Supplementary Materials: Application of GUITAR on the Negative Electrode of the Vanadium Redox Flow Battery: Improved $V^{3+/2+}$ Heterogeneous Electron Transfer with Reduced Hydrogen Gassing

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Calculation of "smooth" (or true) surface area of KFD graphite felt and GUITAR/KFD felt:

In regards to the Smith *et al.* [1] calculation method (Equations (1) to (3) therein) our values are given in the table below

Table S1. Values for calculation of "smooth" (or true) surface area of KFD graphite felt and GUITAR/KFD felt.

Properties	KFD Graphite Felt	GUITAR/KFD Felt
Density of the felt (g/cm^3)	1.8 [1]	1.8 [1]
Radius of the graphite fiber (μm)	4.35	6.17
Areal weight of the felt (g/cm^2)	0.025 [a]	0.034 [b]
Total volume of the graphite fiber (cm^3) ($V_{gf} = m/d_{gf}$)	0.014	0.019
The equivalent length of the graphite fiber (cm) ($V_{gf} = \pi r^2 L_{gf}$)	23562.4	15894.7
"Smooth" surface area of the felt (cm^2) ($A_{gf} = 2\pi r L_{gf}$)	64.4	61.6

[a] Reported by SGL Group, [b] Measured.

Determination of electrochemical surface area of KFD graphite felt and GUITAR/KFD felt using Randles–Sevcik equation:

Randles-Sevcik equation for a reversible process is

$$sI_p = 268{,}600\ n^{3/2} A C \sqrt{(Dv)}$$

where, I_p = Peak current (A)
n = # of electron transferred in the redox process
A = Electrochemical surface area of the electrode (cm^2)
C = Concentration of the redox species (mol/cm^3)
D = Diffusion constant of the redox species (cm^2/s)
v = Scan rate (V/s)

A plot of I_p vs $\sqrt{v}$ gives slope which is equal to $268{,}600\ n^{3/2} A C \sqrt{D}$ from which the electrochemical surface area (A) of the electrode can be calculated and shown in table S2. The I_p vs $\sqrt{v}$ for both the KFD graphite felt and GUITAR coated KFD graphite felt electrode are shown in figure S1 (in 1 mM $Fe(CN)_6^{3-/4-}$ in + 1 M KCl).

For $Fe(CN)_6^{3-/4-}$, n = 1, C= 1×10^{-6} mol/cm^3 and D = 7.26×10^{-6} cm^2/s [2]. Both the felts were made hydrophilic using ethanol as described in Smith et al before use.

Table S2. Values for determination of electrochemical surface area of KFD graphite felt and GUITAR/KFD felt using Randles–Sevcik equation.

	KFD Graphite Felt	GUITAR/KFD Felt
Slope of the I_p vs $\sqrt{v}$ plot	0.0089	0.0055
Electrochemical surface area of the felt (cm^2) (slope = $I_p/\sqrt{v} = 268{,}600\ n^{3/2} A C \sqrt{D}$)	12.3	7.6
Geometric area of the felt (cm^2)	0.20	0.15
Electrochemical surface area of the felt/cm^2 of geometric area (cm^2)	61.5	50.6

Scan rate variations on KFD graphite felt and GUITAR/KFD felt:

To distinguish between finite-length (thin-layer) and semi-infinite diffusion behavior on the felt electrodes. Cyclic voltammetry of 1 mM $Fe(CN)_6^{3-/4-}$ (in 1 M KCl) was performed at potential sweep rates (v) between 0.01 to 0.6 V/s (Figure S1). Figure S2 provides the analysis. Thin-layer behavior gives an peak current (Ip) α v (see Equation (11.7.17) [3]), whereas semi-infinite linear diffusion gives Ip α $v^{1/2}$ (Equation (6.3.8) [3]). At 200 mV/s the current was found to be within the v region where semi-infinite linear diffusion predominates to the electrode surface.

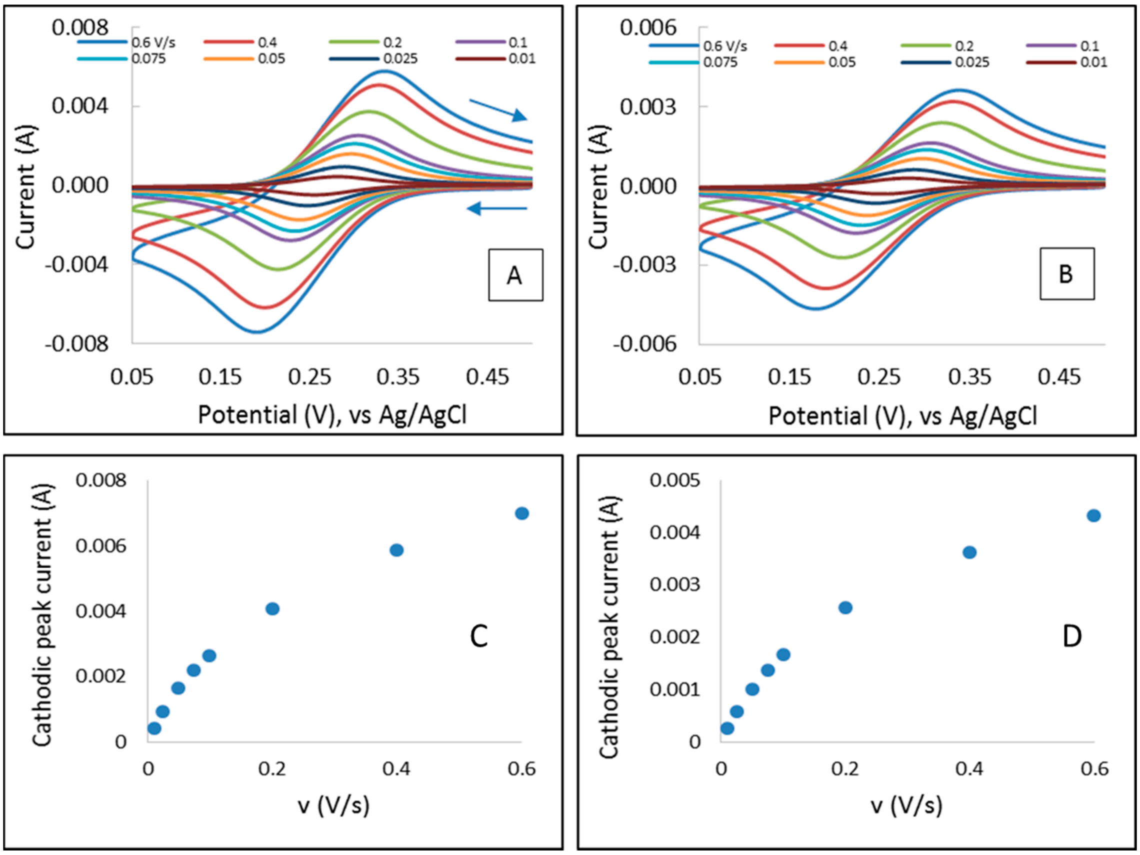

Figure S1. Cyclic Voltammetric scan rate variation on in 1 mM $Fe(CN)_6^{3-/4-}$ (in 1 M KCl) at 0.6, 0.4, 0.2, 0.1, 0.075, 0.05, 0.025 and 0.01 V/s. (**A**) on KFD felt electrode and the corresponding I_p vs v (**C**). (**B**) on GUITAR/KFD felt electrode and the corresponding I_p vs v (**D**).

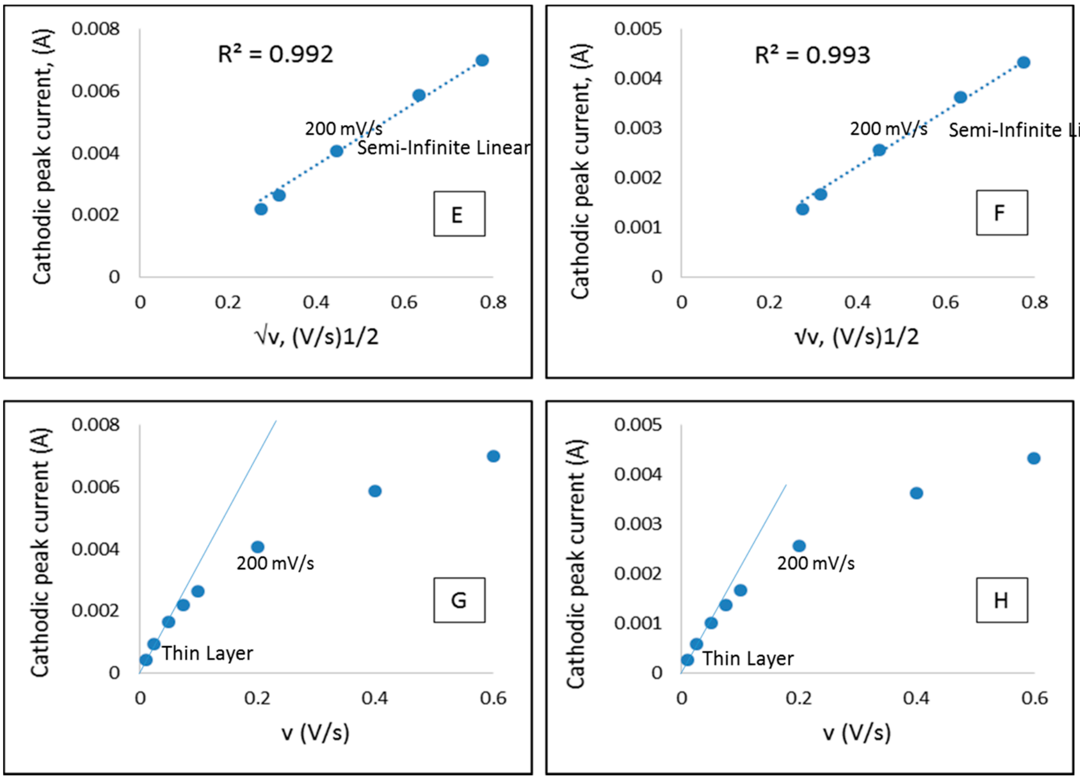

Figure S2. Analysis of cyclic voltammetric peak currents of Figure S1 for thin layer ***vs.*** semi-infinite linear diffusion characteristics. (**E**) Ip *vs.* $v^{1/2}$ on KFD felt electrode, (**F**) Ip *vs.* $v^{1/2}$ on GUITAR/KFD felt. (**G**) Ip *vs.* *v* on KFD felt electrode, (**H**) Ip *vs.* *v* on GUITAR/KFD felt. Thin-layer cell characteristics were found to predominate below 50 mV/s (see Plots **G** and **H**). Semi-infinite linear diffusion were found to predominate over 0.075 V/s (see Plots **E** and **F**).

Working electrode set-up:

Figure S3 shows the working electrode set-up

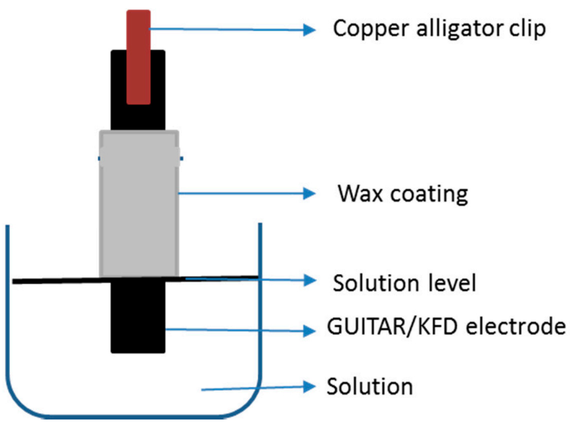

Figure S3. Working electrode set up.

Reference

1. Smith, R.E.G.; Davies, T.J.; Baynes, N.d.; Nichols, R.J. The electrochemical characterisation of graphite felts. *J. Electroanal. Chem.* **2015**, *747*, 29–38.
2. Konopka, S.J.; McDuffie, B. Diffusion Coefficients of Ferri- and Ferrocyanide Ions in Aqueous Media, Using Twin-Electrode Thin-layer Electrochemistry. *Anal. Chem.* **1970**, *42*, 1741–1746.
3. Bard, A.J.; Faulkner, L.R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; John Wiley and Sons: New York, NY, USA, 2001.