

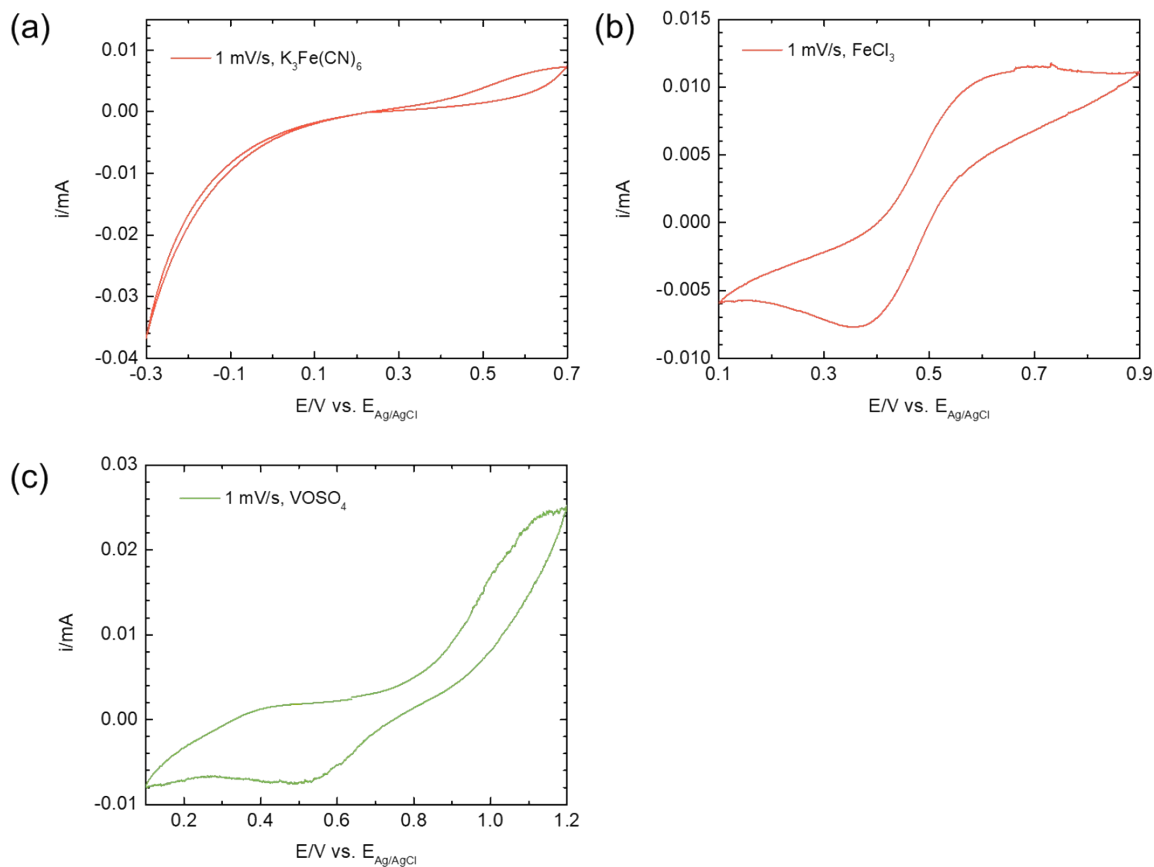
## **Resolving electron transfer kinetics in porous electrodes via diffusion-less cyclic voltammetry**

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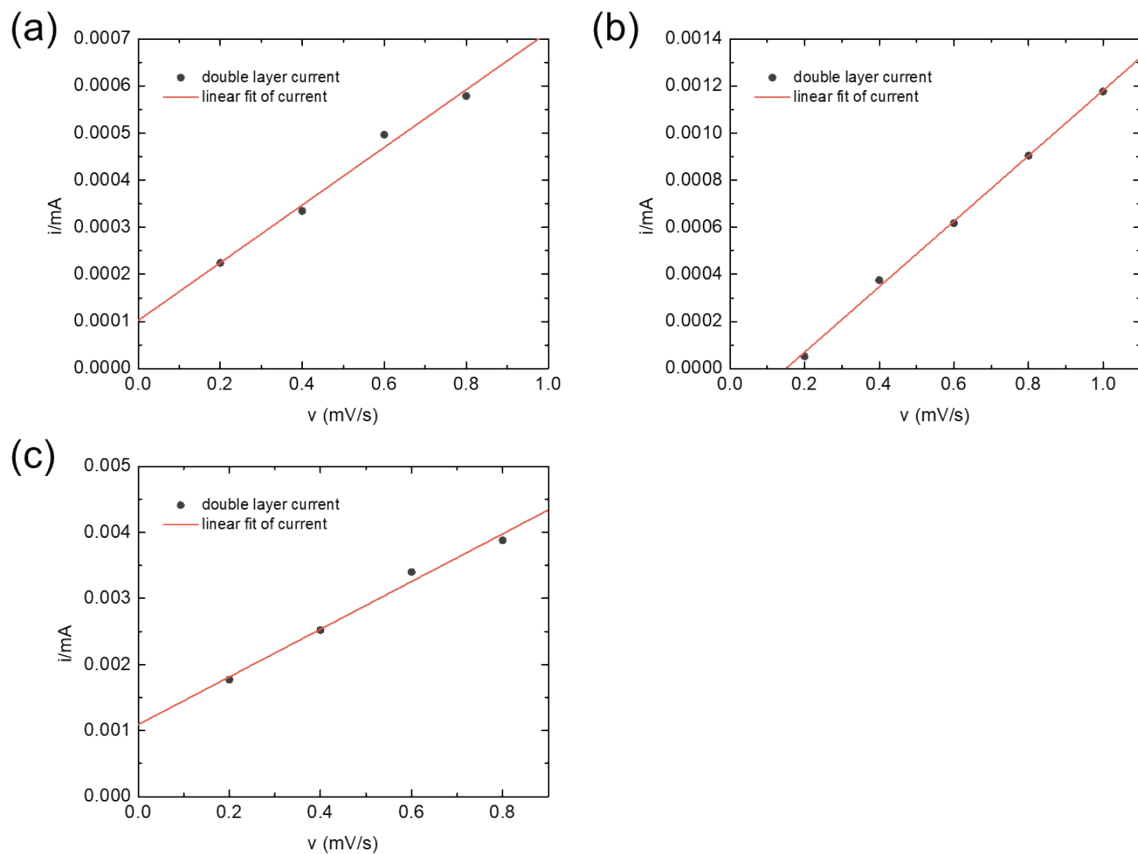
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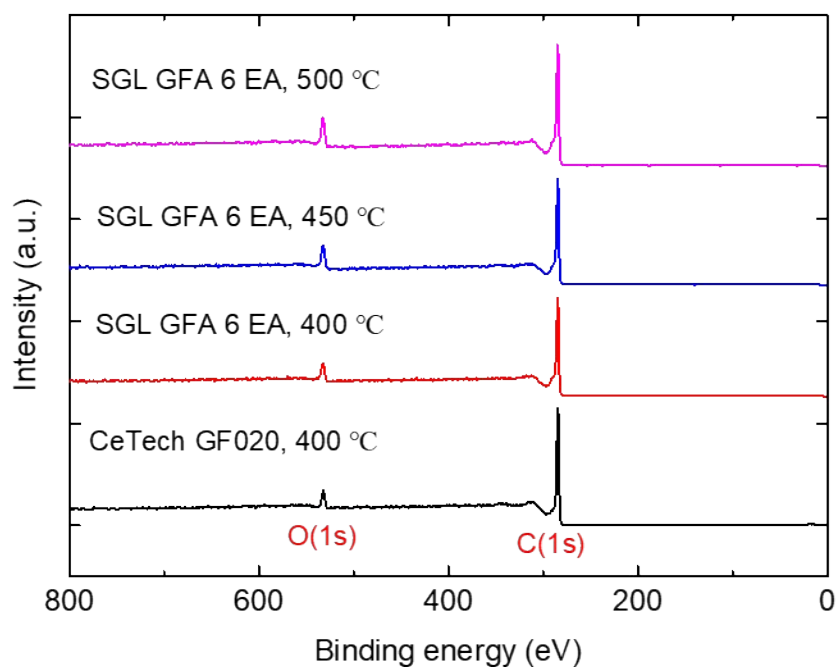
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**Figure S1.** Background current on Ti foil as assembled in the cell with the active electrolyte but without the carbon felt. (a)  $\text{K}_3\text{Fe}(\text{CN})_6$ , (b)  $\text{FeCl}_3$ , and (c)  $\text{VOSO}_4$ . The currents are at least two orders of magnitude lower than those measured with the carbon felt for all three cases, so no background subtraction is necessary for the analysis.



**Figure S2.** Electrochemical surface area measurements of the carbon felt electrode in the electrolytes of (a)  $K_3Fe(CN)_6$ , (b)  $FeCl_3$ , and (c)  $VOSO_4$ . We scan CV in ranges of potential with no visible Faradaic current and plot the average currents against the scan rates. The slopes are divided with a specific capacitance of  $20 \mu F/cm^2$  to derive the areas.

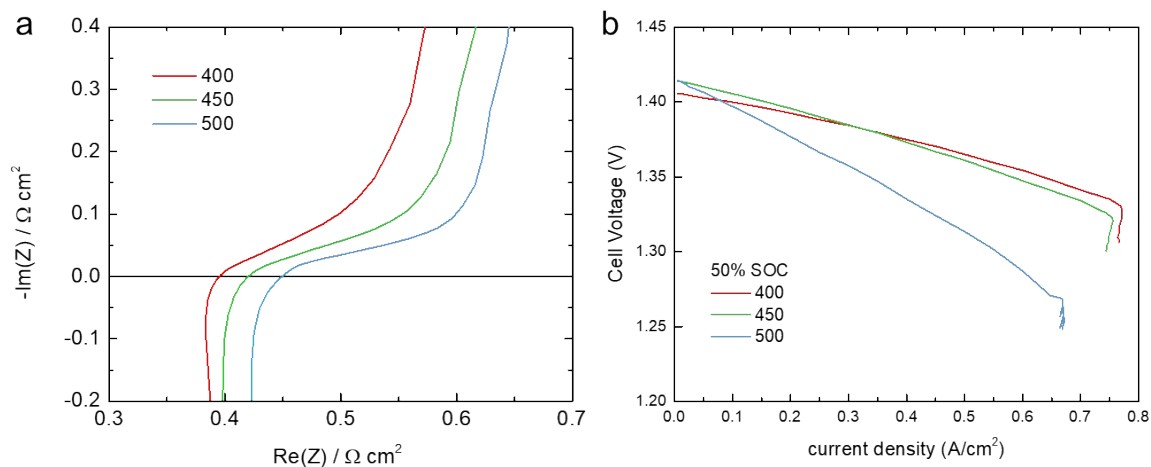


**Figure S3.** X-ray photoelectron spectra of different carbon felts.

**Table S1.** O/C ratio of different carbon felts and the corresponding standard rate constants

$k^0$  of  $\text{VO}^{2+}/\text{VO}_2^+$  on these electrodes.

Carbon Felt	C ratio/%	O ratio/%	O/C	$k^0$ (cm/s)
CeTech CF020, 400 °C	92.51	7.49	0.081	$1.56 \pm 0.15 \times 10^{-6}$
SGL GFA6EA, 400 °C	90.14	9.86	0.109	$1.642 \pm 0.072 \times 10^{-7}$
SGL GFA6EA, 450 °C	89.34	10.66	0.119	$2.095 \pm 0.518 \times 10^{-7}$
SGL GFA6EA, 500 °C	88.93	11.07	0.124	$2.455 \pm 0.216 \times 10^{-8}$



**Figure S4.** Additional results of the RFB tests. (a) Electrochemical impedance spectroscopy (EIS) and (b) IR-corrected polarization curves of VRFB with CF baked at different temperatures.

**Table S2.** Polarization resistance of VRFB with different CF.

SGL CF	$R_u / \Omega \text{ cm}^2$	polarization resistance/ $\Omega \text{ cm}^2$	corrected polarization resistance/ $\Omega \text{ cm}^2$
400°C	0.395	0.487	0.092
450°C	0.421	0.540	0.119
500°C	0.450	0.664	0.214

**Table S3.** Summary of standard rate constants  $k$  of  $\text{VO}^{2+}/\text{VO}_2^+$  reported in literature.

Electrodes	Treatment	Method	Area	$k$ (cm/s)	Ref
SGL Carbon GFD4.6	Baked at 400 °C for 12 hrs	Symmetrical RFB	Electro- chemical	$2.38 \times 10^{-6}$	[1]
Disk made from carbon felt (SigracELL GFA6, SGL carbon)	Baked at 400 °C for 30 hrs	Linear sweep voltammetry (LSV)	Geometric	1.6- $8.8 \times 10^{-8}$	[2]
Ultra- microelectrode made from carbon felts (GrafTech)	Electrochemical oxidation and reduction	LSV and EIS	Electro- chemical	1.7- $17 \times 10^{-5}$	[3]
Carbon felt (Sigratherm GFA5)	Not mentioned	Galvanic charging / discharging	Calculated	$3 \times 10^{-7}$	[4]
Carbon felt (Liao Yang Carbon Fiber Sci-tech. Co., Ltd. China)	None	CV and EIS	Geometric	$1.84 \times 10^{-3}$	[5]
Carbon paper (29, SGL group)	Baked at 450 °C for 30 hrs	Polarization curve and EIS in a RFB	Electro- chemical	0.2- $1.8 \times 10^{-7}$	[6]
Carbon paper (10AA, SGL group)	None	Symmetrical RFB	Gas adsorption	$2.05 \times 10^{-6}$	[7]
Carbon paper (Shanghai Hesun, Ltd. HCP030 N)	Electrochemical oxidation and reduction	CV	Gas adsorption	$1.04 \times 10^{-3}$	[8]

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