Supporting Information for:

Anion Storage Behavior of Graphite Electrode in $LiBF_4$/Sulfone/Ethyl Methyl Carbonate Solutions

Yunju Wang[†, ‡], *Jiayu Li*[†, ‡], *Yuhao Huang*[†, ‡], *and Hongyu Wang*[*, †, ‡]

[†]State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences,5625 Renmin Street, Changchun 130022, Jilin, China

[‡]School of Applied Chemistry and Engineering, University of Science and Technology of China, Hefei 230026, Anhui, China

[*]Phone/Fax: 86-431-85262287; E-mail: hongyuwang@caic.ac.cn

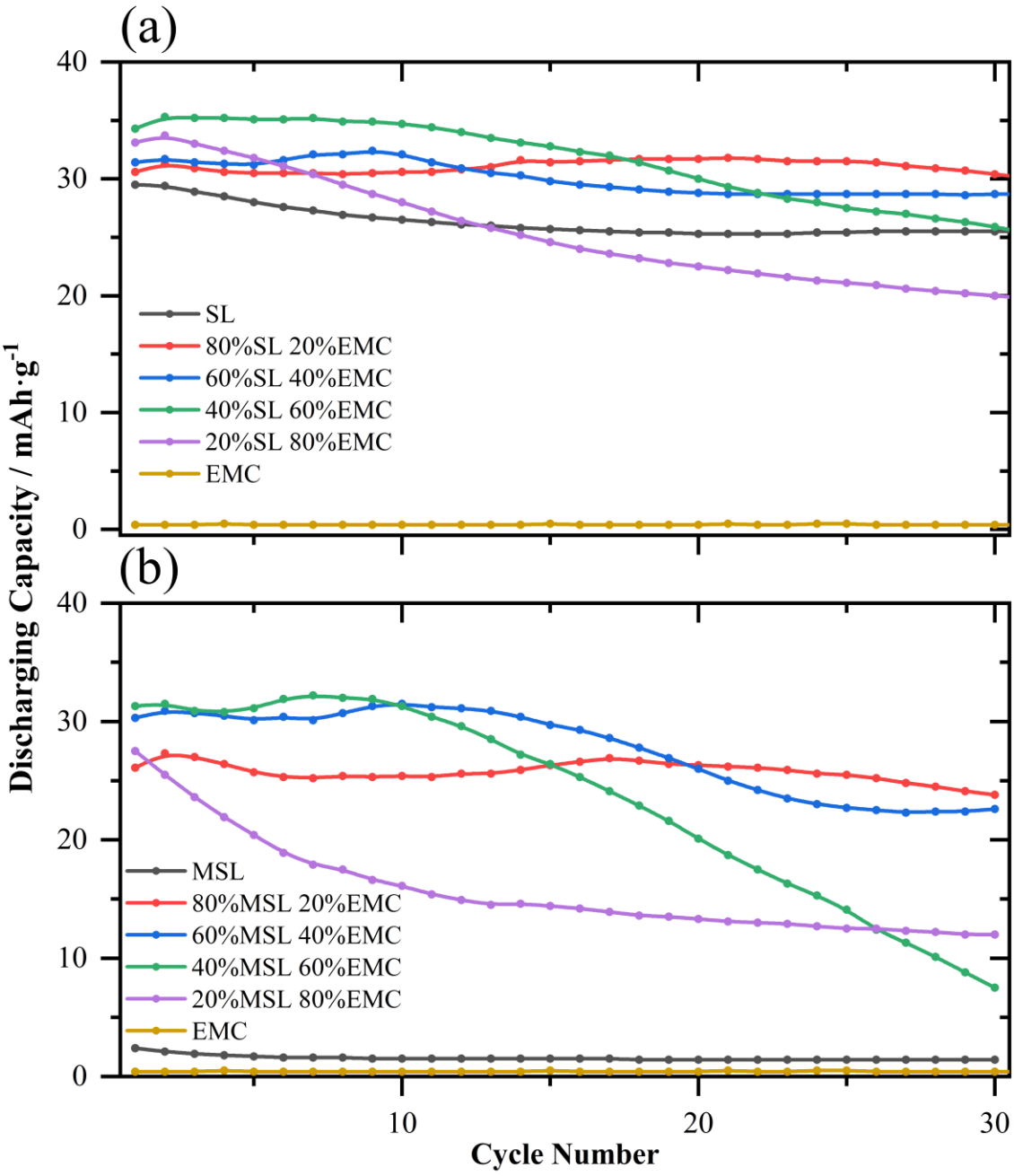


Figure S1. Cycle performance of the Li/graphite cells using different solutions: (a) 1M $LiBF_4$/EMC/SL (b). 1M $LiBF_4$/EMC/MSL.

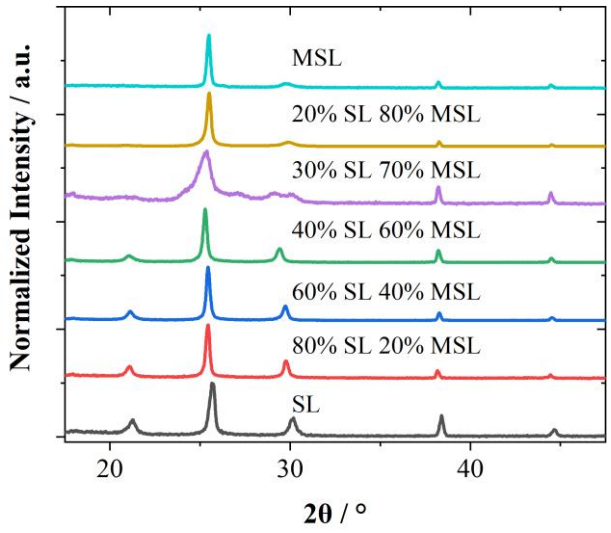


Figure S2. Ex situ XRD patterns of graphite electrodes in 1M $LiBF_4$/SL/MSL electrolyte. The graphite electrodes were charged to 5.0V (vs. Li^+ / Li) and then held for 30 minutes in solutions before XRD test.

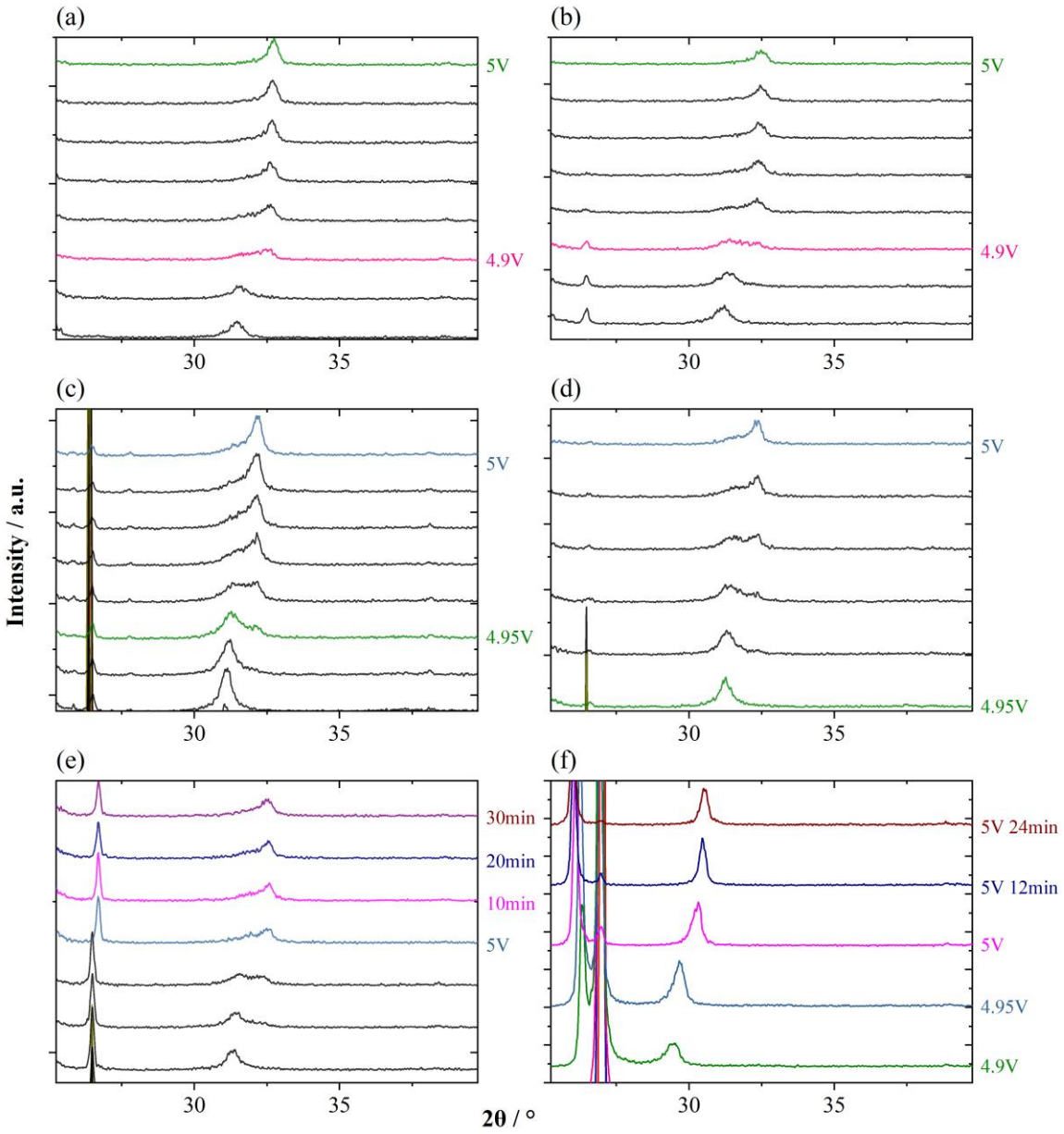
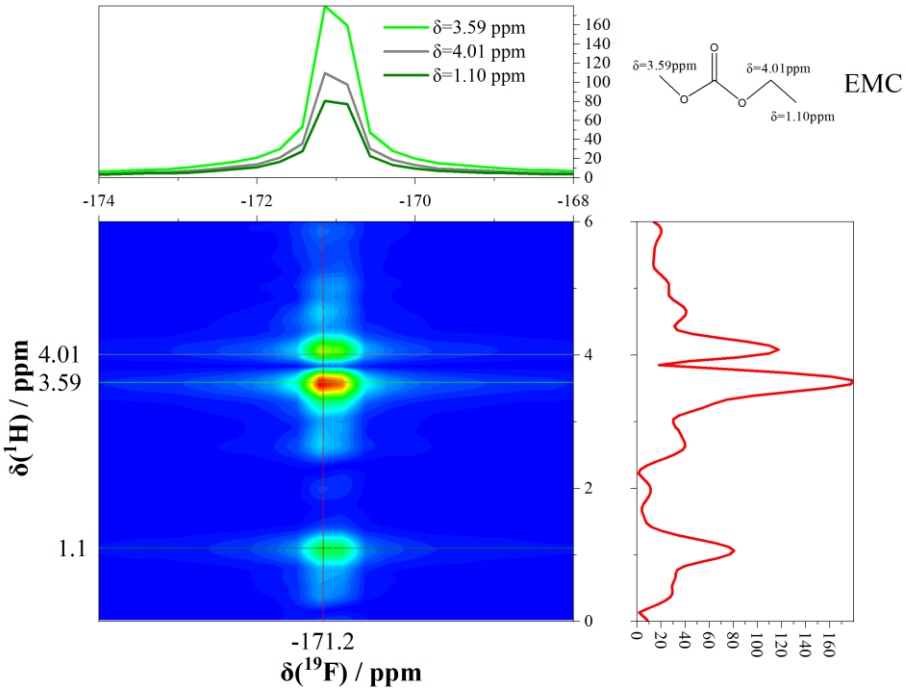
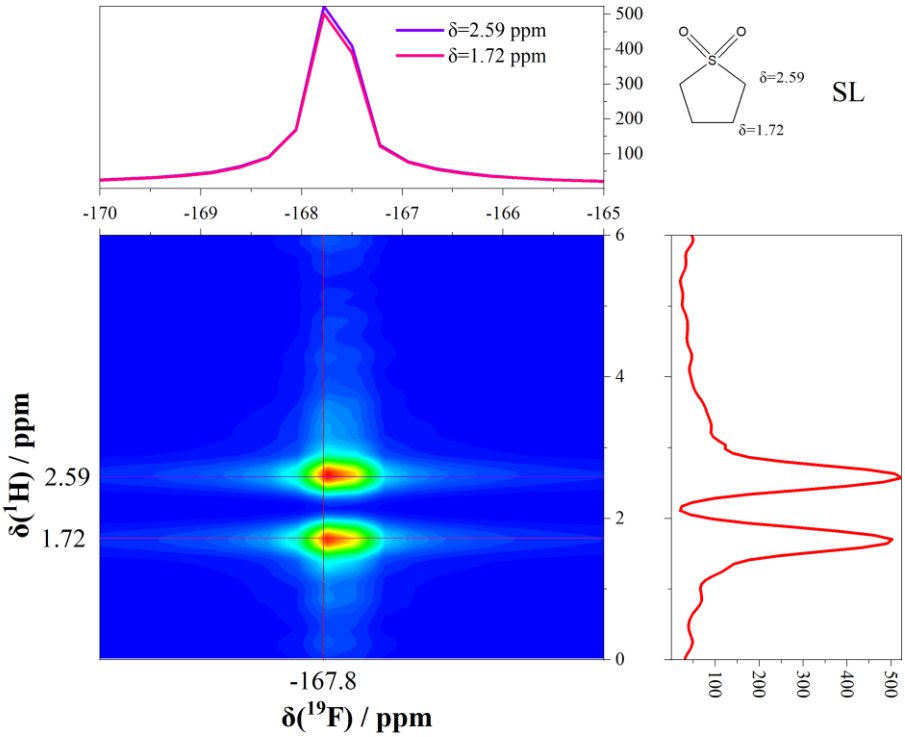


Figure S3. Enlargement of the rectangular areas where the phase transformations proceed in Figure 5. As a reference, Figure S3 (f) stands for the case in the absence of such transformation where the peaks of graphite charged in pure SL keep symmetrical and smooth.

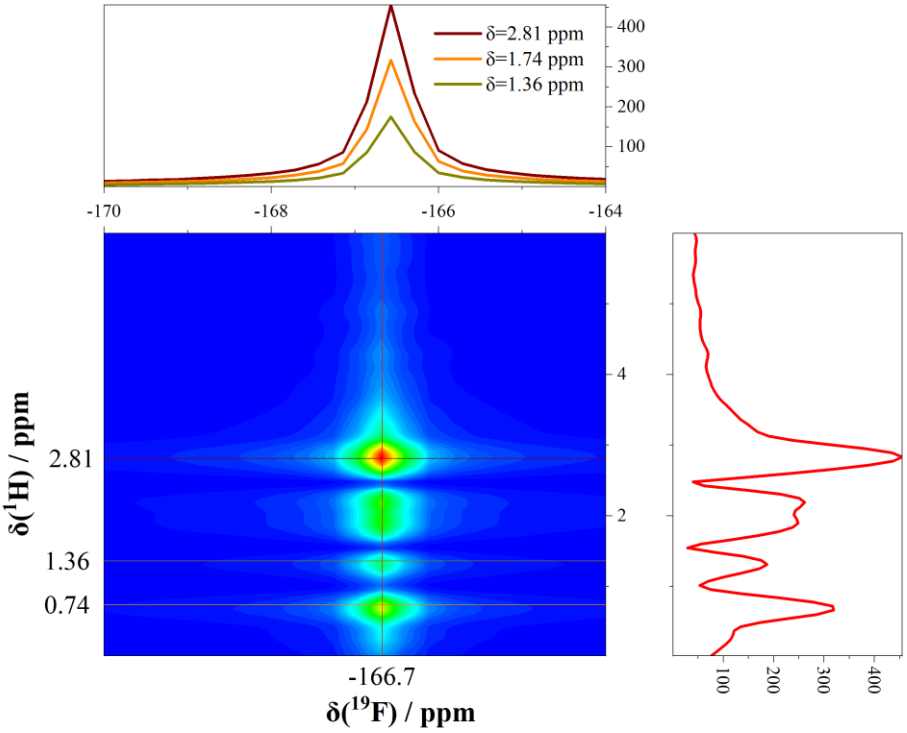
(a)


δ=3.59 ppm
δ=4.01 ppm
δ=1.10 ppm
δ=3.59ppm
δ=4.01ppm
δ=1.10ppm
EMC
δ(1H) / ppm
4.01
3.59
1.1
-171.2
δ(19F) / ppm

(b)


δ=2.59 ppm
δ=1.72 ppm
δ=2.59
δ=1.72
SL
δ(1H) / ppm
2.59
1.72
-167.8
δ(19F) / ppm

(c)


δ=2.81 ppm
δ=1.74 ppm
δ=1.36 ppm
400
300
200
100
-170
-168
-166
-164
4
2
2.81
1.36
0.74
δ(1H) / ppm
-166.7
δ(19F) / ppm
100
200
300
400

(d)

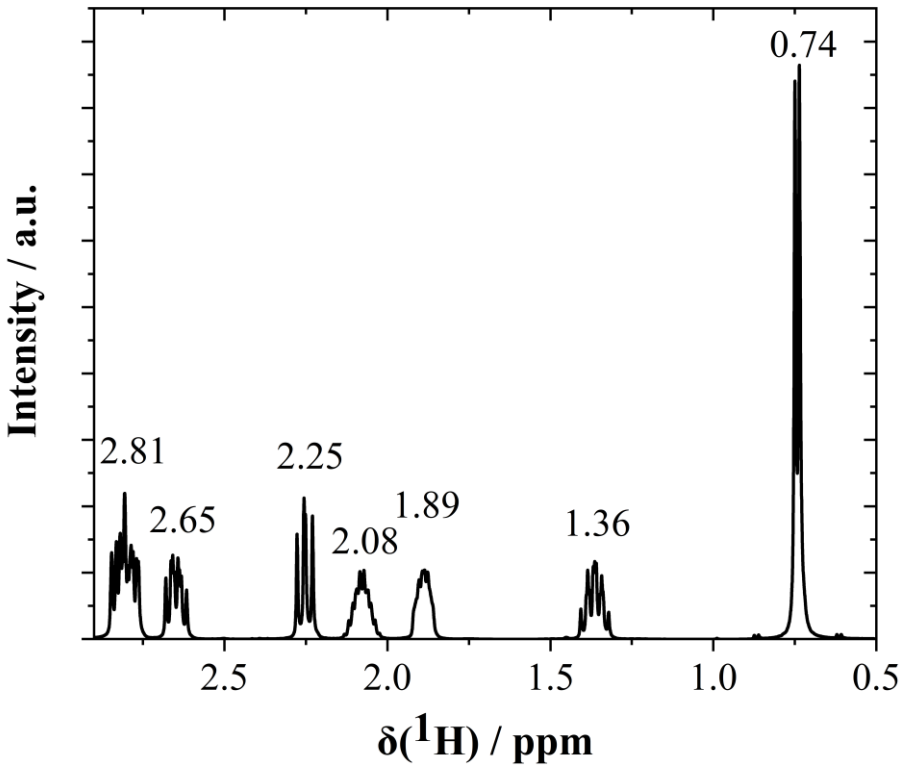

0.74
2.81
2.65
2.25
2.08
1.89
1.36
Intensity / a.u.
2.5
2.0
1.5
1.0
0.5
δ(1H) / ppm

Figure S4. $^{1}H - ^{19}F$ HOESY spectra of 1M $LiBF_4$ in (a). EMC (b). SL (c). MSL and (d)^{1}H NMR spectrum of 1M $LiBF_4$ in MSL. The chemical shifts of ^{1}Hs labeled near the structure formula are gotten from ^{1}H NMR spectra for pure solvents. In Figure S4 (a), (b) and (c), the stronger signals appear in the positions with higher chemical shifts. Besides the number of the atoms also affect the intensity in Figure S4 (a).

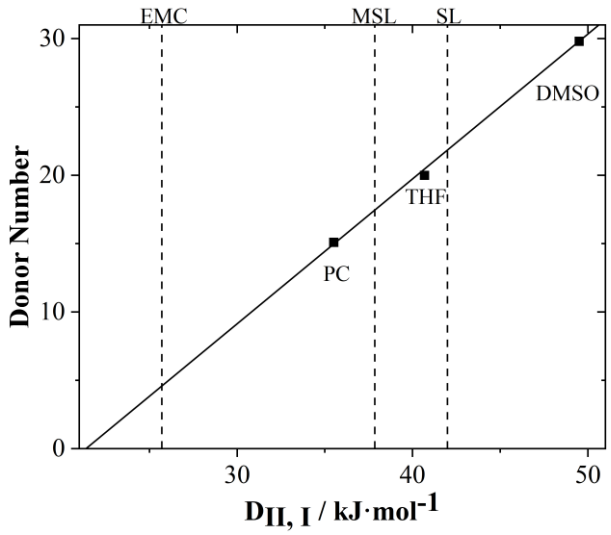


Figure S5. The relationship between donor number and $D_{II, I}$ ($D_{II, I} = 119600(\lambda_2^{-1} - \lambda_1^{-1})$). λ_1 and λ_2 are the wave lengths (in nm) of the two maximum absorption peaks of bis-(1,3-propanediolato) vanadium ($VO(acac)_2$) in a desired solvent. The PC, THF and DMSO were selected as references to plot the liner relationship. The data of SL was collected at 40℃ due to the high melting temperature. While higher temperature could decrease the $D_{II, I,}$ we could rank the solvents by donor numbers from high to low as SL>MSL>EMC.

Volume percentage of EMC / %	R_Ω/Ω	R_{ct}/Ω	Q_1		Q_2	
			$Y_{01}/S\cdot s^{n1}$	n_1	$Y_{02}/S\cdot s^{n2}$	n_2
100	111.6	49.04	$1.64x10^{-5}$	0.84	$4.64x10^{-3}$	0.38
90	51.72	19.69	$9.3x10^{-6}$	0.91	$8.26x10^{-3}$	0.32
80	35.63	14.4	$8.04x10^{-5}$	0.72	$2.7x10^{-2}$	0.42
60	30.48	14.94	$3.61x10^{-5}$	0.80	$4.6x10^{-2}$	0.34
40	28.83	13.47	$3.34x10^{-5}$	0.80	$4.3x10^{-2}$	0.33
20	32.66	20.42	$5.36x10^{-5}$	0.73	$4.2x10^{-2}$	0.39
0	30.33	21.11	$8.25x10^{-5}$	0.70	$4.9x10^{-2}$	0.39

Table S1. Element values in the $R_\Omega(Q_1(R_{ct}Q_2))$ equivalent circuit of impedance spectra of Figure 11 (a).

Volume percentage of EMC / %	R_Ω/Ω	R_{ct}/Ω	Q_1		Q_2	
			$Y_{01}/S\cdot s^{-n1}$	n_1	$Y_{02}/S\cdot s^{-n2}$	n_2
100	111.6	49.04	$1.64x10^{-5}$	0.84	$4.64x10^{-3}$	0.38
80	46.98	26.74	$1.27x10^{-4}$	0.63	$1.51x10^{-2}$	0.45
60	44.23	30.25	$6.72x10^{-5}$	0.72	$2.62x10^{-2}$	0.44
50	43.35	21.72	$4.84x10^{-5}$	0.75	$2.5x10^{-2}$	0.33
40	55.27	21.02	$3.17x10^{-5}$	0.80	$2.1x10^{-2}$	0.38
20	64.58	21.34	$1.81x10^{-5}$	0.87	$1.4x10^{-2}$	0.33
0	67.33	43.75	$7.25x10^{-5}$	0.72	-	-

Table S2. Element values in the $R_\Omega(Q_1(R_{ct}Q_2))$ equivalent circuit of impedance spectra of Figure 11 (b).