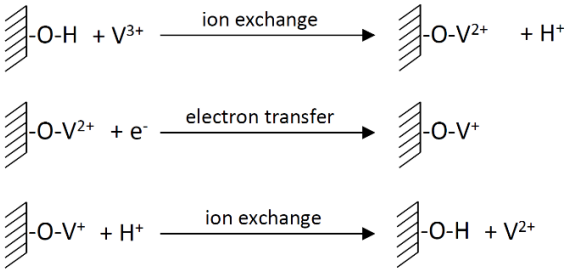
- Strong dependence of V-reactions on carbon electrode surface
- Still unclear reason for this behavior
  - Functional groups
  - Edges, surface roughness,...
- It is known that power density of VRFB can be increased dramatically be electrode treatment
- Higher power density decreases the cost of the batteries
- Electrode behavior changes with potential!

➢ *Study of the most simple systems*
➢ *Linear sweeps at glassy carbon electrodes*
➢ *Study of the influence of electrochemical treatment on the behavior of vanadium reactions*

Oxidation of VO^{2+} at phenolic C-OH groups



Reduction of V^{3+} at phenolic C-OH groups



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Experimental

Electrolytes:

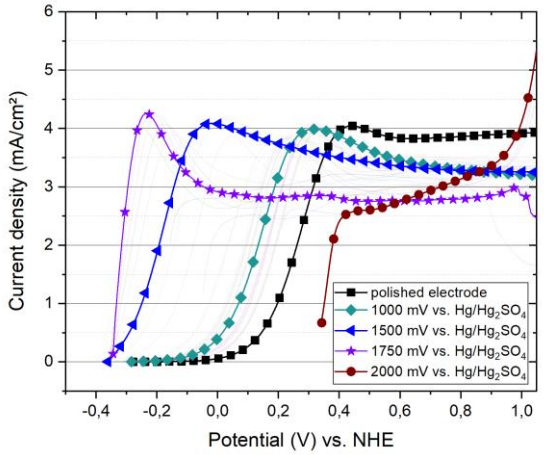
- 0.1 M VSO_4 and 0.1 M $V_2(SO_4)_3$ in 2 M H_2SO_4 (Made by re-crystallisation!)
- 0.1 M & 1.6 M $VOSO_4$ in 2 M H_2SO_4
- 0.1 M V_2O_5 in 2 M H_2SO_4

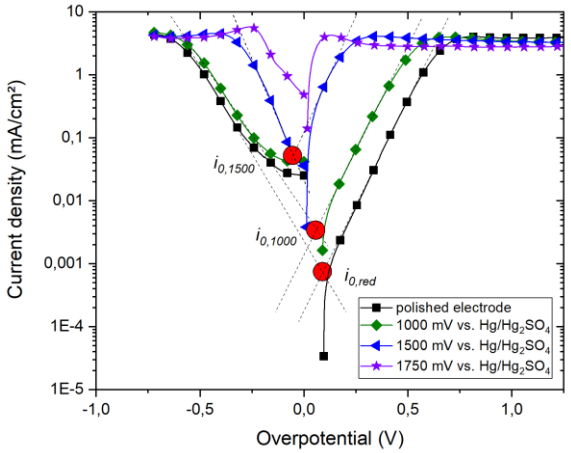
Electrochemical measurement procedure:

1. Polished glassy carbon disc 1 mm diameter (30 x 6 micron, 30 x 1 micron, 30 x 0.25 micron diamond polishing paste, MetaDi II, Buehler, Germany)
   - ➢ Polished electrode (virtual value of 450 mV treatment potential!)
2. Electrochemical treatment in 2 M H_2SO_4 for 30 s at potentials from +500 mV to +2000 mV vs. Hg/Hg_2SO_4, difference 50 mV
3. Linear sweep voltammetry from OCP in direction of reduction or oxidation with scan rate of 10 mV/s
4. Caclulation of reference current density i_{ref} and 3D heat map plots

- **XPS measurements** (Axis Ultra, Kratos Analytical, Manchester, UK)
- **Laser confocal microscopy** (µsurf custom, Nanofocus AG, Germany

LSVs and Tafel plots, ox. 0.1 M V^{2+}





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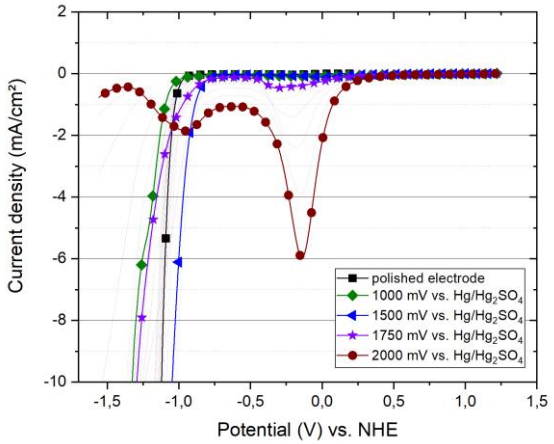
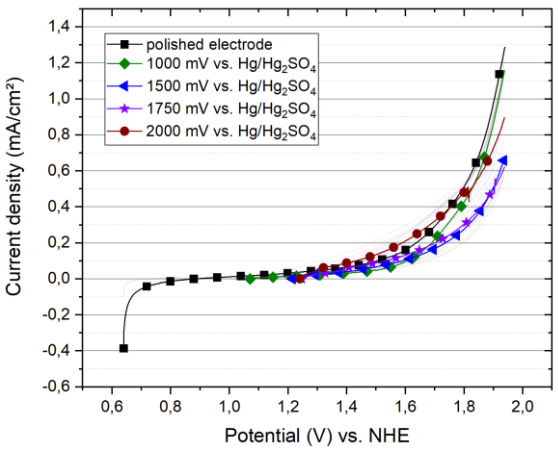
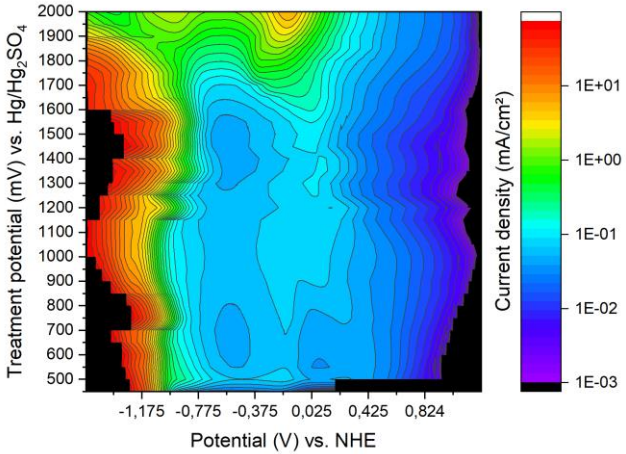
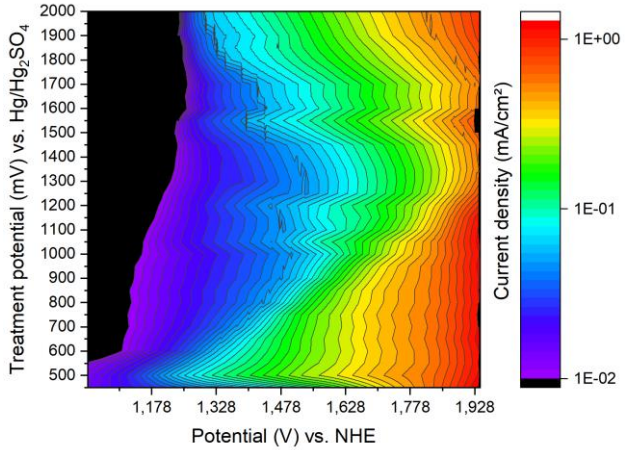
Results & Discussion - Background 2 M H_2SO_4









- Hydrogen and oxygen evolution (or CO_x)
- Strong dependence of the general behavior on treatment potential
- Peaks at around +0.3 V (Q/HQ)
- Additional peaks clearly visible at high treatment potentials

- Several peaks and plateaus in the cathodic area without clear tendency, except appearance of peak at -0.1 V
  - Perhaps O_2 reduction
  - Plateaus with reduction of surface oxides ?
- Clear tendencies in the anodic area!
  - Peak of low oxygen evolution kinetics at ~1.3 V

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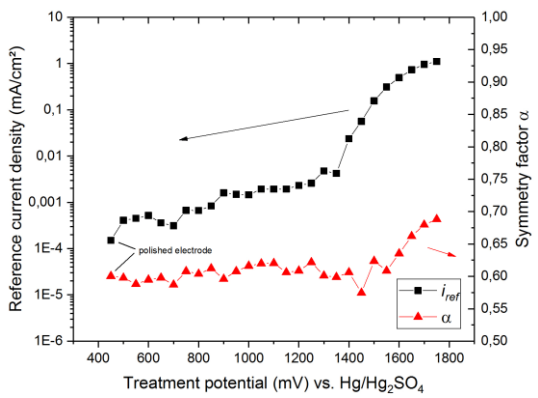
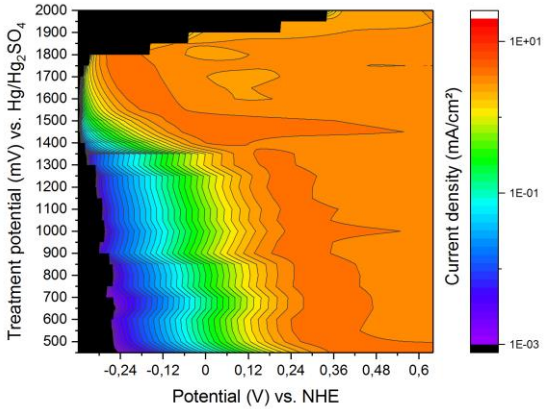
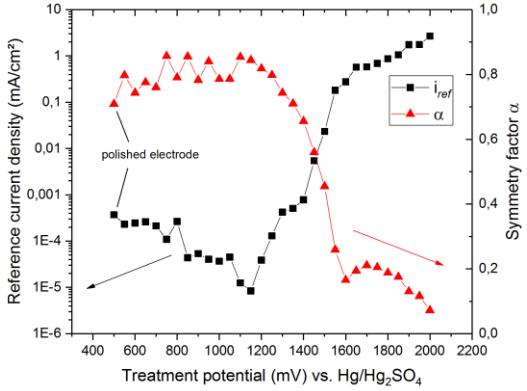
Results & Discussion - Oxidation processes V(II) -> V(III), V(IV) -> V(V)

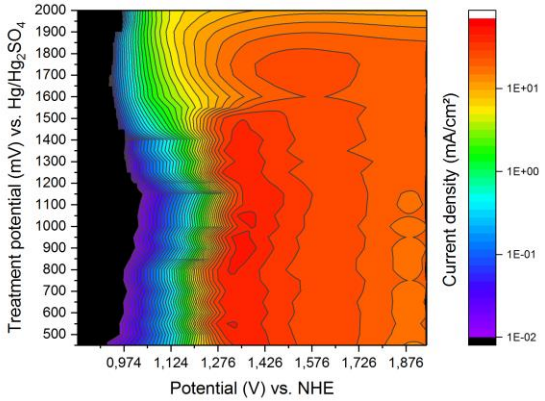
Oxidation of 0.1 M V^{2+} at glassy carbon



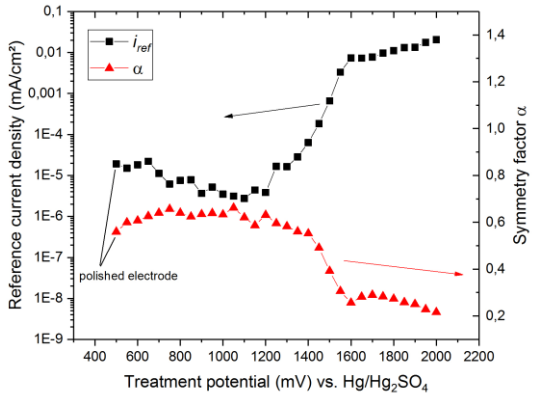


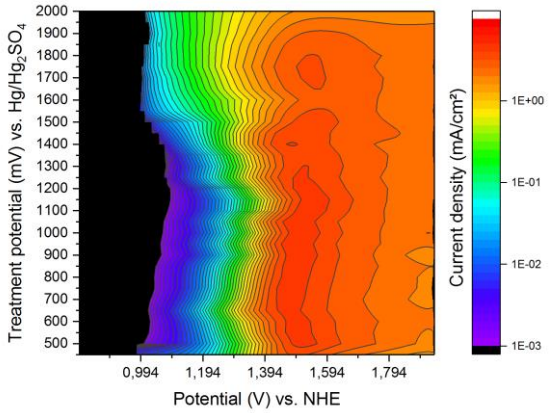
Oxidation of 1.6 M VO^{2+} at glassy carbon





Oxidation of 0.1 M VO^{2+} at glassy carbon





- Not shown here: Oxidation of V(III) is a very special process!
- Significant tendencies for all reactions
  - Kinetics of all reactions increases dramatically
  - V^{2+} -> V^{3+} kinetics continuously increases
  - V(IV) -> V(V) kinetics has a minium
  - 1.6 M and 0.1 M V(IV) show the same behavior

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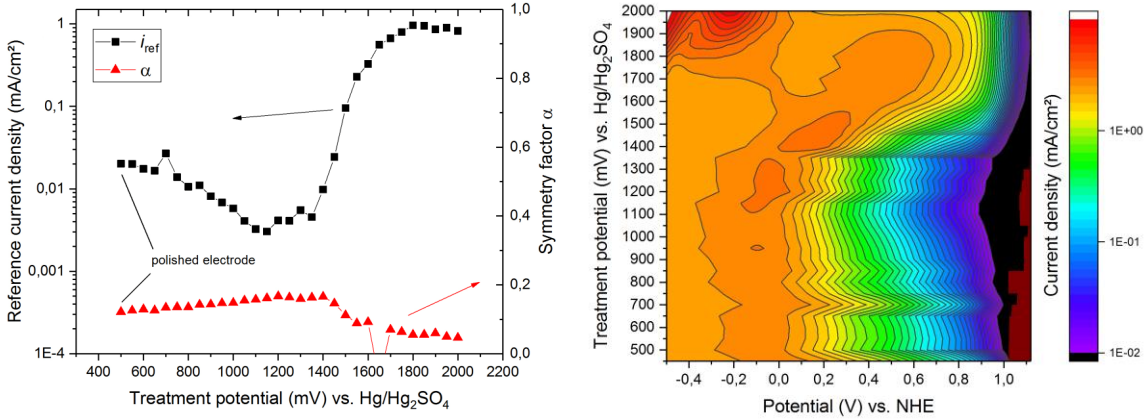
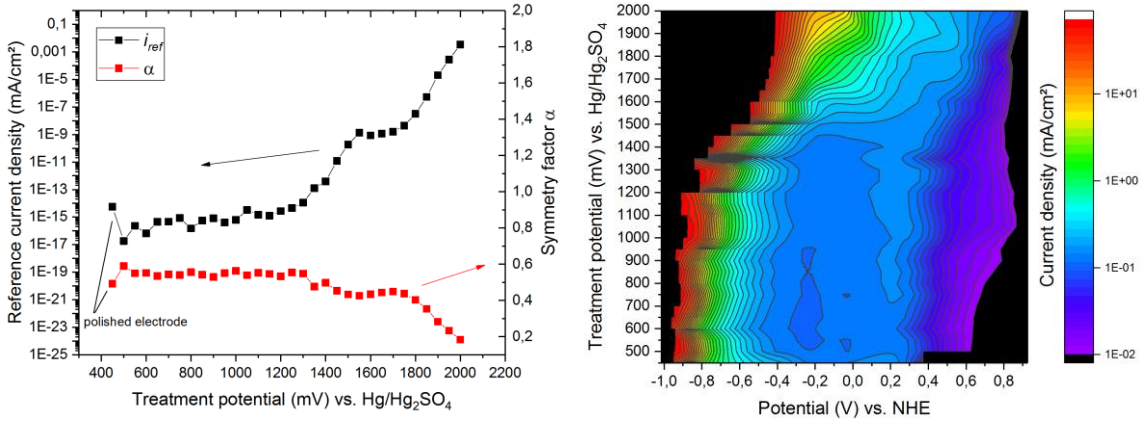
Results & Discussion - Reduction processes

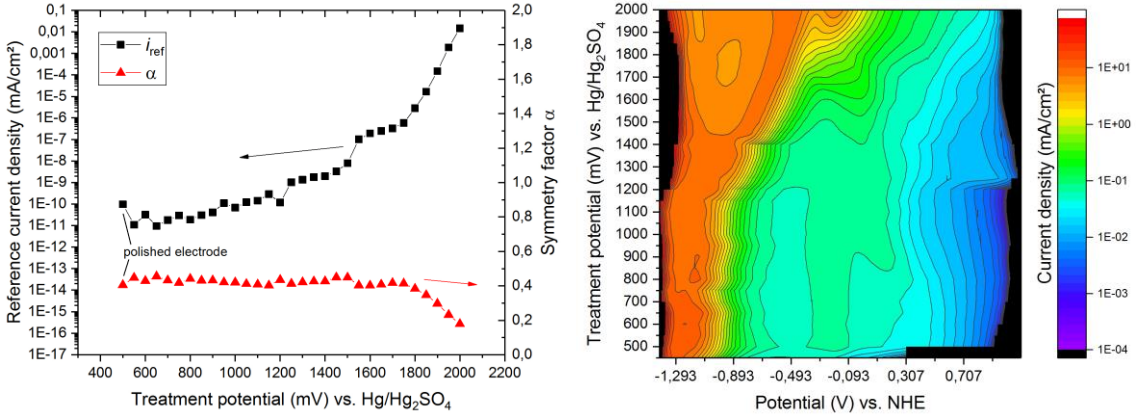
Reduction of 0.1 M VO_2^+ at glassy carbon



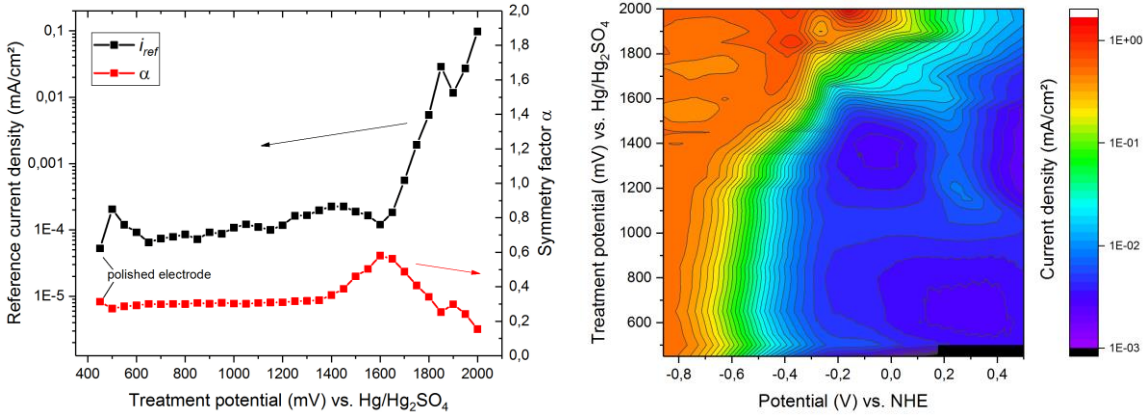
Reduction of 1.6 M VO^{2+} at glassy carbon



Reduction of 0.1 M VO^{2+} at glassy carbon



Reduction of 0.1 M V^{3+} at glassy carbon



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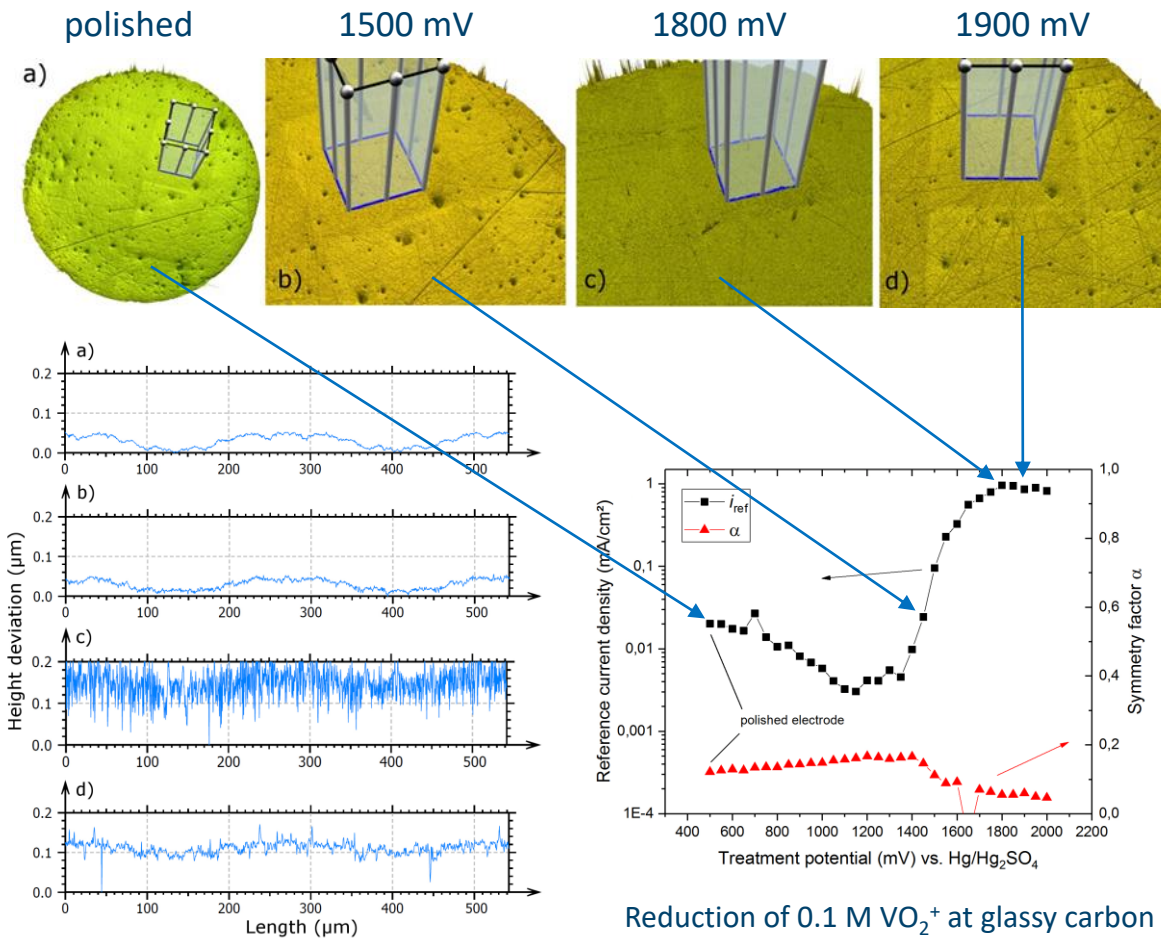
Results & Discussion - Reduction of V(IV) & Laser confocal microscopy

- Oxo-vanadium - Continuous increase of kinetics with treatment potential
- Non-oxo-vanadium - Minimum of kinetics at ~ 1200 mV vs. NHE
- Exception: Reduction of V(IV):

A-1:	$VO^{2+} + 2H^+ + 2e^- \rightarrow V^{2+} + H_2O$	E	fast
B-1:	$V^{2+} + VO^{2+} + 2H^+ \rightarrow V^{3+} + H_2O$	C‘	fast
C-1:	$V^{3+} + e^- \rightarrow V^{2+}$	E	slow
A-2:	$VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O$	E	fast
B-2:	$V^{3+} + e^- \rightarrow V^{2+}$	E	slow
C-2:	$V^{2+} + VO^{2+} + 2H^+ \rightarrow V^{3+} + H_2O$	C‘	fast

- Two path ways possible
- Similar trend to reduction of V^{3+} -> C-1 and B-2 must be speed determinig steps

Laser confocal microscopy



Reduction of 0.1 M VO_2^+ at glassy carbon

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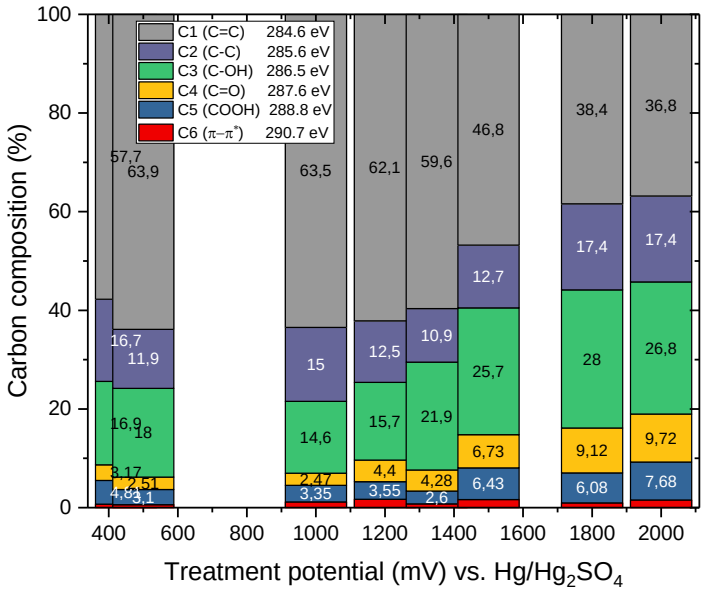
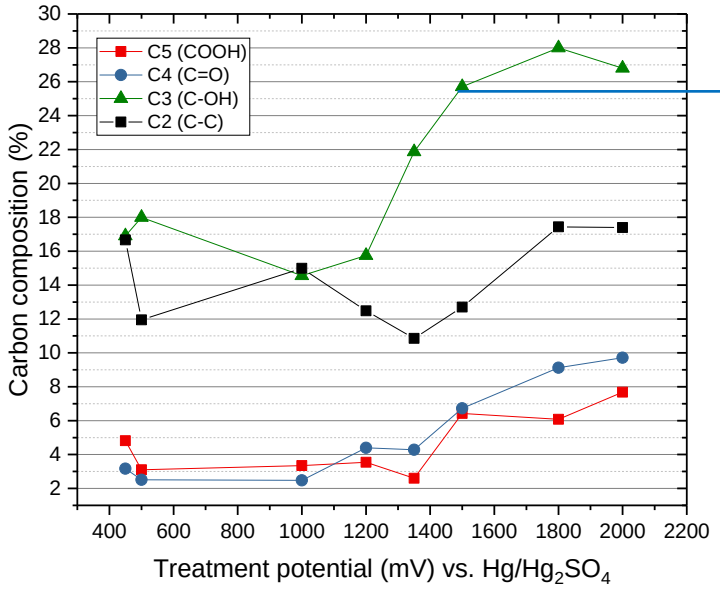
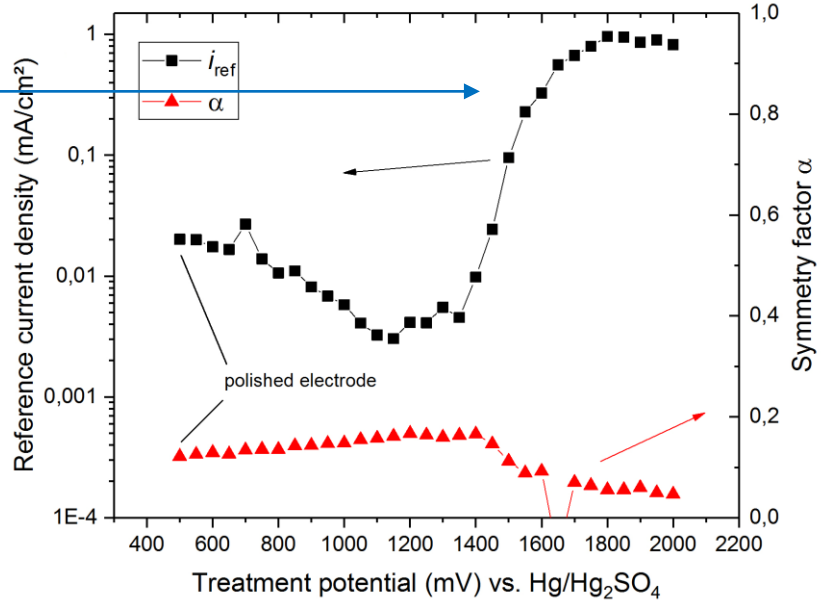
Results & Discussion - XPS Measurements





Reduction of 0.1 M VO_2^+ at glassy carbon



-> No correlation with surface roughness but weak correlation with functional groups:

-C-OH for VO^{2+}/VO_2^+,
-COOH for V^{2+}/V^{3+}

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Conclusions & further work

Conclusions

- Studied electrochemical reactions of V(II) -> V(III), V(IV) -> V(V), V(V) -> V(IV), V(IV) -> V(III), V(III) -> V(IV) on GC
- All reactions are strongly surface sensitive
- Electrochemical surface treatment is able to increase kinetics of all reactions dramatically
- No correlation with confocal microscopy electrode surface
- Non-oxo-vanadium reactions V(II) -> V(III), V(III) -> V(II)
  - Continous increase of kinetics with treatment potential
  - Weak correlation with -COOH functional surface groups
- Oxo-vanadium reactions V(IV) -> V(V), V(V) -> V(IV)
  - Increase of kinetics with treatment potential, but minimum at ~1200 mV vs. Hg/Hg_2SO_4
  - Weak correlation with -C-OH functional surface groups

Further work

- More XPS values needed for significant tendencies
- Different techniques could give more additional information
- In-Situ activation of reactions in a battery possible?

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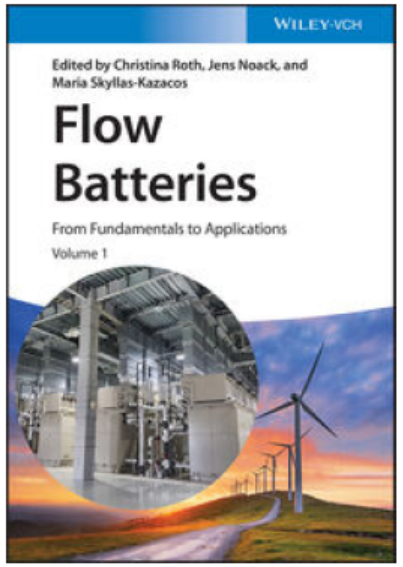
WILEY VCH - Flow Batteries



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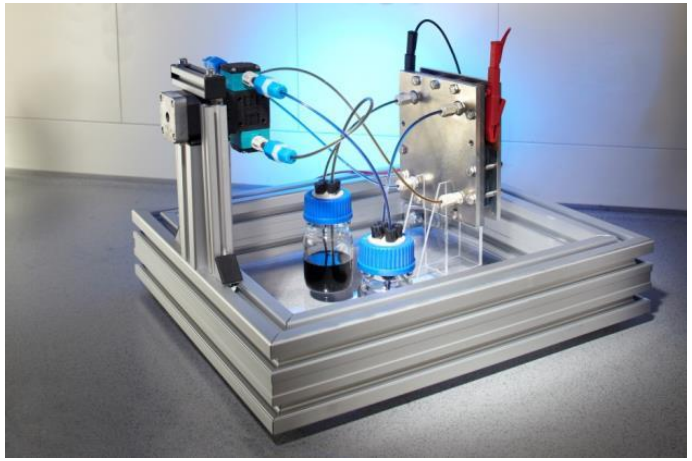

Jens Noack

Adj. Assoc. Prof. (UNSW) Dr.-Ing. Dipl.-Ing. (FH)

Fraunhofer ICT
Joseph-von-Fraunhofer-Str. 7
76327 Pfinztal/Germany

jens.noack@ict.fraunhofer.de

CENELEST
University of New South Wales
UNSW Sydney NSW 2052 Australia

info@cenelest.org

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