

Rapid wet-chemical oxidative activation of graphite felt electrodes for vanadium redox flow batteries

Brian Shanahan^{§a}, Khaled Seteiz^{§a}, Philipp A. Heizmann^{a,b}, Susanne Koch^{a,c}, Jan Büttner^{b,d,e}, Siham Ouardi^f, Severin Vierrath^{a,b,c}, Anna Fischer^{b,d,e,g} and Matthias Breitwieser^{a,c*}*

- a) Electrochemical Energy Systems, IMTEK-Department of Microsystems Engineering, University of Freiburg, Georges-Koehler-Allee 103, 79110 Freiburg, Germany
- b) FIT, University of Freiburg, Georges-Koehler-Allee 105, 79110 Freiburg, Germany
- c) Hahn-Schickard, Georges-Koehler-Allee 103, 79110 Freiburg, Germany
- d) Institute for Inorganic and Analytical Chemistry, University of Freiburg, Alberstr. 21, 79104 Freiburg, Germany
- e) Cluster of Excellence livMatS, University of Freiburg, 79104 Freiburg, Germany
- f) Fraunhofer Institute for Solar Energy Systems ISE, Heidenhofstr. 2, 79110 Freiburg, Germany
- g) FMF—Freiburg Materials Research Center, University of Freiburg, Stefan-Meier Str. 21, 79104 Freiburg, Germany

[§]authors contributed equally

*corresponding authors

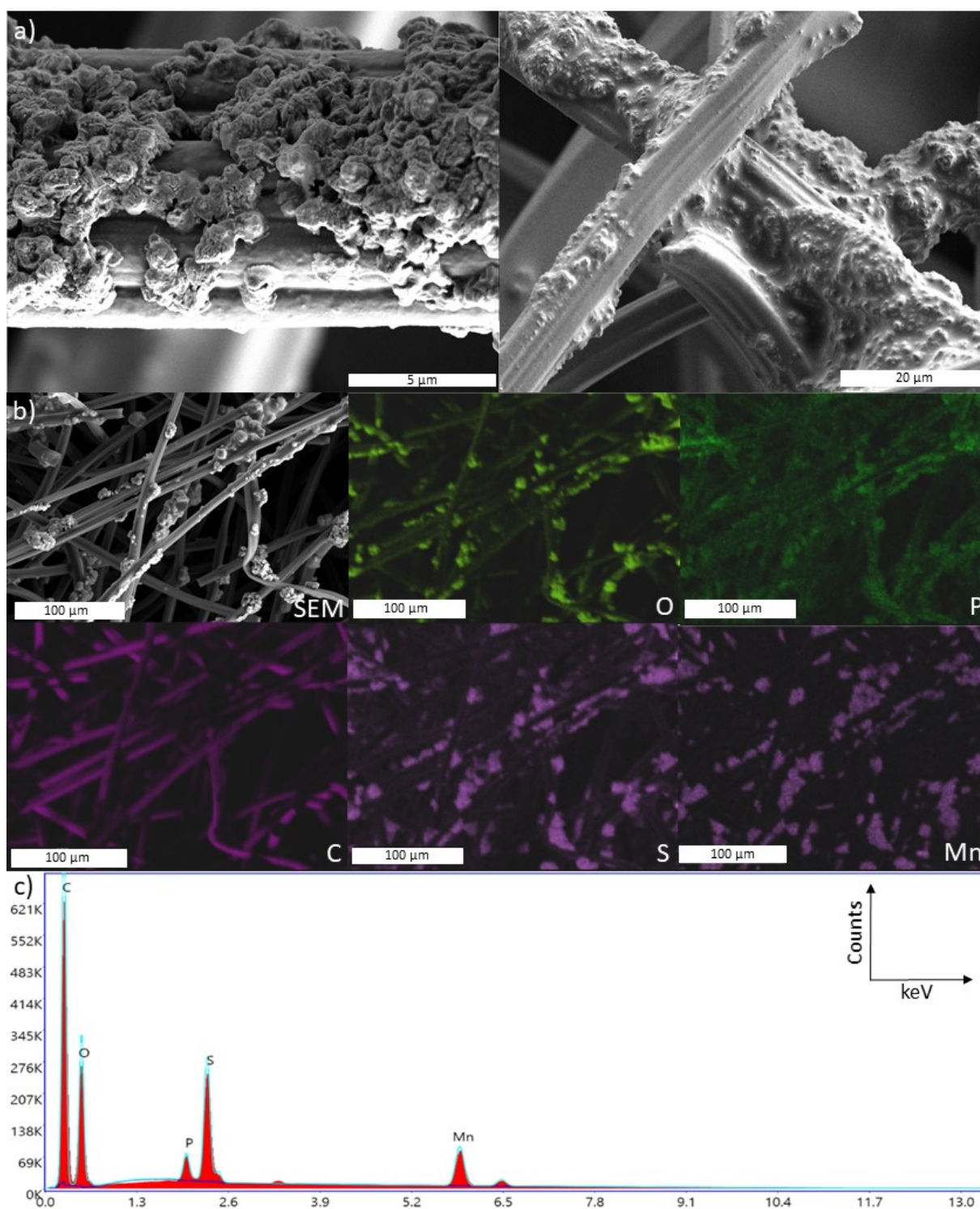


Figure S1: a) SEM imaging of a MnO_x decorated P-GF after step 1 in Figure 1 and b) SEM-EDX mapping of multiple fibers (Top left: Raw SEM image, Top middle: Oxygen, Top right: Phosphorus, Bottom left: Carbon, Bottom middle: Sulfur, Bottom right: Manganese).

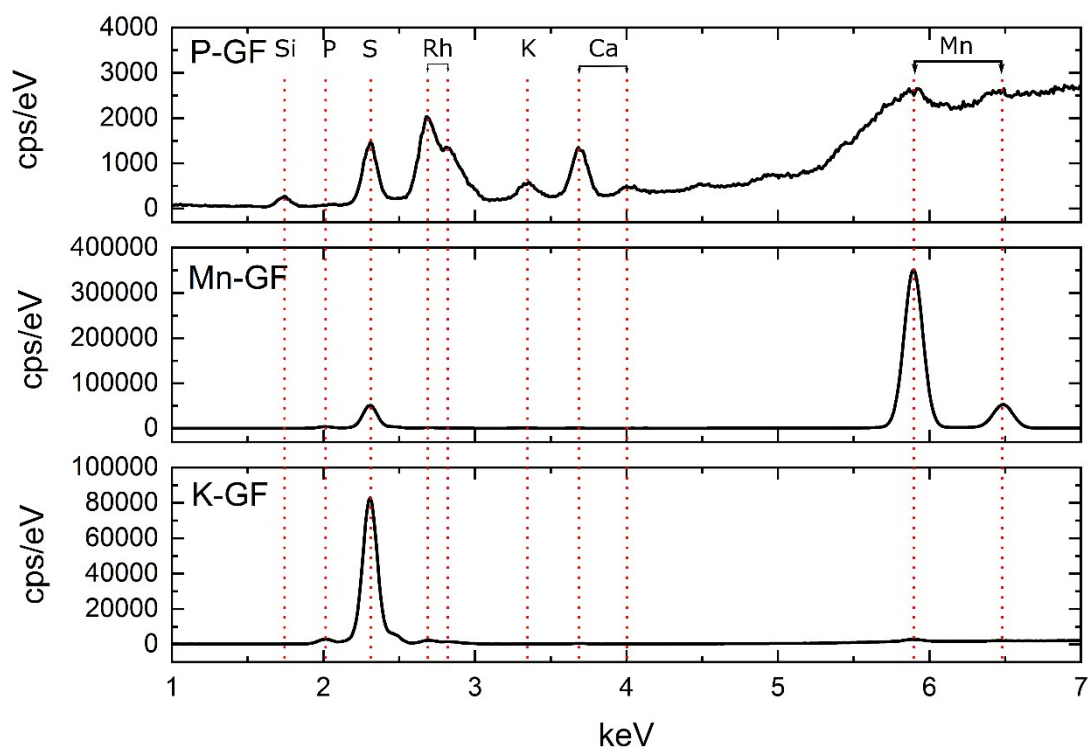


Figure S2: XRF analysis of the P-GF, MnO_x coated GF (denoted as Mn-GF) and the K-GF electrodes. Special attention must be paid to the y-axis scale bar.

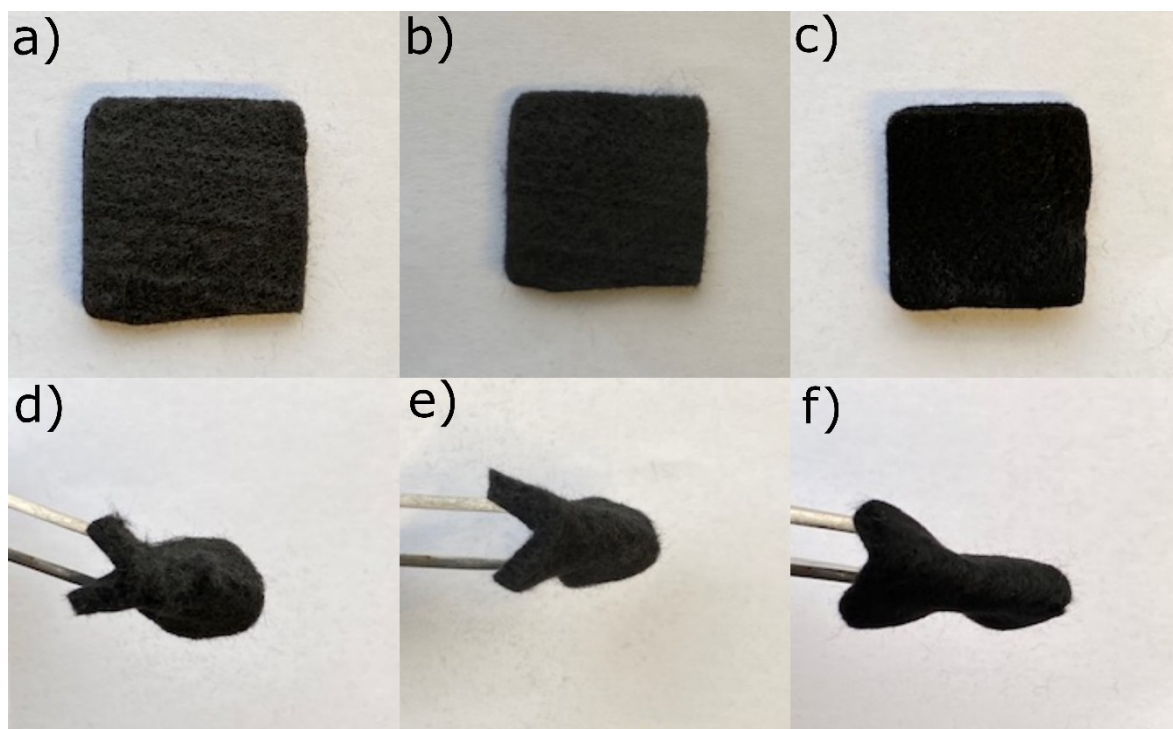


Figure S3: Photographs depicting the physical condition of electrodes used in this study. a) P-GF before treatment, b) T-GF electrode after treatment, c) K-GF electrode after treatment, d) P-GF electrode bent with tweezers, e) T-GF electrode bent by tweezers and f) K-GF electrode bent by tweezers.

Table S1: Cyclic voltammetry results for the optimization of the KMnO₄ treatment process as described in Table 1 and Figure 2. The best result for each testing group is marked with an *.

Test Number	Test Type	$E_{peak\ ox}$ V	$E_{peak\ red}$ V	ΔE_{peak} V	$I_{peak\ ox}$ A/g	$I_{peak\ red}$ A/g
1*	KMnO ₄ Conc.	0.880	0.724	0.156	2.69	-3.14
2		0.893	0.687	0.206	2.07	-2.80
3		0.903	0.677	0.226	1.84	-2.57
4	Time	0.908	0.685	0.223	2.58	-3.01
5*		0.873	0.722	0.151	2.99	-3.03
6		0.916	0.682	0.234	2.44	-3.01
7		0.926	0.685	0.241	1.86	-2.85
8		0.920	0.667	0.253	1.78	-2.44
9	Temperature	1.010	0.634	0.376	1.41	-1.54
10		0.889	0.708	0.181	2.11	-3.07
11*		0.882	0.717	0.165	2.75	-3.11
12		0.907	0.698	0.209	2.22	-2.95
13*	Acid	0.873	0.714	0.159	2.51	-3.07
14		0.892	0.710	0.182	2.46	-2.95
15		0.883	0.714	0.169	2.40	-2.94

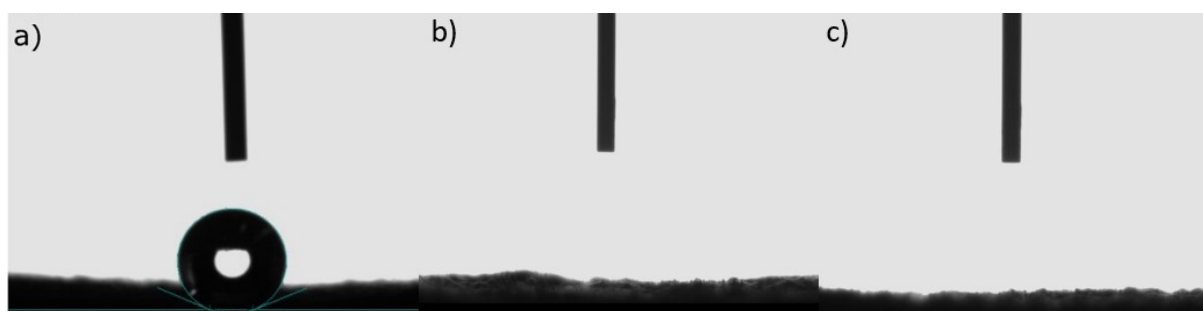


Figure S4: Contact angle of DI water on the a) P-GF electrode, b) T-GF electrode and b) K-GF electrode. Sample sizes of 1 cm² were used and each water droplet volume is 5 μ L.

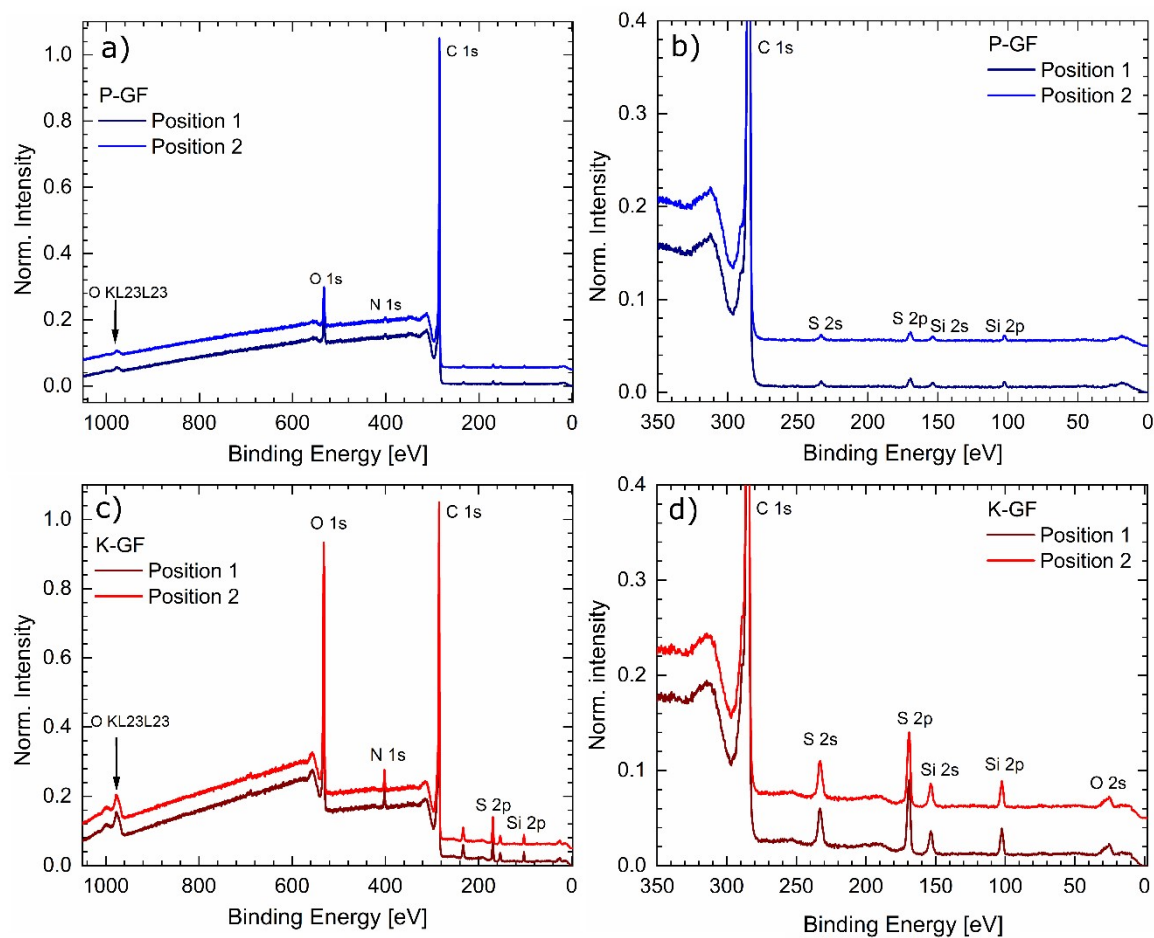


Figure S5: XPS spectra of the P-GF electrode survey (a) and semicore states (b) and K-GF electrode survey (c) and semicore states (d).

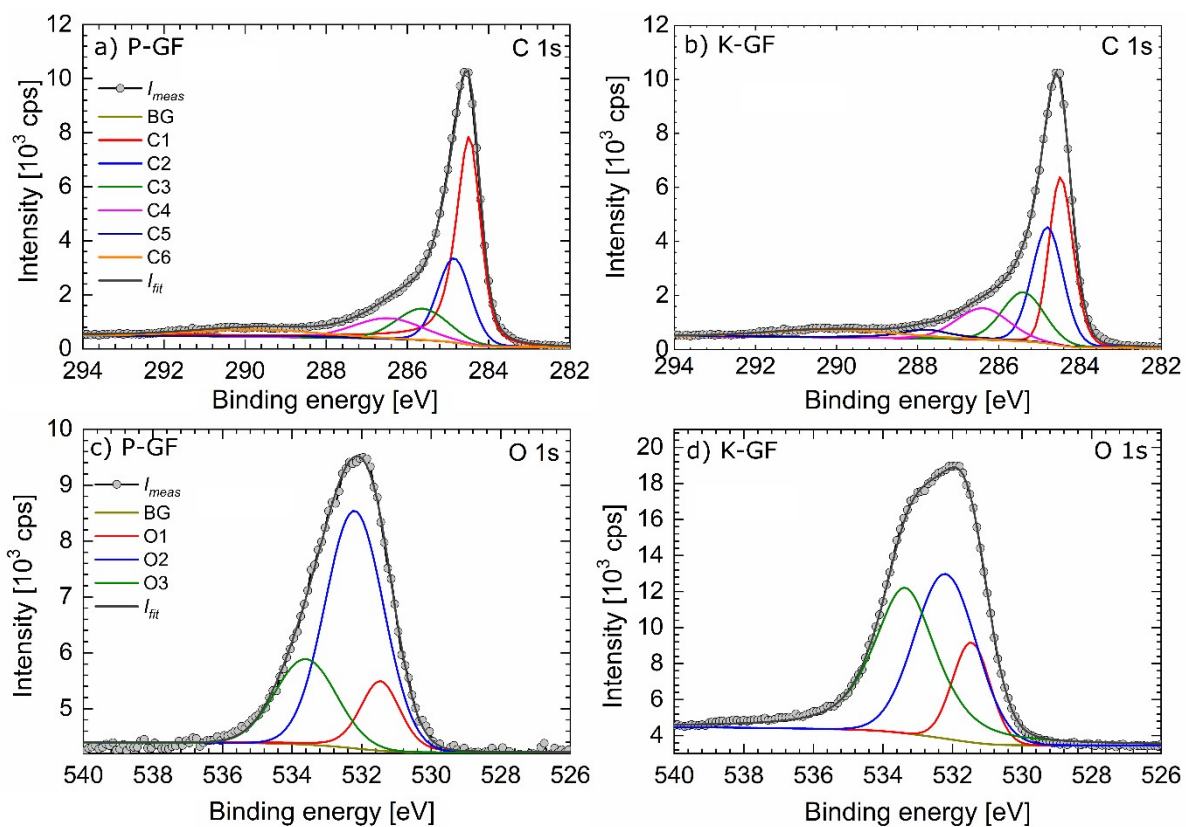


Figure S6: Peak fitting of C1s (a, b) and O1s (c, d) of the P-GF and K-GF samples. Special attention must be given to the y-axis scale on (c) and (d).

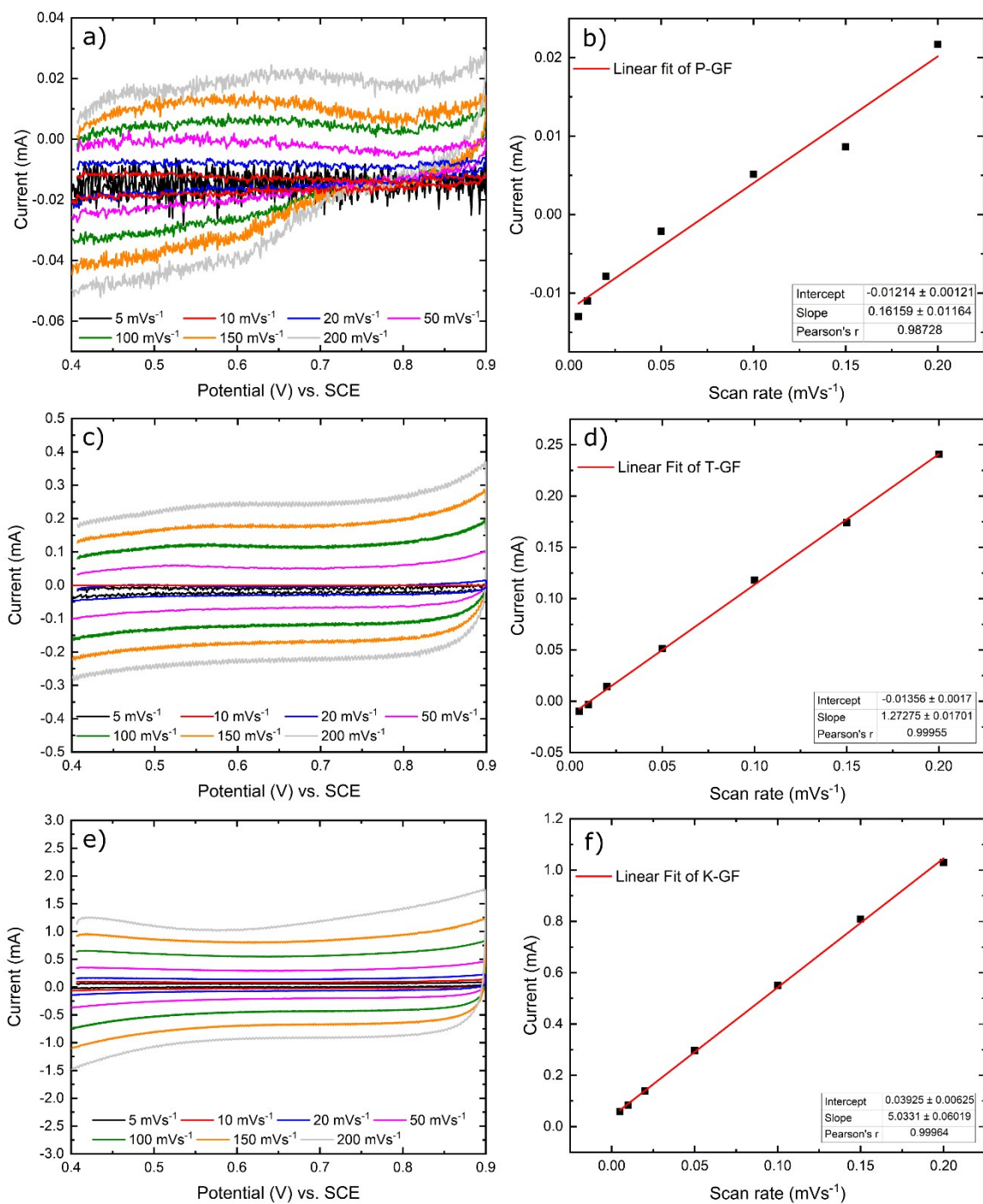


Figure S7: EDLC measurement of the P-GF, T-GF and K-GF electrodes. CV was performed in a potential range of 0.4 to 0.9 V vs. SCE with different scan rates (200, 150, 100, 50, 20, 10, and 5 mVs⁻¹) in 2 M H₂SO₄. The peak currents of a) P-GF, c) T-GF and e) K-GF at 0.6 V were plotted against scan rates and fitted linearly in b), d) and f) respectively.

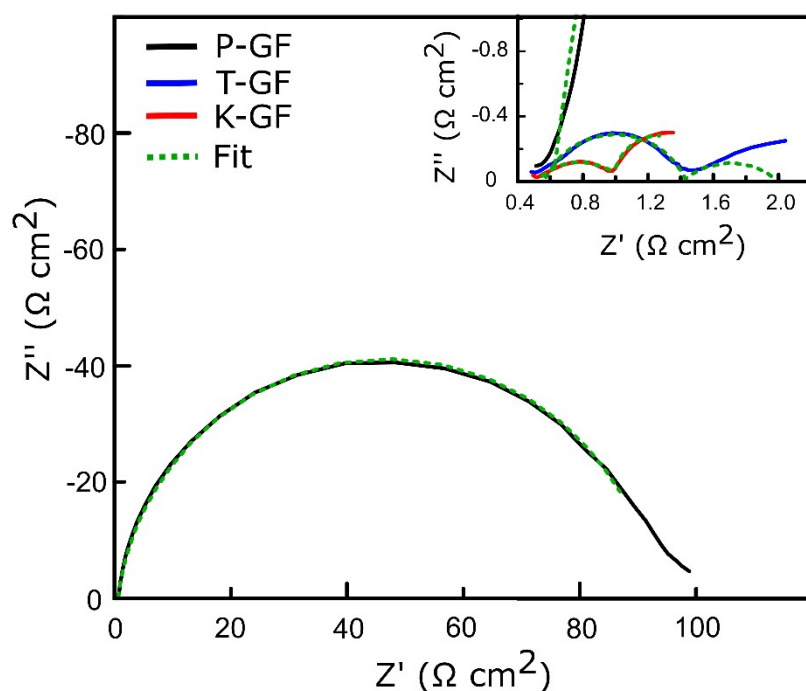


Figure S8: EIS curves of P-GF, T-GF and K-GF electrodes in the frequency range of 10^{-1} to 10^4 Hz. Inset: Focused view of the T-GF and K-GF electrodes. Real and Imaginary ohmic values were multiplied by the active geometric cell electrode area (4 cm^2). Equivalent circuit fits are displayed as dashed green lines.

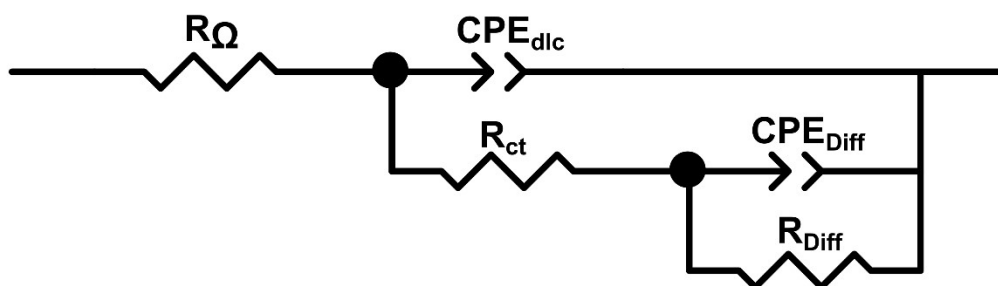


Figure S9: Equivalent circuit used to fit T-GF and K-GF EIS data of Figure S8. R_Ω corresponds to the ohmic resistance of the cell and is equal to the HFR. R_{ct} is the charge transfer resistance and R_{Diff} is the finite diffusion resistance. CPE_{dlc} and CPE_{Diff} correspond to the double layer capacitance of the electrode/electrolyte interface and the diffusion capacitance of the vanadium ions into the electrode structure, respectively.

Table S2: Obtained values from fitting Nyquist plots displayed in Figure S7 using the equivalent circuit shown in Figure S8.

Electrode	R_Ω ($\Omega \text{ cm}^2$)	R_{ct} ($\Omega \text{ cm}^2$)
P-GF	0.65	90.50
T-GF	0.56	0.88
K-GF	0.51	0.53