HIGREEW

First Project Workshop

In Pilsen and Online

Activated vs non-activated: quantitative assessment of reactivity for optimizing RFB electrodes

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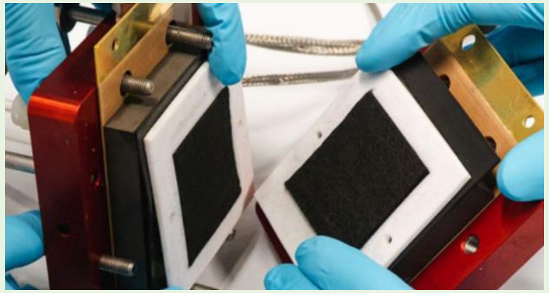
CNRS, 3.02.2022

The research leading to these results has received funding from the European Union under Grant Agreement no. 875613

Carbon Felt
characterization

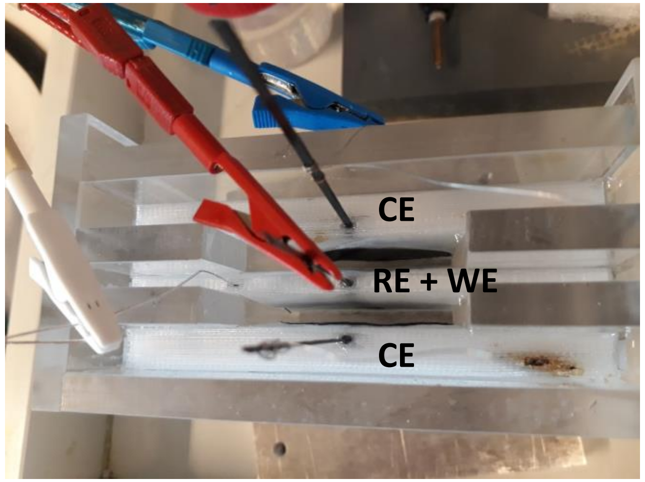
Macroscale | **Microscale** | **Local**



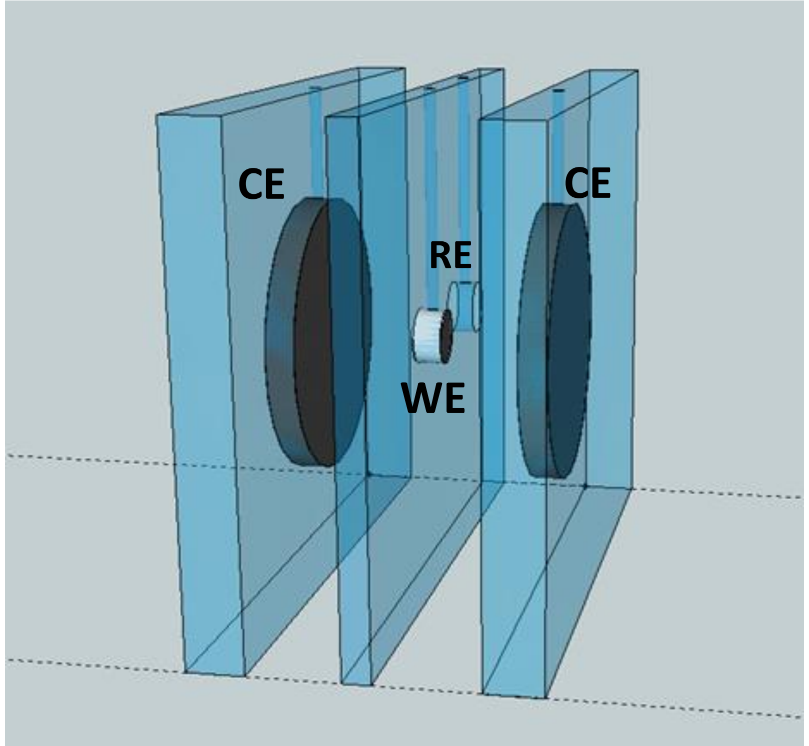
- In-situ and operando measurements, close to real-device applications
- Geometry complexity (porosity, compact tangled fibers, high specific surface)
- Difficult to quantify certain parameters (e.g. kinetics)

Experimental setup for porous macro felt studies

Top view

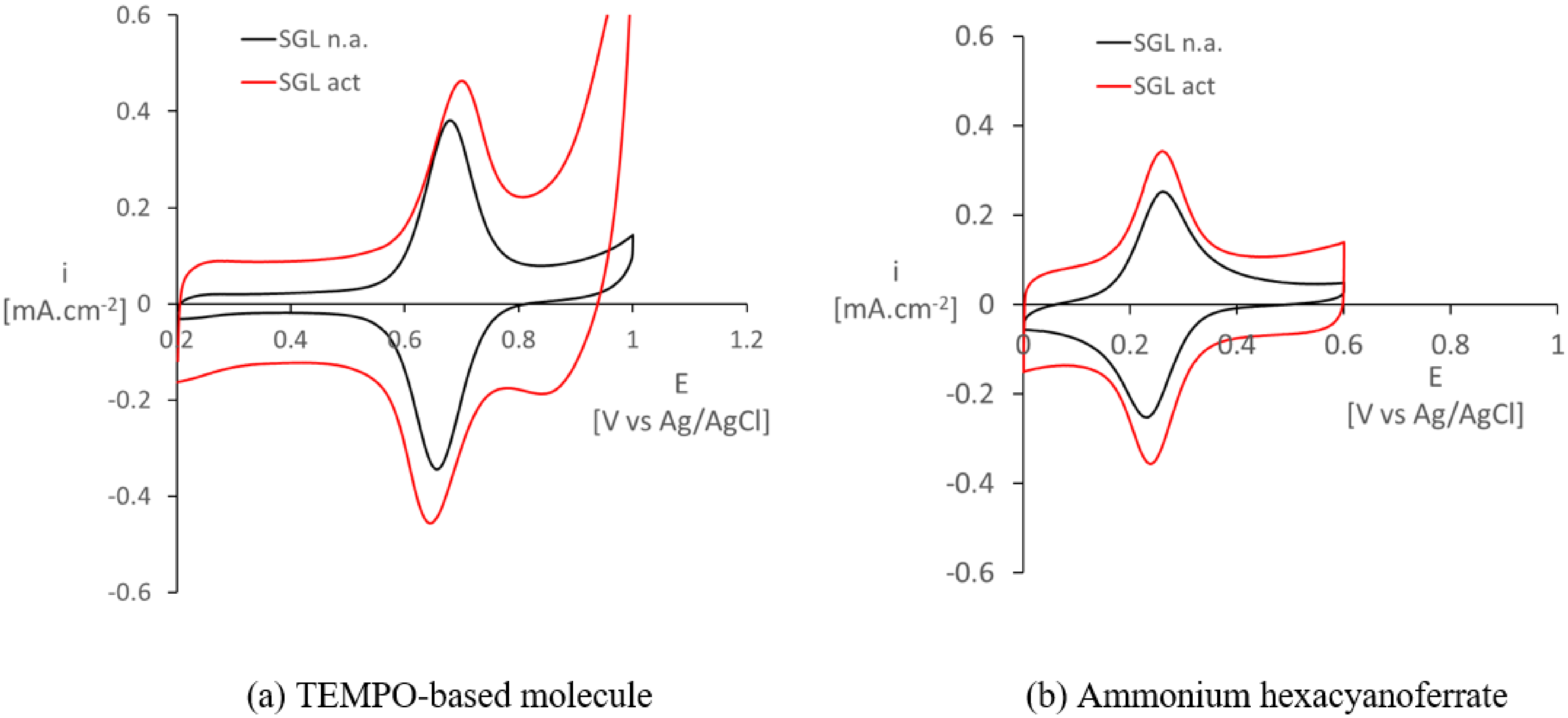


Side/3D view



- Working electrode: studied carbon felt (SGL GFD 4.6 mm, non-activated and commercially activated); d = 1 cm
- Reference electrode: Ag/AgCl pseudo-reference
- Counter electrodes: carbon felt; d = 5 cm

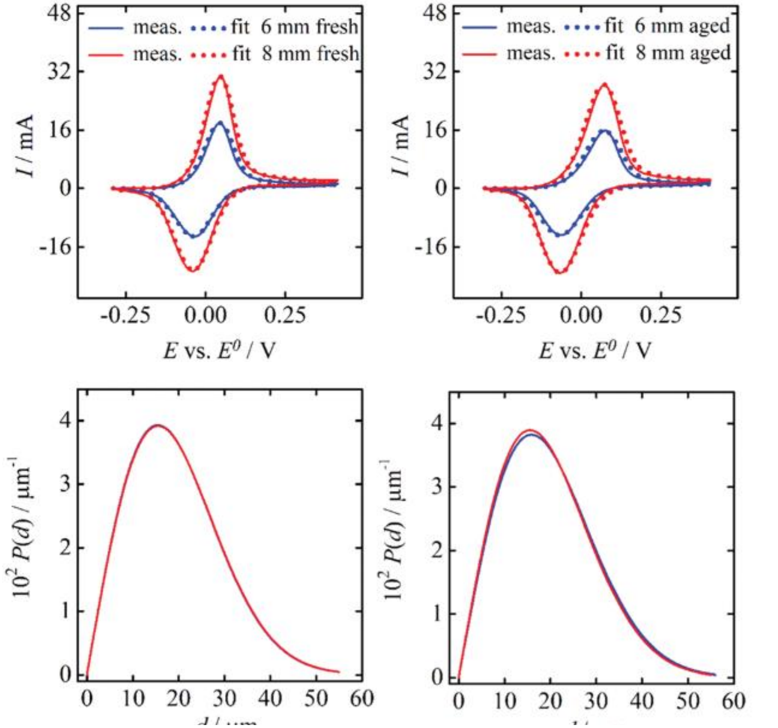
<u>Studied electrolytes</u>:
TEMPO derivate molecule: 10^{-4} M in 1 M NaCl
Ammonium ferrocyanide: 10^{-4} M in 1 M NH_4Cl



(a) TEMPO-based molecule (b) Ammonium hexacyanoferrate

Figure 1: Typical cyclic voltammograms (scan rate: 10 mV.s^{-1}*) on SGL graphite felts with (a) TEMPO-based molecule and (b) ammonium hexacyanoferrate*

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



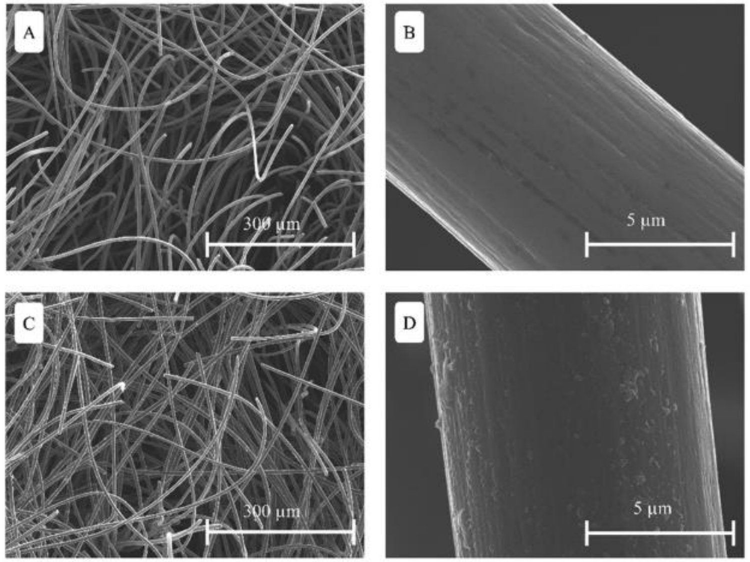


Fig. 4 SEM data acquired for pristine (A and B) and electrochemically aged (C and D) GFD4.6 carbon felt electrodes. From A and C it can be seen, that the assumption of just one fiber radius is sufficient. From B and D the approximate fiber radius of 4.2 µm was extracted.

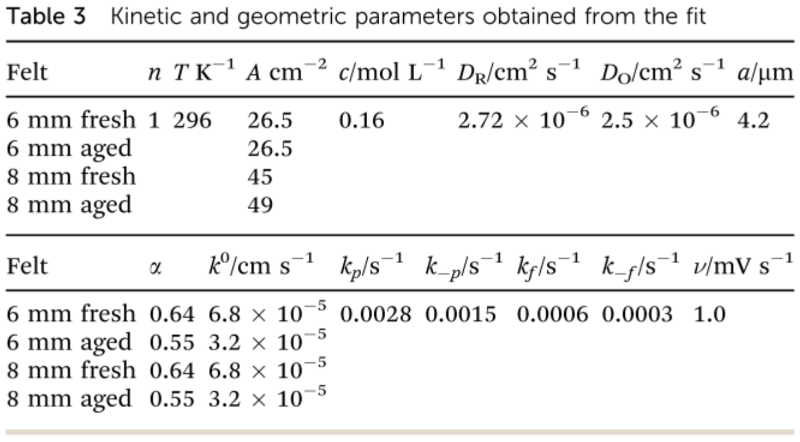


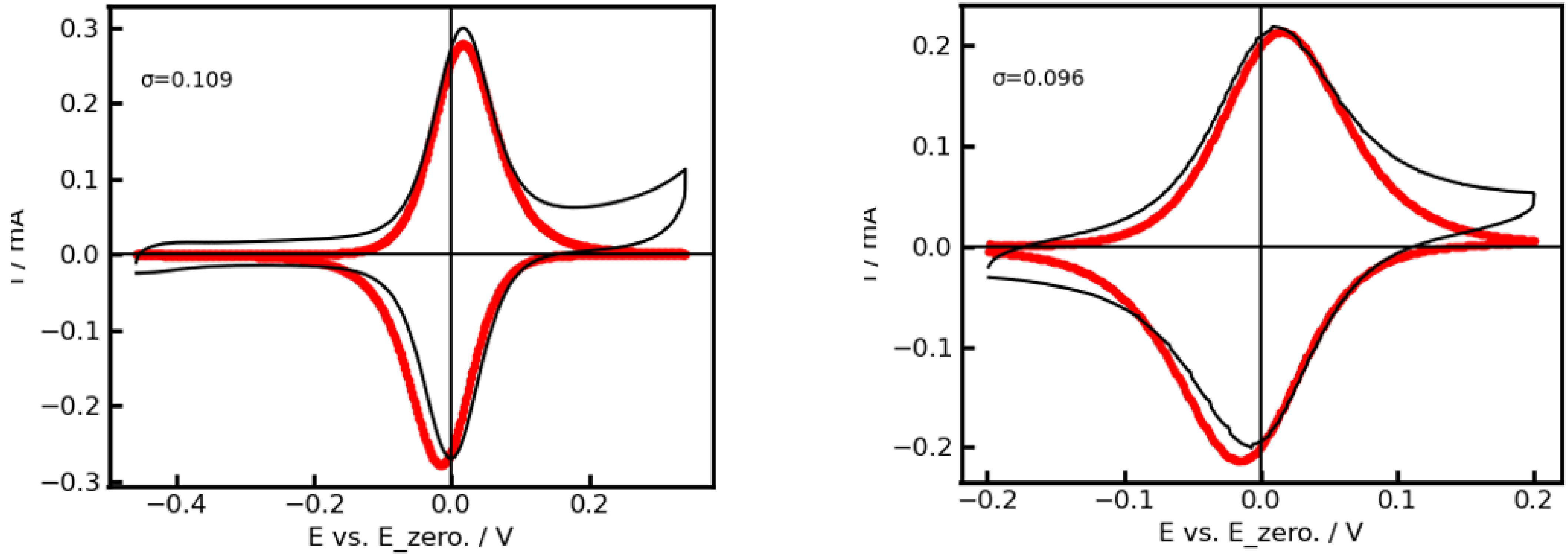
Table 3 Kinetic and geometric parameters obtained from the fit

Felt	n	T K^{-1}	A cm^{-2}	c/mol L^{-1}	D_R/cm^2 s^{-1}	D_O/cm^2 s^{-1}	a/µm
6 mm fresh	1	296	26.5	0.16	2.72×10^{-6}	2.5×10^{-6}	4.2
6 mm aged			26.5				
8 mm fresh			45				
8 mm aged			49				

Felt	α	k^0/cm s^{-1}	k_p/s^{-1}	k_{-p}/s^{-1}	k_f/s^{-1}	k_{-f}/s^{-1}	ν/mV s^{-1}
6 mm fresh	0.64	6.8×10^{-5}	0.0028	0.0015	0.0006	0.0003	1.0
6 mm aged	0.55	3.2×10^{-5}					
8 mm fresh	0.64	6.8×10^{-5}					
8 mm aged	0.55	3.2×10^{-5}					

Système VO^{2+}/VO_2^+

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.



(a) TEMPO-based

(b) $(NH_4)Fe(CN)_6$

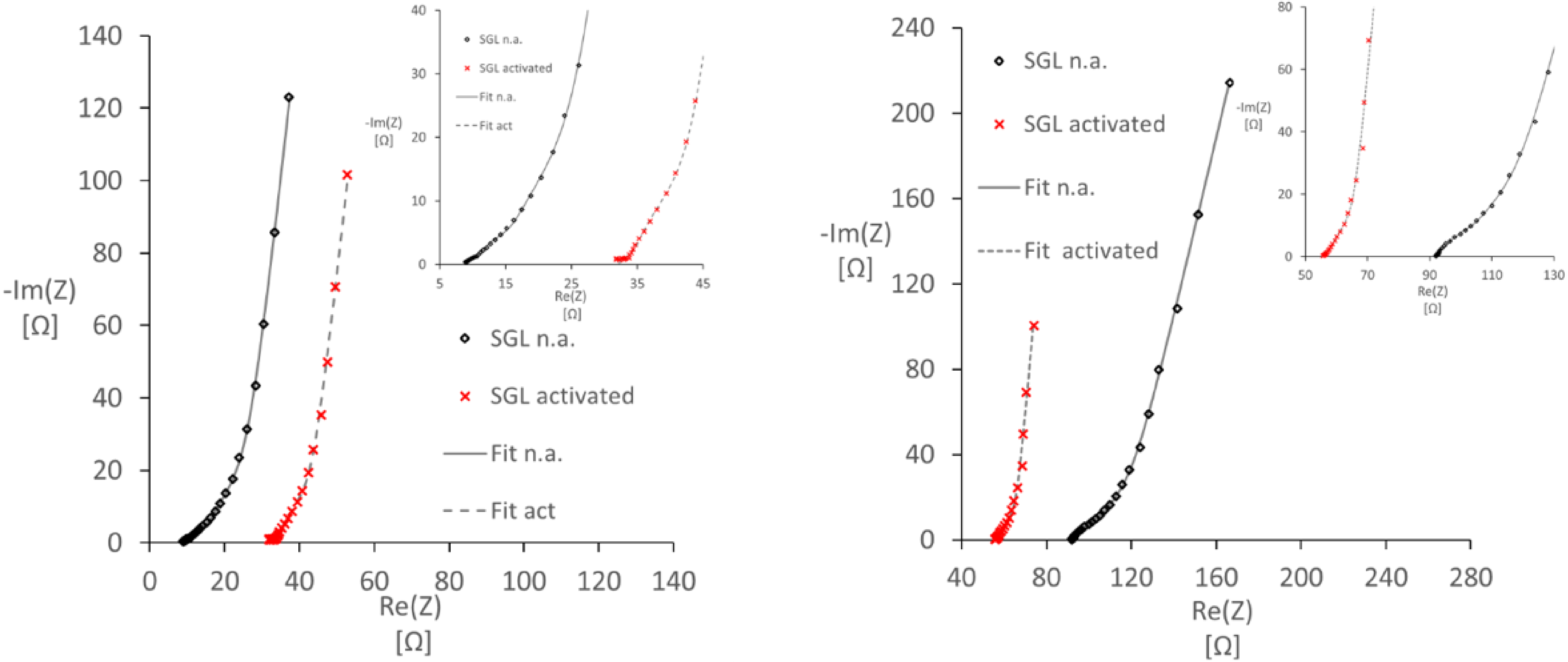
$k^0 = 1.0\ 10^{-2}$ cm.s^{-1}

$k^0 = 1.0\ 10^{-2}$ cm.s^{-1}

$A_{total} = 60$ cm^2

$A_{total} = 45$ cm^2

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.



(a) TEMPO-based Nyquist diagram

(b) $(NH_4)_4Fe(CN)_6$ Nyquist diagram

Figure 3: Nyquist diagrams of EIS experiments on SGL graphite felt with TEMPO-based molecule (left) at estimated formal potential ($E^{0\prime}$ = 0.66 V vs Ag/AgCl quasi-reference) and with $(NH_4)_4Fe(CN)_6$ molecule (right) at estimated formal potential ($E^{0\prime}$ = 0.25 V vs Ag/AgCl quasireference)

For analysis of the impedance spectra with graphite felts, the macrohomogeneous model developed by Paasch, Micka and Gersdorf was used, in addition to some minor modifications.

R_{ohm}: Ohmic resistance [Ω]

C: *Double-layer capacitance* [F.cm^{-2}]

γ: CPE exponent

k^0: *Heterogeneous charge transfer kinetic constant* [cm.s^{-1}]

l_p: *Diffusion layer thickness* [cm]

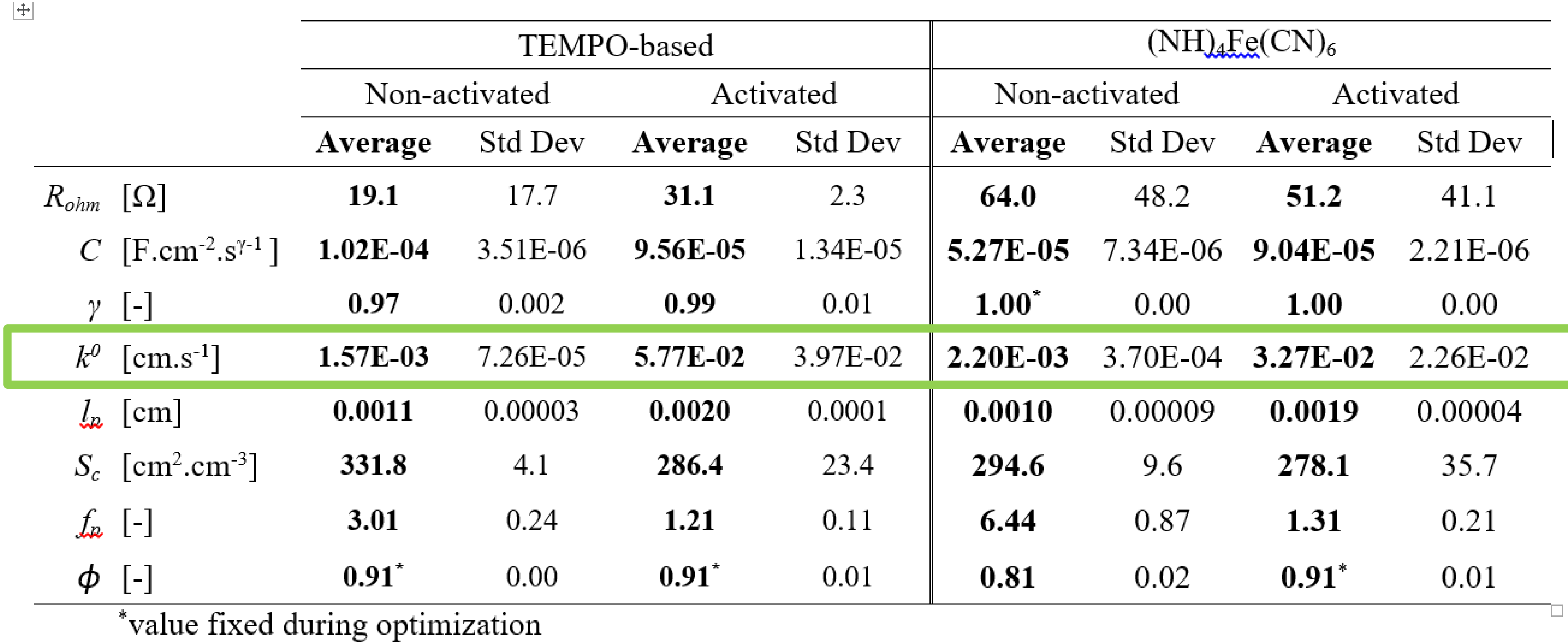
S_c: *Specific surface area* [cm^2.cm^{-3}]

f_p: *Tortuosity coefficient*

ϕ: *Non-uniform diffusion exponent*

G. Paasch, K. Micka, and P. Gersdorf, “Theory of the electrochemical impedance of macrohomogeneous porous electrodes,” *Electrochim. Acta*, vol. 38, no. 18, pp. 2653–2662, 1993, doi: 10.1016/0013-4686(93)85083-B.

Table 2: Averaged optimized parameters' values (calculated from the three replications) and their standard deviation values for EIS experiments carried out on SGL graphite felt with TEMPO-based molecule (left) at estimated formal potential of 0.66 V vs Ag/AgCl and with ammonium hexacyanoferrate (right) at estimated formal potential of 0.25 V vs Ag/AgCl



	TEMPO-based				$(NH_4)_4Fe(CN)_6$			
	Non-activated		Activated		Non-activated		Activated	
	Average	Std Dev	**Average**	Std Dev	**Average**	Std Dev	**Average**	Std Dev
R_{ohm} [Ω]	**19.1**	17.7	**31.1**	2.3	**64.0**	48.2	**51.2**	41.1
C [$F.cm^{-2}.s^{\gamma-1}$]	**1.02E-04**	3.51E-06	**9.56E-05**	1.34E-05	**5.27E-05**	7.34E-06	**9.04E-05**	2.21E-06
γ [-]	**0.97**	0.002	**0.99**	0.01	**1.00***	0.00	**1.00**	0.00
k^0 [$cm.s^{-1}$]	**1.57E-03**	7.26E-05	**5.77E-02**	3.97E-02	**2.20E-03**	3.70E-04	**3.27E-02**	2.26E-02
l_p [cm]	**0.0011**	0.00003	**0.0020**	0.0001	**0.0010**	0.00009	**0.0019**	0.00004
S_c [$cm^2.cm^{-3}$]	**331.8**	4.1	**286.4**	23.4	**294.6**	9.6	**278.1**	35.7
f_p [-]	**3.01**	0.24	**1.21**	0.11	**6.44**	0.87	**1.31**	0.21
ϕ [-]	**0.91***	0.00	**0.91***	0.01	**0.81**	0.02	**0.91***	0.01

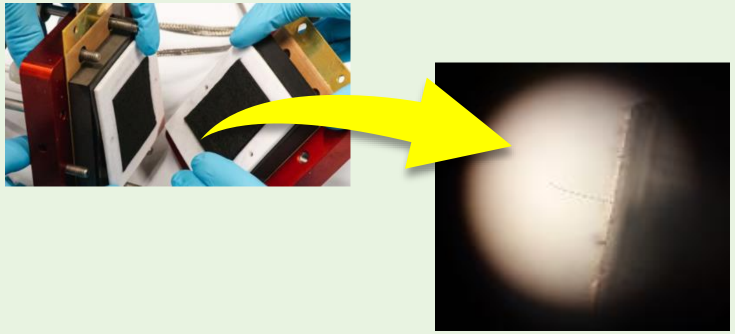
*value fixed during optimization

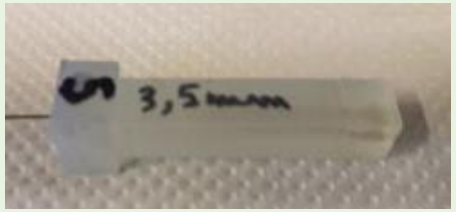
Carbon Felt
characterization

Macroscale

Microscale

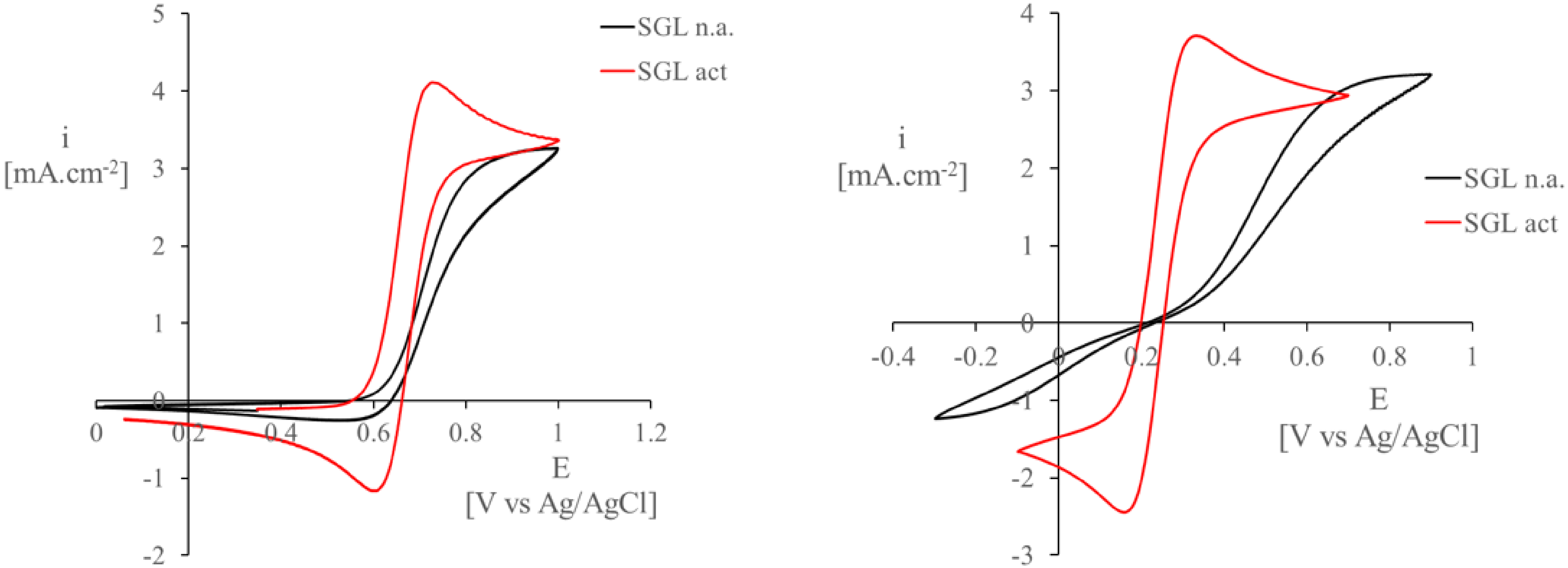
Local





Microelectrodes: Fibers extracted from the same carbon felt

- Ex-situ measurements
- Well-defined geometry
- Relatively more time-consuming process



(a) TEMPO-based molecule (b) Ammonium hexacyanoferrate

Figure 4: Typical cyclic voltammograms (scan rate: 100 mV.s^{-1}) on carbon fibre microelectrode plotted on micro-fibres extracted from SGL graphite felt with (a) TEMPO-based molecule and (b) ammonium hexacyanoferrate

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.

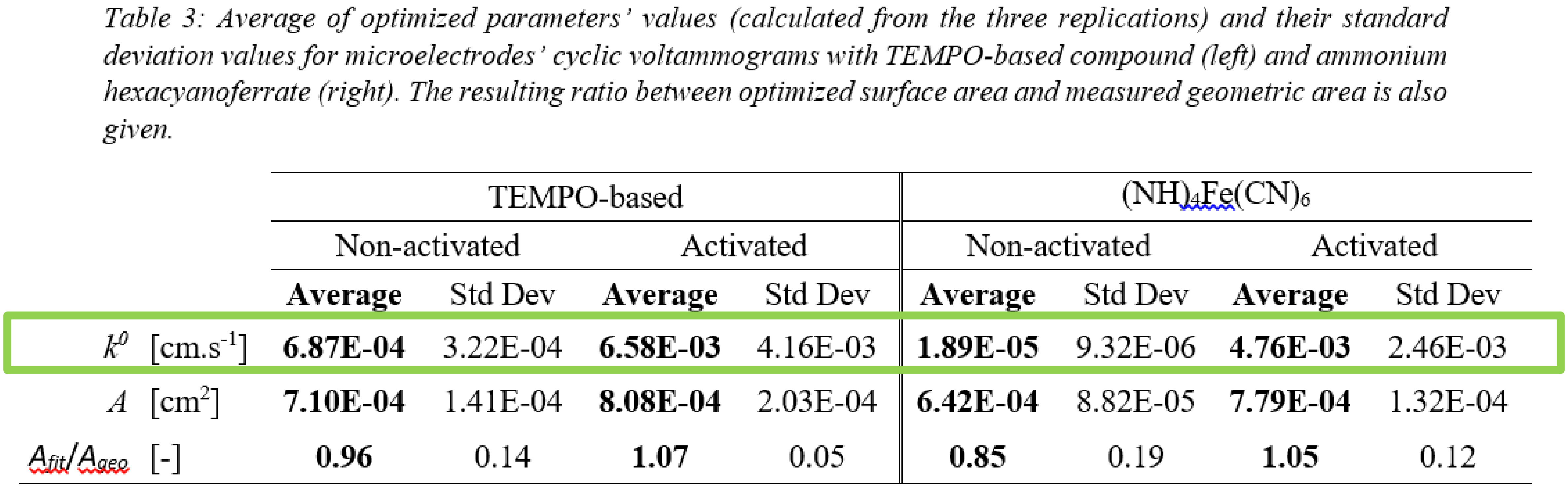
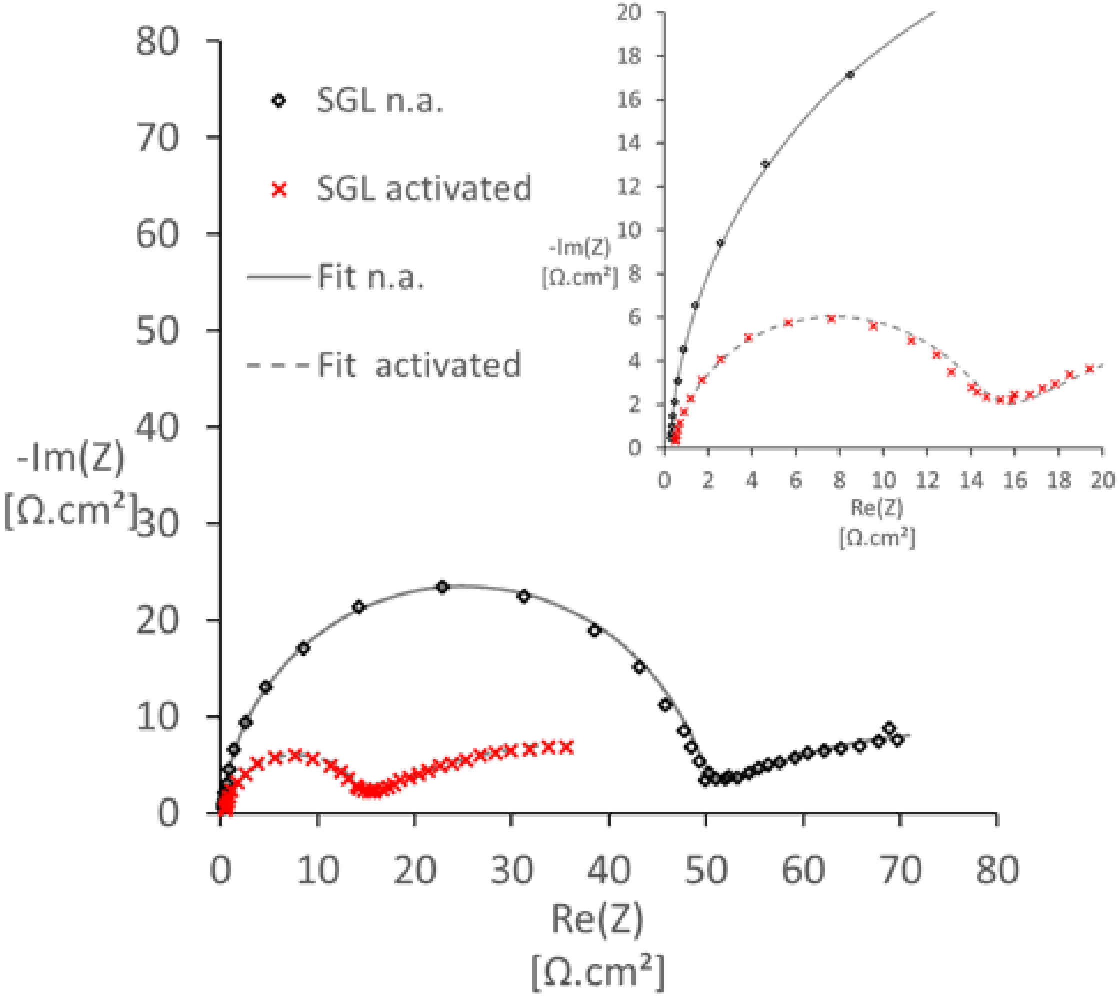


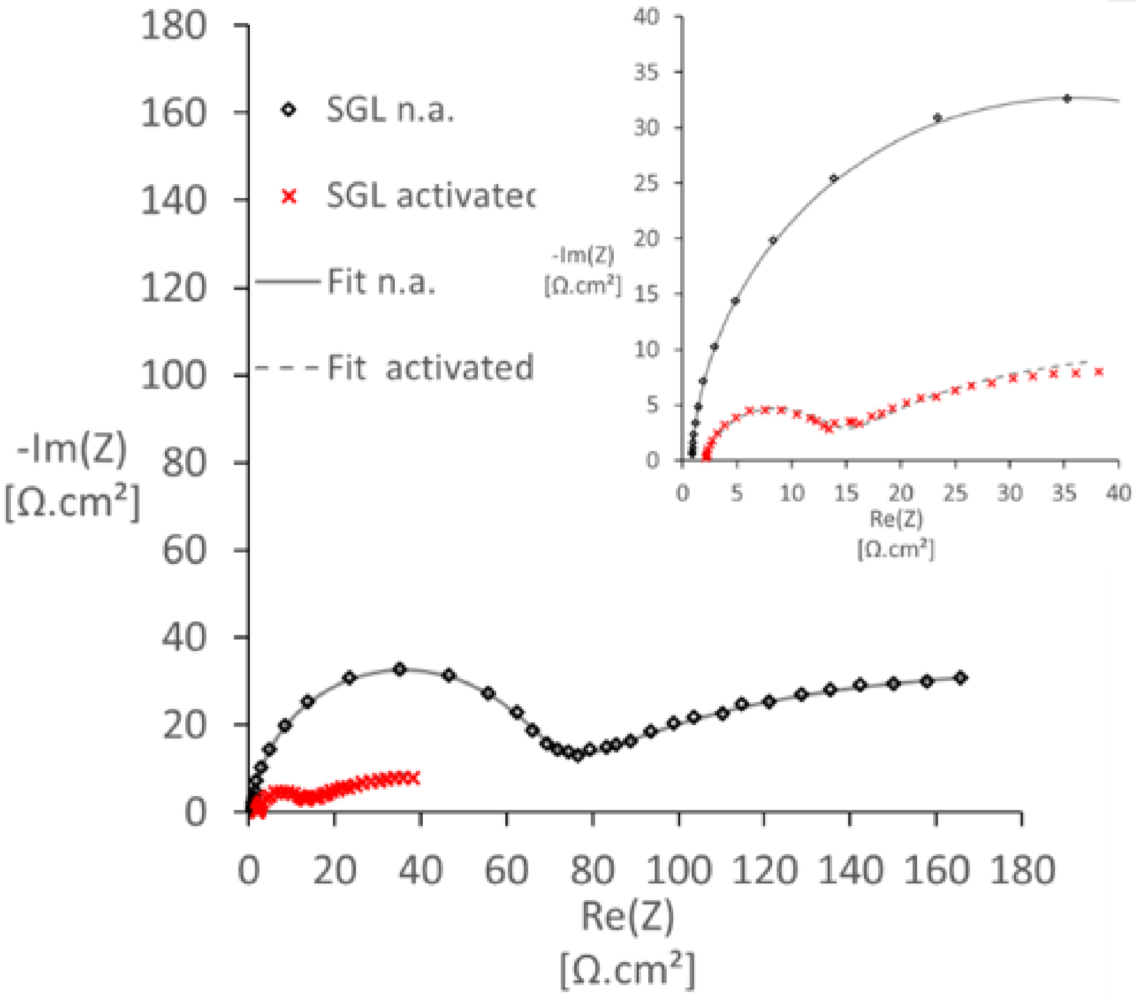
Table 3: Average of optimized parameters' values (calculated from the three replications) and their standard deviation values for microelectrodes' cyclic voltammograms with TEMPO-based compound (left) and ammonium hexacyanoferrate (right). The resulting ratio between optimized surface area and measured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

	TEMPO-based				$(NH)_4Fe(CN)_6$			
	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
A_{fit}/A_{geo} [-]	**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) TEMPO-based Nyquist diagram



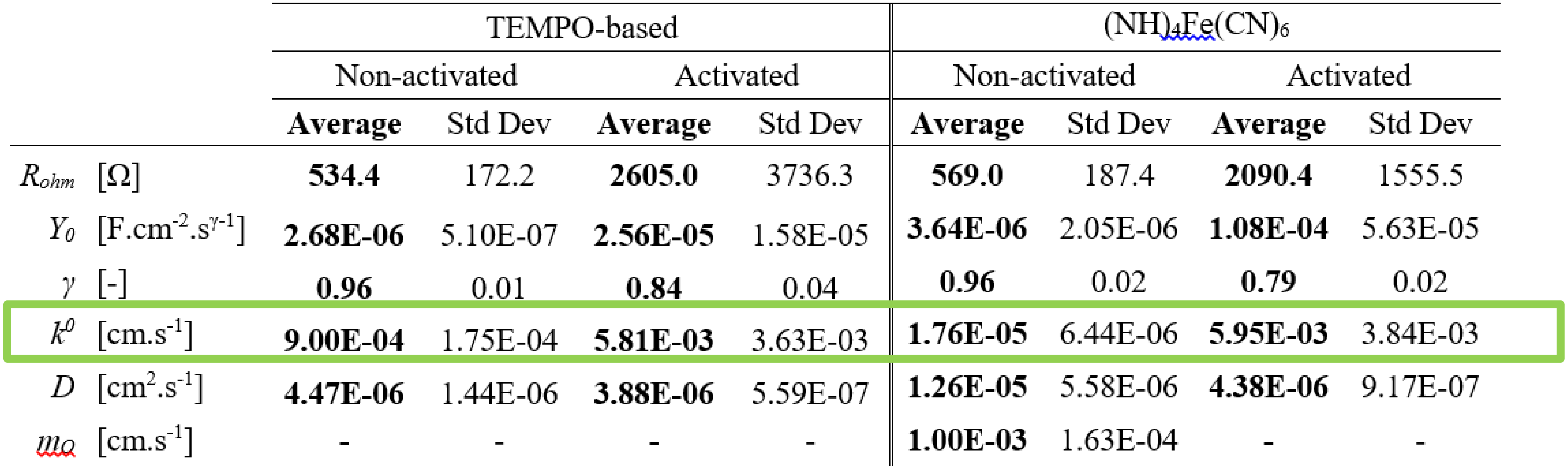
(b) $(NH_4)_4Fe(CN)_6$ Nyquist diagram

Carbon fibres microelectrodes can be reasonably represented as cylindrical electrodes and impedance at their surface can then simply be modelled with a Randle circuit.

Landon-Lane and co-authors mentioned problems in convergence when using this expression and suggested the use of a simplified equation with errors in real and imaginary parts not exceeding 4% of their original values [21].

[21] L. Landon-Lane, A. T. Marshall, and D. A. Harrington, “EIS at carbon fiber cylindrical microelectrodes,” *Electrochem. commun.*, vol. 109, no. September, p. 106566, 2019, doi: 10.1016/j.elecom.2019.106566.

R_{ohm}: Ohmic resistance [Ω]
Y_0: Pseudo-capacitance (for microelectrode model)[$F.cm^{-2}.s^{(\gamma-1)}$]
γ: CPE exponent
D: Diffusion coefficient [$cm^2.s^{-1}$]
m_O: Mass transfer coefficient [$cm.s^{-1}$]



		TEMPO-based				$(NH)_4Fe(CN)_6$			
		Non-activated		Activated		Non-activated		Activated	
		Average	Std Dev	**Average**	Std Dev	**Average**	Std Dev	**Average**	Std Dev
R_{ohm}	[Ω]	**534.4**	172.2	**2605.0**	3736.3	**569.0**	187.4	**2090.4**	1555.5
Y_0	[$F.cm^{-2}.s^{\gamma-1}$]	**2.68E-06**	5.10E-07	**2.56E-05**	1.58E-05	**3.64E-06**	2.05E-06	**1.08E-04**	5.63E-05
γ	[-]	**0.96**	0.01	**0.84**	0.04	**0.96**	0.02	**0.79**	0.02
k^0	[$cm.s^{-1}$]	**9.00E-04**	1.75E-04	**5.81E-03**	3.63E-03	**1.76E-05**	6.44E-06	**5.95E-03**	3.84E-03
D	[$cm^2.s^{-1}$]	**4.47E-06**	1.44E-06	**3.88E-06**	5.59E-07	**1.26E-05**	5.58E-06	**4.38E-06**	9.17E-07
m_O	[$cm.s^{-1}$]	-	-	-	-	**1.00E-03**	1.63E-04	-	-

Conclusions

k^0 values analysed from micro-fibres are systematically lower than that analysed from macro-felts where the differences may reach *ca.* two orders of magnitude in some cases.

The reason for these discrepancies is unclear but one possible explanation could be the analytical model for macro-felts, where the geometrical approximations might not always correspond well to the experimental systems.

From the practical point of view, direct measurements on macro-felts are more convenient and straightforward.

On the other hand, measurements on extracted micro-fibres may reveal more sensitively the kinetic difference for electrode materials undergoing different treatments. Moreover, they may also provide information on the heterogeneity of the felt by extracting fibres randomly from different areas

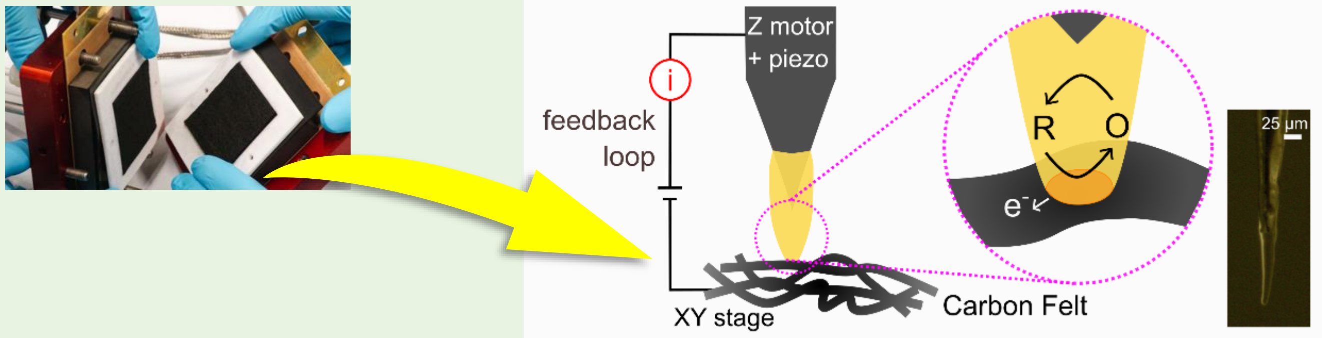
Possible outlook: non destructive measurement at microscale to extract kinetic information

Carbon Felt
characterization

Macroscale

Microscale

Local



Targeting individual fibers in the felt: Scanning Gel Electrochemical Microscope

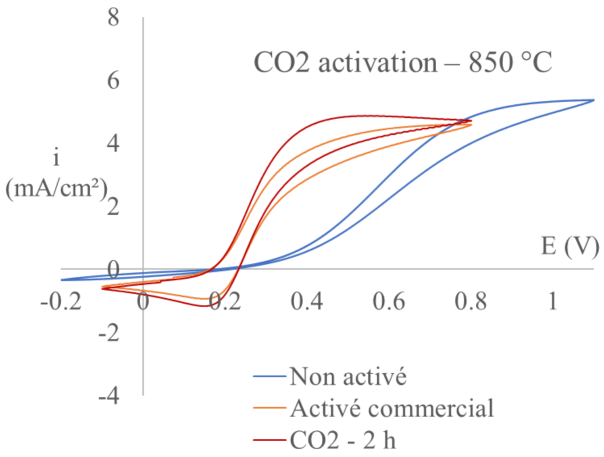
- Target particular areas of the substrate (e.g. bending parts)
- In-situ measurements
- Non-destructive
- Fast kinetics

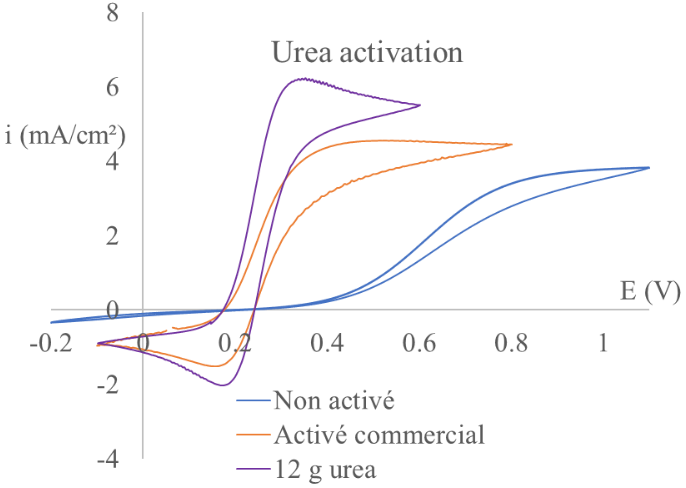
Quantitative assessment of several activation protocols

Thermal activation
- CO_2 atmosphere at 850 °C
- Air atmosphere at 400 °C

Activation in solution
- Acidic 5 M HNO_3 at 70 °C
- Fenton’s reagent at ambient temperature

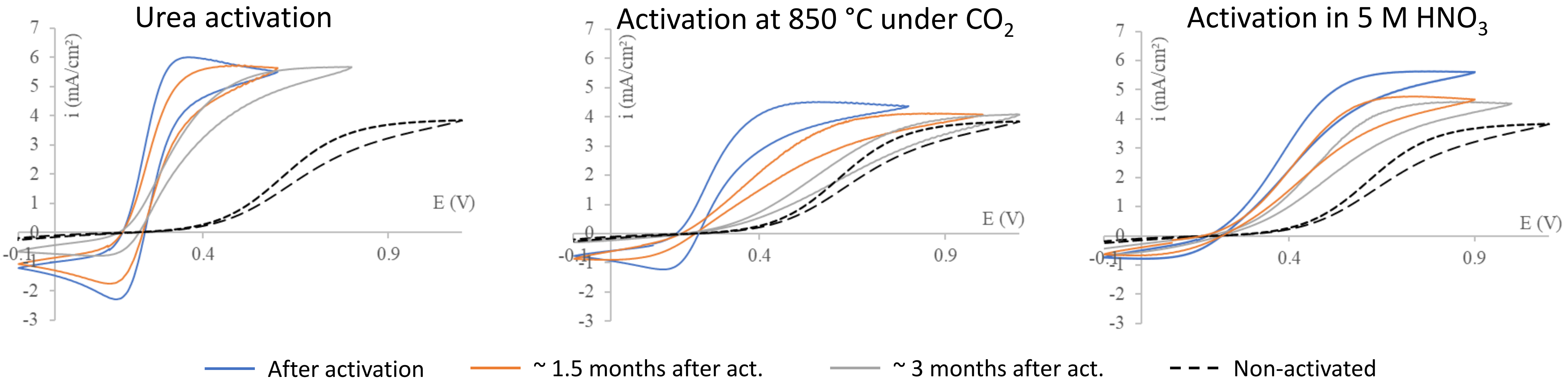
Mixed activation in 2 steps: 1) soaking in urea solution at ambient temperature
2) thermal treatment at 500 °C





Degradation of activation over time

- Degradation of the kinetic response of ferrocyanide was noticed some time after activation of the initial carbon felt
- Measurement 1.5 and 3 months after activation for the “optimal” activation of each technique



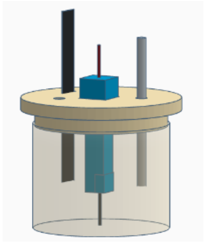
Urea activation

Activation at 850 °C under CO_2

Activation in 5 M HNO_3

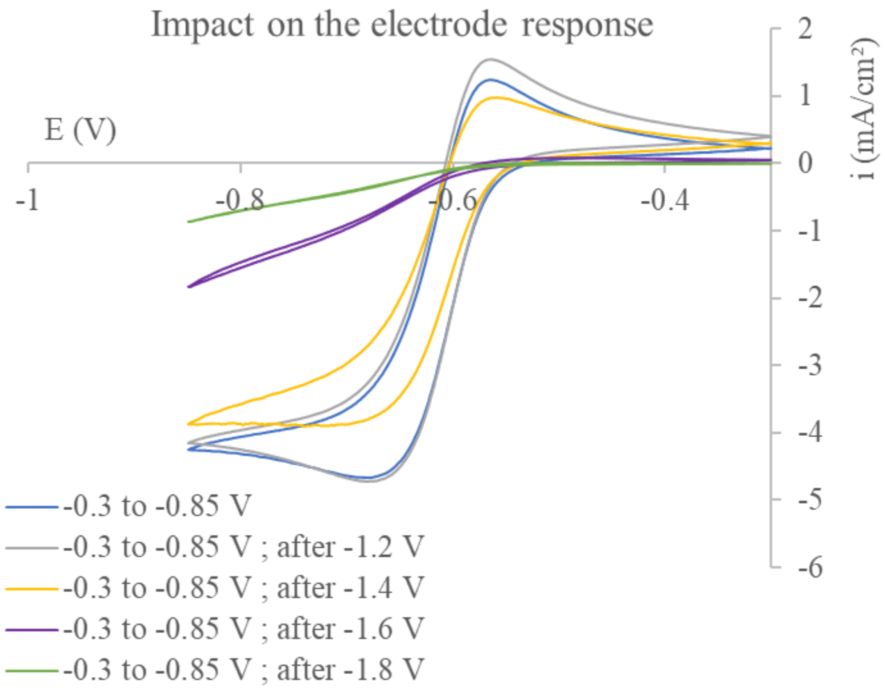
Degradation during characterization

$[SPr_2V] = 10^{-2}$ M in 2 M NH_4Cl



v = 100 mV/s

Ag/AgCl pseudo-ref
Graphite composite CE



Any reaction beyond -1.4 V impacts irreversibly the electrode

In the operating potential range of the battery, the electrode appears to be stable

Conclusions:

- Quantitative kinetic data were obtained for graphite felt materials
- Different material treatments were tried, and their influence on the electron transfer kinetic was determined
- Optimal materials for the Higreew electrolytes were determined
- Microscale measurement gives also an opportunity to evaluate aging/degradation of the electrodes

Thank you!

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Disclaimer/ Acknowledgment

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 875613. The information and views set out in this publication does not necessarily reflect the official opinion of the European Commission. Neither the European Union institutions and bodies nor any person acting on their behalf, may be held responsible for the use which may be made of the information contained therein.