

Workshop -Flow batteries, bringing the technology to the market

Vitoria-Gasteiz

How active can be the graphite felt electrode in redox flow battery electrolyte?

Mathieu ETIENNE

CNRS

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Ranine El Hage, Vincent Feynerol, Mariela Brites Helú, Liang Liu, Rafael-Luan Sehn-Canevesi, Vanessa Fierro



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Introduction



Redox flow battery

Conversion and storage of energy from renewable sources

The electrolytes must be stable, low cost, scalable, highly energetic redox systems

Electrochemical studies to assess the reactivity of the active species

Fast and reversible systems are required

In the battery, the reactions are performed on porous carbon electrode, e.g. carbon paper or graphite felt

The challenge is here to determine how fast can be this electron transfer kinetic on porous electrode materials

Quantification would also allow studying aging phenomena





Determination of the intrinsic kinetic constant of ferrocyanide (Fe(CN)₆⁴⁻ ≒ Fe(CN)₆³⁻ + 1 e⁻) Also viologen and tempo derivatives

Three approaches for the analysis at different scales:

MACRO = graphite felt \Rightarrow cm²

Micro-fiber^[1-2] = graphite fiber extracted from the felt ⇒ mm²

Gel-probe = using SECM to approach the fiber in the felt $\Rightarrow \mu m^2$

Mathematical modelling for quantification

^[1] L. Landon-Lane, A. T. Marshall, D. A. Harrington, 109 (2019) 106566, doi: 10.1016/j.elecom.2019.106566
[2] L. Landon-Lane, A. J. Downard, A. T. Marshall, Electrochimica Acta, 354, 2020, 136709, doi: 10.1016/j.electacta.2020.136709



MAcro-scale analysis: graphite felt





Attempt of fitting of CVs on Polarographica^[3-4]

[3] V. Feynerol, R. El Hage, M. Brites Helú, V. Fierro, A. Celzard, L. Liu, M. Etienne, Electrochimica Acta, 421, 2022, 140373, doi: 10.1016/j.electacta.2022.140373
 [4] T. Tichter, J. Schneider, D. Andrae, M. Gebhard, and C. Roth, ChemPhysChem, 21 (5), 2020, 428–441, doi: 10.1002/cphc.201901113

Theory of cyclic voltammetry in random arrays of cylindrical microelectrodes applied to carbon felt electrodes for vanadium redox flow batteries



Table 3 Kinetic and geometric parameters obtained from the fit

Felt	п	$T \mathrm{K}^{-1}$	$A \ \mathrm{cm}^{-2}$	c/mol I	$L^{-1} D_{\rm R}/c$	$m^2 s^{-1}$	$D_{\rm O}/{\rm cm}^2$	$s^{-1} a/\mu$	m
6 mm fresh 6 mm aged 8 mm fresh 8 mm aged	1	296	26.5 26.5 45 49	0.16	2.72	imes 10 ⁻⁶	2.5×1	0^{-6} 4.2	
Felt	α	$k^{0}/$	cm s ⁻¹	k_p/s^{-1}	k_{-p}/s^{-1}	k_f/s^{-1}	k_{-f}/s^{-1}	$\nu/mV s$	-1
6 mm fresh 6 mm aged 8 mm fresh 8 mm aged	0. 0. 0.	.64 6.8 .55 3.2 .64 6.8 .55 3.2	$egin{array}{c} 8 imes 10^{-5} \ 8 imes 10^{-5} \end{array}$	0.0028	0.0015	0.0006	0.0003 HIC	1.0 GREEW - 3	87



Fig. 4 SEM data acquired for pristine (A and B) and electrochemically aged (C and D) GFD4.6 carbon felt electrodes. From A and C it can be seen, that the assumption of just one fiber radius is sufficient. From B and D the approximate fiber radius of 4.2 μ m was extracted.

Système VO²⁺/VO₂+

T. Tichter, D. Andrae, J. Mayer, J. Schneider, M. Gebhard, C. Roth, Theory of cyclic voltammetry in random arrays of cylindrical microelectrodes applied to carbon felt electrodes for vanadium redox flow batteries, Phys. Chem. Chem. Phys. 21 (2019) 9061–9068. doi:10.1039/c9cp00548j.



Figure 2: Simulation of Cyclic Voltammetry with "Statistically Weighted External Cylindrical Finite Diffusion" model using Polarographica software (in red) compared with compensated experimental data (in black) on non-activated SGL graphite felt with TEMPO-based system (left) and ammonium hexacyanoferrate (right). Scan rate: 10 mV.s⁻¹. Concentration: 10⁻⁴ M in supporting electrolyte.



MAcro-scale analysis: graphite felt



Additional analysis: Electrochemical Impedance Spectroscopy



[3] V. Feynerol, R. El Hage, M. Brites Helú, V. Fierro, A. Celzard, L. Liu, M. Etienne, *Electrochimica Acta*, 421, 2022, 140373, doi: 10.1016/j.electacta.2022.140373
 [5] G. Paasch, K. Micka, P. Gersdorf, Electrochimica Acta, 38 (18), 1993, 2653-2662, doi: 10.1016/0013-4686(93)85083-B





Micro-scale analysis

Does it illustrate properly the real kinetics of the species ?

Change of the analysis strategy: Micro-fiber electrodes extracted from the same carbon felt

Why micro-fiber electrodes?

- Geometrical surface easier to determine (1D system cylindrical coordinates)
- Study of the electrochemical reaction on a single carbon fiber
- Study of higher electrolyte concentrations
- Study of the homogeneity of the felt activation on fibers extracted from different places











$$\label{eq:v} \begin{split} \nu &= 100 \ mV/s \\ \text{Ag/AgCl pseudo-ref} \\ \text{Graphite composite CE} \end{split}$$

A clear effect of the activation of the fiber is observed on the shape of the curves ∀ concentration

CV modelling for k⁰ determination for 10⁻² M solution



* Mathematical models for simulation in: V. Feynerol et al., Electrochimica Acta, 421, 2022, DOI: 10.1016/j.electacta.2022.140373



The representation of cyclic voltammograms was done according to the method presented by Compton, Laborda and Ward [2]

[2] R. G. Compton, E. Laborda, and K. R. Ward, Understanding Voltammetry. 2014.

Table 3: Average of optimized parameters' values (calculated from the three replications) and their standard deviation values for microelectrodes' cyclic voltammograms with TEMPO-based compound (left) and ammonium hexacyanoferrate (right). The resulting ratio between optimized surface area and measured geometric area is also given.

		TEMP	O-based		(NH) ₄ Fe(CN) ₆			
	Non-activated		Activated		Non-activated		Activated	
	Average	Std Dev	Average	Std Dev	Average	Std Dev	Average	Std Dev
k ⁰ [cm.s ⁻¹]	6.87E-04	3.22E-04	6.58E-03	4.16E-03	1.89E-05	9.32E-06	4.76E-03	2.46E-03
$A [cm^2]$	7.10E-04	1.41E-04	8.08E-04	2.03E-04	6.42E-04	8.82E-05	7.79E-04	1.32E-04
Atit/Ageo [-]	0.96	0.14	1.07	0.05	0.85	0.19	1.05	0.12
A: Electrode geometric area (cross section for carbon felt, cylinder area for microelectrode) [cm ²]								

A: Electrode geometric area (cross section for carbon felt, cylinder area for microelectrode) [cm²]



Quantitative assessment of several activation protocols





Effect of the activation technique on the ferrocyanide kinetics



Activation	<u>к° (ст/s)</u>
In 5 M HNO ₃	6.9×10 ⁻⁴
At 850 °C under CO ₂	3.2×10 ⁻³
In urea + 500 °C in air	8.5×10 ⁻³

Evaluation of aging of activation with time

Urea activation



— After activation	8.5×10⁻³ cm/s
— ~ 1.5 months later	5.1×10 ⁻³ cm/s
—— ~ 3 months later	2.3×10 ⁻³ cm/s

Undergoes possible modifications during cycling in the battery

In this work: effect of cycling on the aging of the graphite felt properties

Chosen electrolytes for cycling:





Posolyte: Ferrocyanide \rightarrow 0.9 M in water

Negolyte: Viologen derivative \rightarrow 0.9 M in 2 M NH₄Cl



Double half-cell reactor

• Evaluation of the effect of 1 redox system at a time



Double half-cell cycling

Experimental protocol



Analysis performed under 50 % SOC for both systems divided into 4 periods:

3 days initial stabilization at OCV
8 days at 150 mA cm⁻²
1 day at OCV
1 day at OCV after electrolyte exchange

EIS and load curves performed each 6 hours, when the cell was held at selected current density (0 or 150 mA cm^{-2}).

Felts tested: SGL non-activated and commercially activated

Membrane: FS950 used in dry form S_g = 20 cm² Flow rate: 40 mL/min T = 20 °C



Performed at UCT and UWB in Czech Republic



Electrode characterization

Ferrocyanide results

- Three electrodes setup: 1: WE = Micro-fiber electrode 2: RE = Ag/AgCl wire 3: WE = Graphite composite rod
- *v* = 100 mV/s





Micro-fiber electrodes: Triplicas prepared from the provided felt



Compared to the corresponding (act. or non-act. before cycling)

	350	$[K_4[Fe(CN)_6]] =$	0.75 M in	H_2O
	300	Neg. (Comp.	$\overline{}$
$\sqrt{cm^2}$	250	-		
i (mA	200	-		
	150			
	100			
	50			
_	0			E (V)
-0	.2	0.3	0.8	1.3
	-	$-\mu$ elec #1 $-\mu$ elec #2	—µelec #4	—SGL n.a.

	Non-ac	tivated	Commercially activated				
	E ½ (average) (V)	Raman: D/G ratio	E ½ (average) (V)	Raman: D/G ratio			
Before cycling	0.679 (± 0.010)	1.11 (± 0.06)	0.42 (± 0.060)	1.45 (± 0.07)			
Negative compartmen t	0.707 (± 0.038)	0.89 (± 0.07)	0.454 (± 0.080)	1.42 (± 0.04)			
Positive compartmen t	0.703 (± 0.043)	0.80 (± 0.10)	0.469 (± 0.073)	1.39 (± 0.05)			

Practically no impact on the kinetics \rightarrow i.e. no subsequent "activation"

Slight decrease of the E $\frac{1}{2}$ \rightarrow Not significant to consider impact on the kinetics



Electrode characterization

Non activated

Viologen results

-1



Commercially activated



[Viologen] = $1.22 \text{ M in } 2\text{M } \text{NH}_4\text{Cl}$ Pos. Comp.		E ½ (average) (V)	Raman: D/G ratio	E ½ (average) (V)	Raman: D/G ratio
50 - 50 - 50 - 50 - 50 - 50 - 50 - 50 -	Before cycling	-0.509	1.11 (± 0.06)	-0.514	1.45 (± 0.07)
E (V) -1 -0.8 -0.6 -0.4 -0.2 50 -	Negative compartmen t	-0.511 (± 0.001)	0.81 (± 0.08)	-0.509	1.39 (± 0.14)
-100 -	Positive compartmen t	-0.506 (± 0.003)	0.96 (± 0.25)	-0.523	1.33 (± 0.14)
				-	



Activation has no impact on the viologen kinetics \rightarrow fast system

Practically no variation of E $\frac{1}{2}$ \forall the history of the felt \rightarrow no impact on the kinetics \rightarrow no aging of the felt during cycling

Decrease of the Raman D/G ratio with high error values \rightarrow surface of the graphite is not homogeneous \rightarrow adsorption of viologen? Impact of viologen radical?



How active can be the graphite felt electrode in redox flow battery electrolyte? Close to 10^{-2} cm/s

But, quantitative evaluation of this reaction rate is rather challenging on porous electrodes. Different approaches were evaluated including microfiber electrochemistry and scanning electrochemical gel microscopy (not shown today).

Microfiber electrochemistry allows accessing information about the stability of the carbon electrode, when aged in air, and after redox flow battery experiments.

Higreew provided us an excellent opportunity to enhance the methodology used for quantitatively evaluating the rate of electron transfer in redox flow batteries.

This knowledge must now be combined with controlled construction of the 3D structure of porous electrode with high reaction rate for improved mass transfer and power density of aqueous organic redox flow batteries.





Thank you!





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