What Contributes to the Internal Mass-Transport Resistance of Redox Species through Porous Thin-Film Electrodes?

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Supporting Information (SI)

EIS pattern of binder-free carbon-thin film electrode in 1 M H_2SO_4

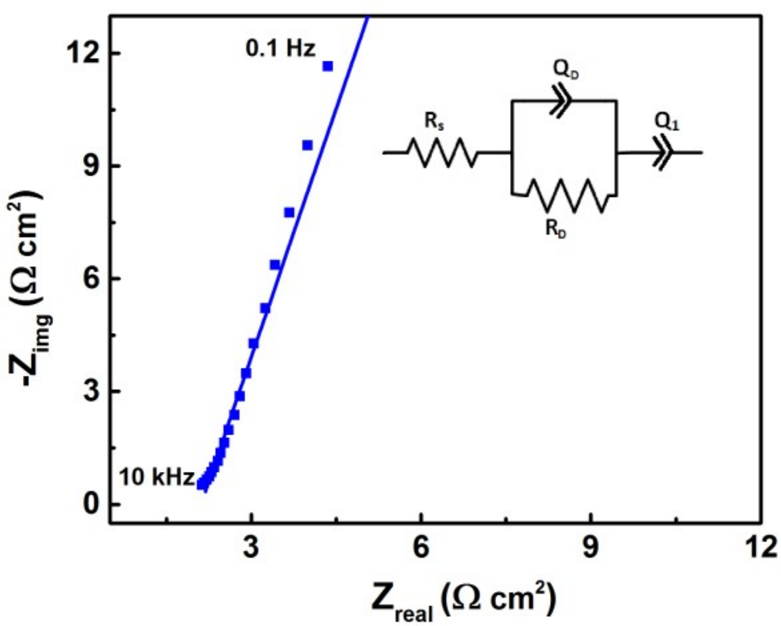


Figure S1 Impedance of the binder-free electrode in the absence of redox species in 1 M H_2SO_4

EIS pattern of BQ/BQH_2 in 1 M H_2SO_4 on binder-free carbon thin-film

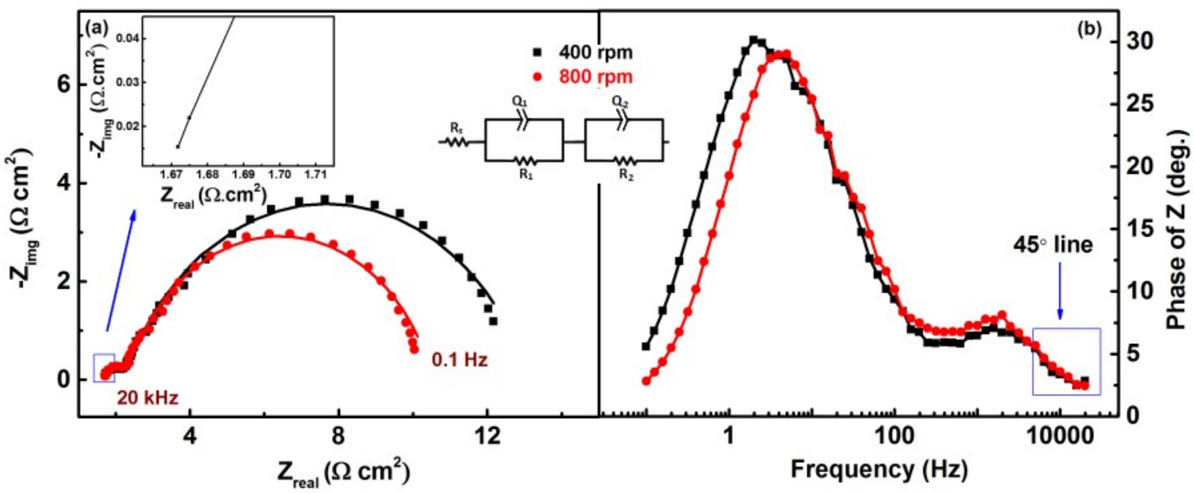


Fig. S2(a) Nyquist and **(b)** Bode plot of equimolar (5 mM) solution of BQ/BQH_2 in 1 M H_2SO_4 on binder-free carbon thin-film on the GCD at 400 and 800 rpm, recorded at equilibrium potential (~0.7 V).

Fitting parameters of BQ/BQH_2 on binder-free carbon-modified GCD

Table ST1 Parameters obtained by fitting the EIS pattern recorded at equilibrium potential on binder-free carbon-modified GCD in equimolar solution (5 mM) of BQ/BQH_2 in 1 M H_2SO_4.

Rotation Rate (rpm)	Parameter	Obtained fitting value	Relative standard error (%)	χ^2 (Chi-square)	Relative error of the measured impedance
400	R_s (Ω cm^2)	1.86	2.51	0.0005	2.17
	R_1 (Ω cm^2)	0.548	6.32		

	Q_1 (F cm^{-2} $s^{\phi-1}$)	0.002	8.59		
	ϕ_1	0.753	9.76		
	R_2 (Ω cm^2)	10.9	1.39		
	Q_2 (F cm^{-2} $s^{\phi-1}$)	0.024	2.51		
	ϕ_2	0.738	1.25		
800	R_s (Ω cm^2)	1.76	1.10	0.0004	2.09
	R_1 (Ω cm^2)	0.64	6.87		
	Q_1 (F cm^{-2} $s^{\phi-1}$)	0.002	4.47		
	ϕ_1	0.789	6.6		
	R_2 (Ω cm^2)	8.26	1.44		
	Q_2 (F cm^{-2} $s^{\phi-1}$)	0.018	3.06		
	ϕ_2	0.747	1.30		

Optimization of binder (Nafion) content

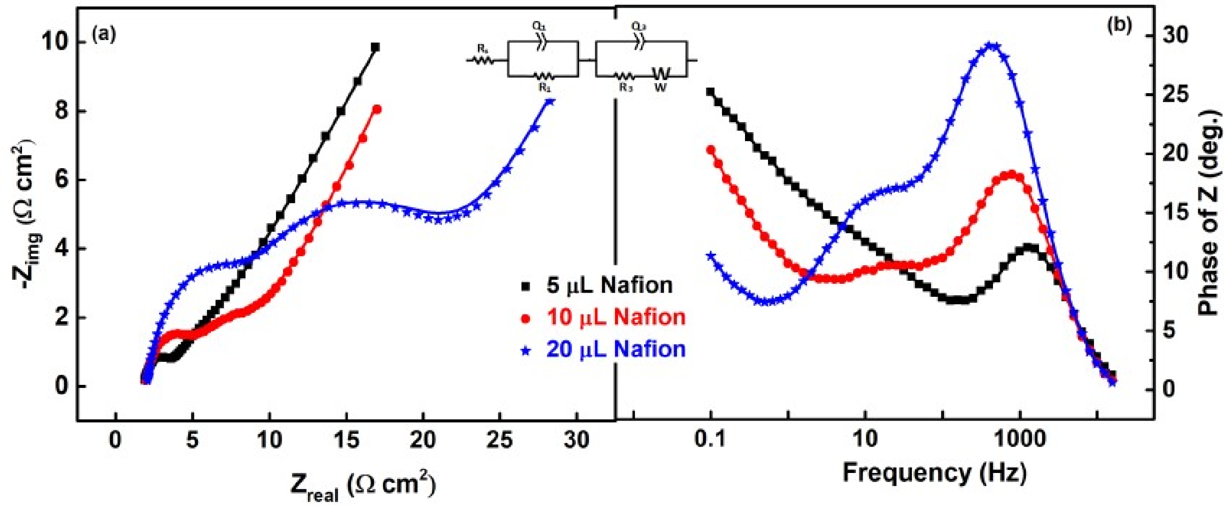


Figure S3 (a) Nyquist and **(b)** Bode plots of equimolar solution of 5 mM BQ/BQH_2 in 1 M H_2SO_4 at static condition of electrode for various Nafion contents.

Fitting parameters of V^{5+}/V^{4+} on Nafion-free and Nafion-containing carbon-modified GCD

Table ST2 Parameters obtained by fitting the EIS pattern recorded at equilibrium potential on Nafion-free and Nafion-containing carbon-modified GCD in equimolar solution (200 mM) of V^{5+}/V^{4+} in 3 M H_2SO_4.

Electrode	Parameter	Obtained fitting value	Relative standard error (%)	χ^2(Chi-square)	Relative error of the measured impedance
Nafion-free	R_s (Ω cm^2)	0.803	0.415	0.00002	0.475
	R_1 (Ω cm^2)	0.41	0.250		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.001	1.85		
	ϕ_1	0.812	0.281		
	R_3 (Ω cm^2)	-	-		
	Q_3 (F cm^{-2} s$^{\phi-1}$)	-	-		
	ϕ_3	-	-		

	W (Ω cm^2 s$^{-1/2}$)	0.008	1.45		
Nafion-containing	R_s (Ω cm^2)	0.93	0.932	0.0001	2.15
	R_1 (Ω cm^2)	1.36	8.71		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.007	9.62		
	ϕ_1	0.872	4.71		
	R_3 (Ω cm^2)	9.94	7.36		
	Q_3 (F cm^{-2} s$^{\phi-1}$)	0.038	7.69		
	ϕ_3	0.772	4.19		
	W (Ω cm^2 s$^{-1/2}$)	0.029	7.18		

Bode plots of V^{5+}/V^{4+} on Nafion-free and Nafion-containing carbon-modified GCD

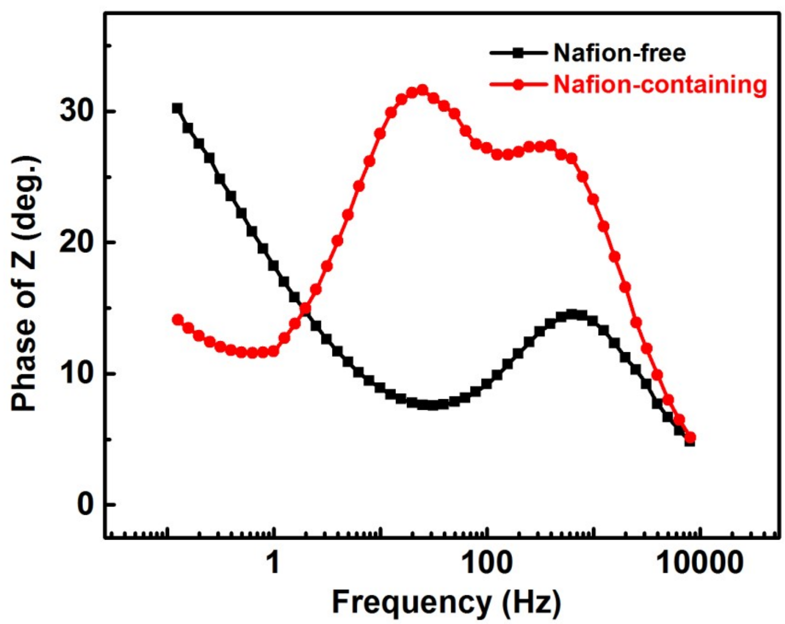


Figure S4 Bode plots of equimolar (200 mM) solution of V^{5+}/V^{4+} in 3 M H_2SO_4 on Nafion-free and Nafion-containing GCD.

Fitting parameters of V^{5+}/V^{4+} on Nafion-containing carbon-modified GCD for various rotation rates

Table ST3 Parameters obtained by fitting the EIS patterns recorded at equilibrium potential (~0.86 V) on Nafion-containing carbon-modified GCD in equimolar (200 mM) solution of V^{5+}/V^{4+} in 3 M H_2SO_4.

Rotation Rate (rpm)	Parameter	Obtained fitting value	Relative standard error (%)	χ^2(Chi-square)	Relative error of the measured impedance
400	R_s (Ω cm^2)	1.55	0.618	0.0004	2.11
	R_1 (Ω cm^2)	2.02	6.79		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.007	8.84		
	ϕ_1	0.917	2.35		
	R_2 (Ω cm^2)	12.1	3.67		
	Q_2 (F cm^{-2} s$^{\phi-1}$)	0.084	2.56		
	ϕ_2	0.692	3.16		
800	R_s (Ω cm^2)	1.59	0.594	0.0005	2.19
	R_1 (Ω cm^2)	2.08	3.39		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.009	3.15		
	ϕ_1	0.873	2.17		
	R_2 (Ω cm^2)	9.6	5.94		
	Q_2 (F cm^{-2} s$^{\phi-1}$)	0.069	8.98		
	ϕ_2	0.788	5.94		
1200	R_s (Ω cm^2)	1.58	0.494	0.0003	1.83
	R_1 (Ω cm^2)	2.17	4.05		

	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.008	8.24		
	ϕ_1	0.874	1.63		
	R_2 (Ω cm^2)	8.59	2.53		
	Q_2 (F cm^{-2} s$^{\phi-1}$)	0.063	2.69		
	ϕ_2	0.849	2.16		
1600	R_s (Ω cm^2)	1.53	0.354	0.0002	1.32
	R_1 (Ω cm^2)	2.15	3.02		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.008	6.26		
	ϕ_1	0.881	1.24		
	R_2 (Ω cm^2)	7.08	1.91		
	Q_2 (F cm^{-2} s$^{\phi-1}$)	0.058	2.12		
	ϕ_2	0.869	1.61		
2000	R_s (Ω cm^2)	1.52	0.313	0.0001	1.17
	R_1 (Ω cm^2)	2.20	2.64		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.008	5.68		
	ϕ_1	0.886	1.10		
	R_2 (Ω cm^2)	6.73	1.67		
	Q_2 (F cm^{-2} s$^{\phi-1}$)	0.054	1.93		
	ϕ_2	0.885	1.40		
2400	R_s (Ω cm^2)	1.54	0.410	0.0002	1.41
	R_1 (Ω cm^2)	2.32	3.08		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.008	6.57		
	ϕ_1	0.907	1.65		

	R_2 (Ω cm^2)	6.45	2.03		
	Q_2 (F cm^{-2} $s^{\phi-1}$)	0.053	2.37		
	ϕ_2	0.876	1.29		

Fitting parameters of BQ/BQH_2 on Nafion-free and Nafion-containing carbon-modified GCD

Table ST4 Parameters obtained by fitting the EIS pattern recorded at equilibrium potential on Nafion-free and Nafion-containing carbon-modified GCD in equimolar solution (5 mM) of BQ/BQH_2 in 1 M H_2SO_4.

Electrode	Parameter	Obtained fitting value	Relative standard error (%)	χ^2(Chi-square)	Relative error of the measured impedance
Nafion-free	R_s (Ω cm^2)	1.74	1.79	0.0006	2.37
	R_1 (Ω cm^2)	0.225	7.68		
	Q_1 (F cm^{-2} $s^{\phi-1}$)	0.0001	5.19		
	ϕ_1	1	8.35		
	R_3 (Ω cm^2)	1.71	4.53		
	Q_3 (F cm^{-2} $s^{\phi-1}$)	0.073	9.2		
	ϕ_3	0.85	5.18		
	W (Ω cm^2 $s^{-1/2}$)	0.004	3.25		
Nafion-containing	R_s (Ω cm^2)	2.01	0.377	0.0001	0.989
	R_1 (Ω cm^2)	5.80	5.57		
	Q_1 (F cm^{-2} $s^{\phi-1}$)	0.0003	6.24		
	ϕ_1	0.87	1.27		

	R_3 (Ω cm^2)	14.2	3.96		
	Q_3 (F cm^{-2} s$^{\phi-1}$)	0.005	4.88		
	ϕ_3	0.73	2.99		
	W (Ω cm^2 s$^{-1/2}$)	0.004	1.78		

Bode plots of BQ/BQH$_2$ on Nafion-free and Nafion-containing carbon-modified GCD

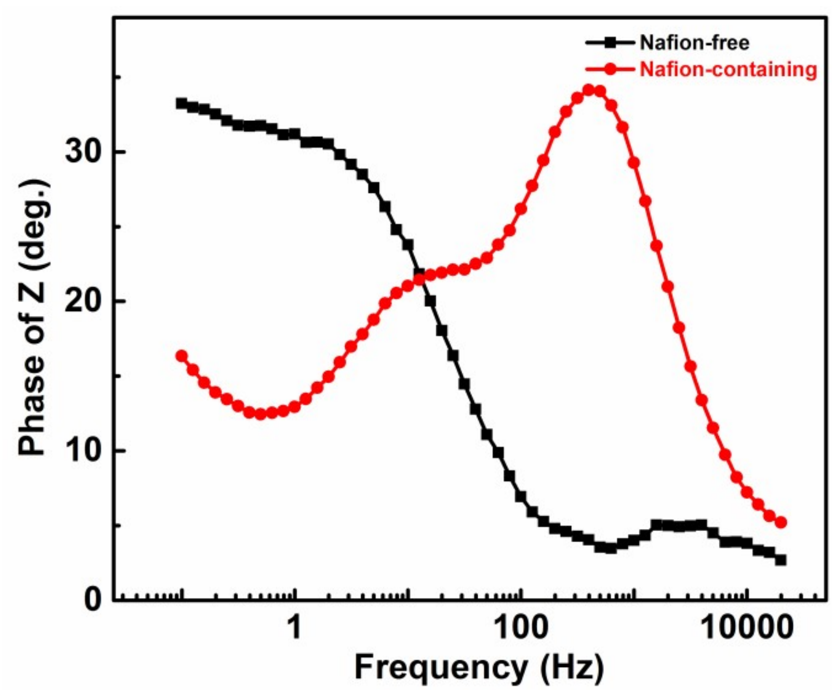


Figure S5 Bode plots of equimolar (5 mM) solution of BQ/BQH$_2$ in 1 M H_2SO_4 on Nafion-free and Nafion-containing GCD.

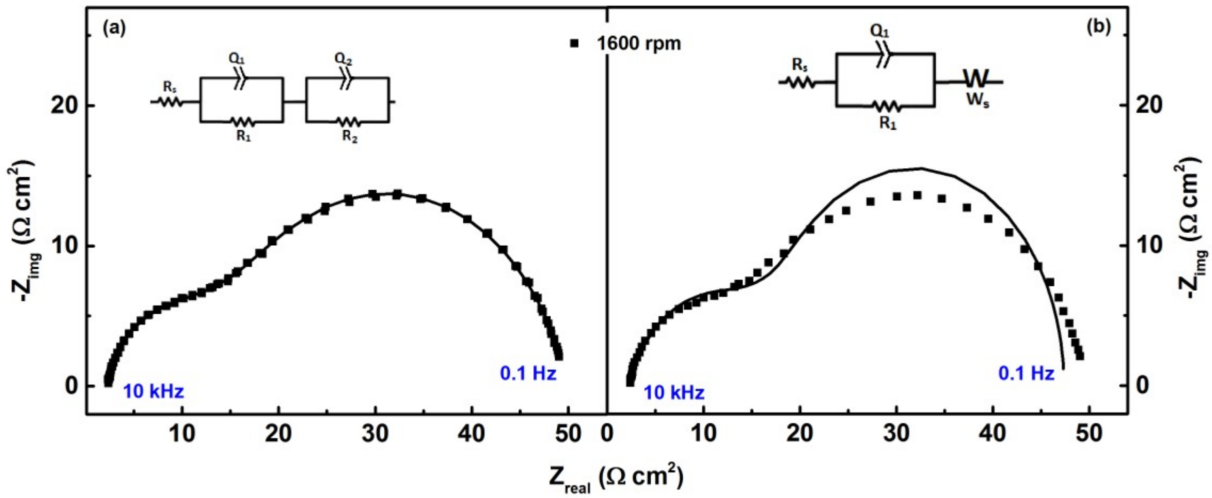


Figure S6 Nyquist plots recorded at equilibrium potential on Nafion-containing electrode (20 µL) in equimolar solution (5 mM) of BQ/BQH_2 (1:1) in 1 M H_2SO_4. The respective equivalent circuits are shown in the inset.

The EIS patterns recorded at 1600 rpm are fitted with (a) a series combination of R_s (solution resistance), (R_1, Q_1) element (charge-transfer process at the high frequency region), and (R_2, Q_2) element (mass-transfer process; unresolved and distorted semicircle); (b) a series combination of R_s (solution resistance), (Q_1, (R_1, W_s)) element (charge-transfer process at the high frequency region and finite length transmissive mass-transport at the low frequency region). The χ^2 (Chi-square) is lower when the equivalent circuit consists of two (R, Q) elements. Their respective circuit parameters are given below.

Table ST5 Parameters obtained by fitting the EIS pattern recorded at equilibrium potential on Nafion-containing (20 µL) electrode at 1600 rpm in equimolar solution of 5 mM BQ/BQH_2 in 1 M H_2SO_4. The EC used for fitting the data is shown in Fig. S6(a).

Parameter	Obtained fitting	Relative		Relative error of

	value	standard error (%)	χ^2(Chi-square)	the measured impedance
R_s (Ω)	10.4	0.99		
R_1 (Ω)	50.94	3.68		
Q_1 (F $s^{\phi-1}$)	0.00006	6.37		
ϕ_1	0.845	1.13	0.0002	1.38
R_2 (Ω)	201.1	1.61		
Q_2 (F $s^{\phi-1}$)	0.0006	2.39		
ϕ_2	0.784	1.47		

Table ST6 Parameters obtained by fitting the EIS pattern recorded at equilibrium potential on Nafion-containing (20 μL) electrode at 1600 rpm in equimolar solution of 5 mM BQ/BQH_2 in 1 M H_2SO_4. The EC used for fitting the data is shown in Fig. S6(a).

Parameter	Obtained fitting value	Relative standard error (%)	χ^2(Chi-square)	Relative error of the measured impedance
R_s (Ω)	10.35	2.45		
R_1 (Ω)	45.77	6.54		
Q_1 (F $s^{\phi-1}$)	0.00007	20.2	0.002	4.75
ϕ_1	0.889	3.22		
W_s–Y_o	0.002	3.47		
W_s–B	0.393	2.62		

χ^2(Chi-square) value and the relative error in the measure of the impedance are the least for the circuit contains two (R, Q) elements. It appears that the circuit containing two (R, Q) elements are the best suited for fitting of BQ/BQH_2 EIS patterns.

F-test for the EC of EIS patterns recorded under hydrodynamic conditions on Nafion-containing electrode

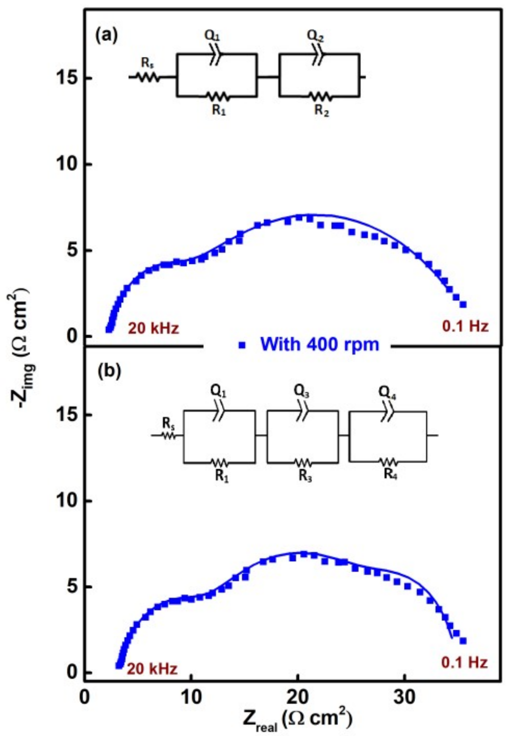


Figure S7 Nyquist plots recorded at equilibrium potential on Nafion-containing electrode in equimolar solution (5 mM) of BQ/BQH_2 (1:1) in 1 M H_2SO_4. The respective equivalent circuits are shown in the inset.

The EIS patterns recorded at 400 rpm are fitted with (a) a series combination of R_s (solution resistance), (R_1, Q_1) element (charge-transfer process at the high frequency region), and (R_2, Q_2)

element (mass-transfer process; unresolved and distorted semicircle); (b) a series combination of R_s (solution resistance), (R_1, Q_1) element (charge-transfer process at the high frequency region), (R_3, Q_3) element (internal mass-transfer process at the mid-frequency region), and (R_4, Q_4) (external mass-transfer process at the low frequency region), respectively. The fitting of mid-frequency and low-frequency features in the Nyquist plots are different in both the cases. The χ^2 (Chi-square) is lower when the equivalent circuit consists of three (R, Q) elements. Further clarification is obtained from F-test.

Table ST7 Parameters obtained by fitting the EIS pattern recorded at equilibrium potential on Nafion-containing electrode at 400 rpm in equimolar solution of 5 mM BQ/BQH_2 in 1 M H_2SO_4. The EC used for fitting the data is shown in Fig. S7(a).

Parameter	Obtained fitting value	Relative standard error (%)	χ^2(Chi-square)	Relative error of the measured impedance
R_s (Ω cm^2)	2.09	2.39	0.0006	2.52
R_1 (Ω cm^2)	5.82	4.17		
Q_1 (F cm^{-2} s$^{\phi-1}$)	0.0002	3.0		
ϕ_1	0.96	5.66		
R_2 (Ω cm^2)	29.14	4.89		
Q_2 (F cm^{-2} s$^{\phi-1}$)	0.006	4.69		
ϕ_2	0.537	4.71		

Table ST8 Parameters obtained by fitting the EIS pattern recorded at equilibrium potential on Nafion-containing electrode at 400 rpm in equimolar solution of 5 mM BQ/BQH_2 in 1 M H_2SO_4. The EC used for fitting the data is shown in Fig. S7(b).

Parameter	Obtained fitting value	Relative standard error (%)	χ^2(Chi-square)	Relative error of the measured impedance
R_s (Ω cm^2)	2.03	1.267	0.0005	2.22
R_1 (Ω cm^2)	6.62	1.61		
Q_1 (F cm^{-2} $s^{\phi-1}$)	0.0003	1.688		
ϕ_1	0.86	3.548		
R_3 (Ω cm^2)	7.69	2.5		
Q_3 (F cm^{-2} $s^{\phi-1}$)	0.050	3.1		
ϕ_3	0.92	1.71		
R_4 (Ω cm^2)	17.46	2.67		
Q_4 (F cm^{-2} $s^{\phi-1}$)	0.0003	2.56		
ϕ_4	0.773	1.236		

F (α, k, 2N-m-k) = 2.68869

Where, k=3, m=7 and N=59, α = 0.05

$$F_{exp} = \frac{\dfrac{S_1 - S_2}{(2N-m)-(2N-m-k)}}{\dfrac{S_2}{(2N-m-k)}} = \frac{\dfrac{S_1 - S_2}{k}}{\dfrac{S_2}{2N-m-k}}$$

$$S_1 = 2.52,\ S_2 = 2.221$$

$$F_{exp} = \frac{\frac{0.299}{3}}{\frac{2.221}{108}} = 4.846$$

Since $F_{exp} > F$ (α, k, 2N-m-k), the model consisting of three (R, Q) elements can be accepted in the manuscript for 20 µl Nafion-concentration.

Equivalent circuit fitting parameters of BQ/BQH_2 on Nafion-containing electrode recorded at various rotation rates

Table ST9 Parameters obtained by fitting the EIS pattern recorded at equilibrium potential on N (20) electrode in equimolar solution of 5 mM BQ/BQH_2 in 1 M H_2SO_4.

Here, at 400 rpm, Nyquist plot is fitted with three (R, Q) elements in the EC. The parameters are shown in Table ST6.

Rotation Rate (rpm)	Parameter	Obtained fitting value	Relative standard error (%)	χ^2(Chi-square)	Relative error of the measured impedance
800	R_s (Ω cm^2)	2.03	1.47	0.0008	2.89
	R_1 (Ω cm^2)	8.53	7.23		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.0003	7.22		
	ϕ_1	0.885	3.06		
	R_2 (Ω cm^2)	32.5	4.23		
	Q_2 (F cm^{-2} s$^{\phi-1}$)	0.003	5.65		

	ϕ_2	0.725	3.91		
1200	R_s (Ω cm^2)	2.13	0.767	0.0002	1.40
	R_1 (Ω cm^2)	9.11	4.27		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.0003	2.52		
	ϕ_1	0.871	1.25		
	R_2 (Ω cm^2)	37.69	1.72		
	Q_2 (F cm^{-2} s$^{\phi-1}$)	0.003	7.20		
	ϕ_2	0.749	1.61		
1600	R_s (Ω cm^2)	2.038	0.99	0.0002	1.38
	R_1 (Ω cm^2)	9.98	3.68		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.0003	6.37		
	ϕ_1	0.845	1.13		
	R_2 (Ω cm^2)	39.4	1.61		
	Q_2 (F cm^{-2} s$^{\phi-1}$)	0.003	2.39		
	ϕ_2	0.784	1.47		
2000	R_s (Ω cm^2)	1.98	0.551	0.00009	0.953
	R_1 (Ω cm^2)	10.39	2.67		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.0003	4.01		
	ϕ_1	0.853	0.723		
	R_2 (Ω cm^2)	40.29	1.16		
	Q_2 (F cm^{-2}s$^{\phi-1}$)	0.003	1.67		
	ϕ_2	0.782	1.03		
2400	R_s (Ω cm^2)	2.11	0.798	0.00001	1.23

	R_1 (Ω cm^2)	11.05	3.86		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.0003	5.43		
	ϕ_1	0.844	1.01		
	R_2 (Ω cm^2)	40.68	1.86		
	Q_2 (F cm^{-2} s$^{\phi-1}$)	0.003	2.48		
	ϕ_2	0.779	1.54		

Interaction of the redox species with Nafion for various rotation rates

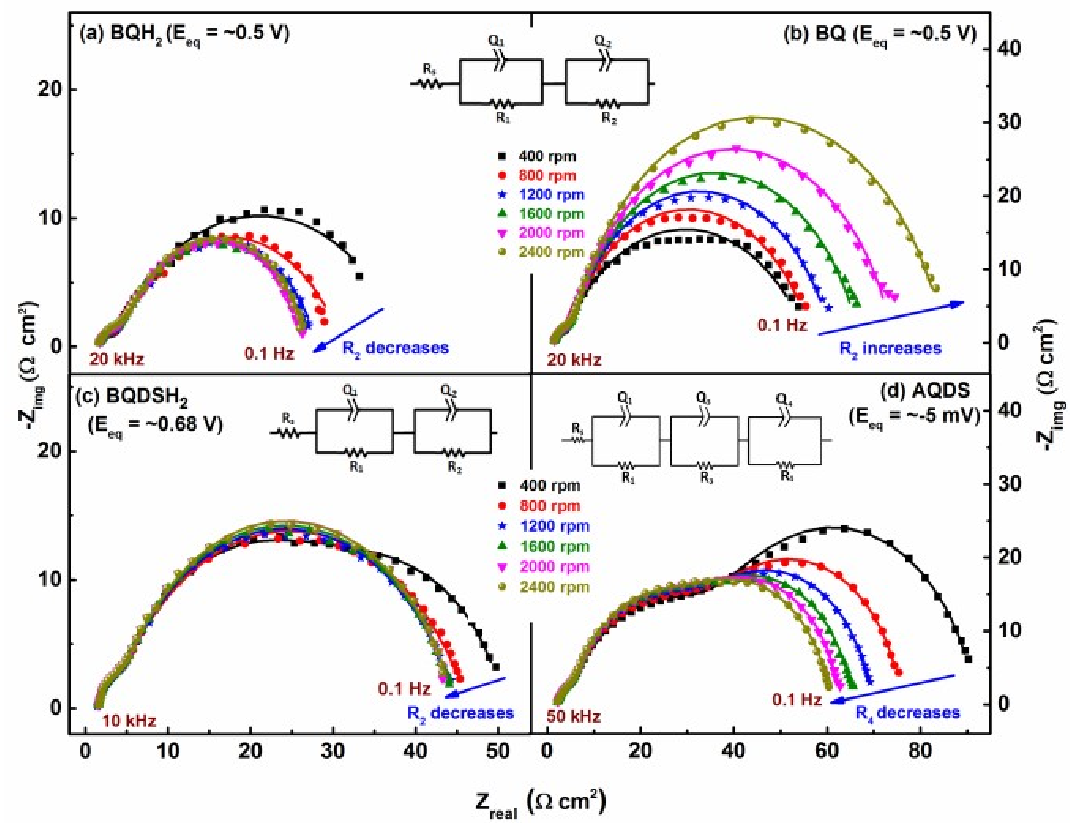


Figure S8 EIS patterns of 5 mM (a) BQH_2 (b) BQ (c) $BQDSH_2$ and (d) AQDS in 1 M H_2SO_4 recorded at equilibrium potential on Nafion-containing carbon thin-film for various rotation rate of the electrode. ECs are given in the inset. The symbols and solid lines show experimental and fitted data, respectively.

Interaction of the redox species with Nafion for various time intervals

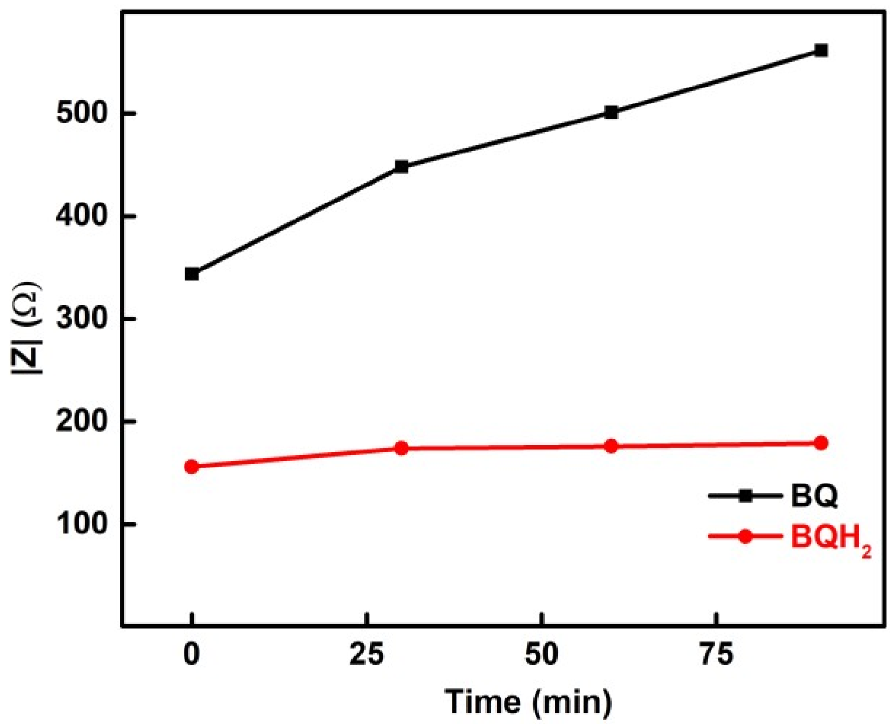
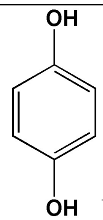
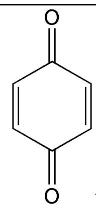
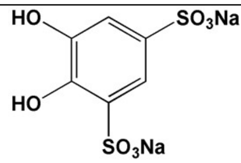
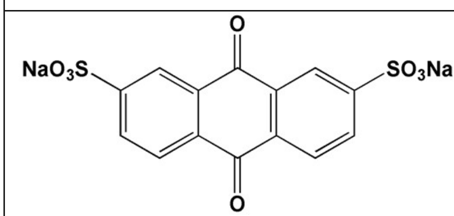


Figure S9 Time dependence on impedance under hydrodynamic condition (1600 rpm) for (a) 5 mM BQ and (b) 5 mM BQH_2 in 1 M H_2SO_4 at equilibrium potential (~700mV) for equal time intervals on Nafion-containing carbon-thin film.

Table ST10 Different organic redox species are checked for Nafion interaction

Redox species	**Interaction with Nafion**

 Hydroquinone (BQH_2)	✕
 p-benzoquinone (BQ)	✓
 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt ($BQDSH_2$)	✕
 Anthraquinone-2,7-disulfonic acid disodium salt (AQDS)	✕

Comparison of kinetics

Table ST11 Comparison of kinetics of the redox couple at stationary condition

Redox system	Electrode modification	R_1 (Ω) *Concentration (M) (Bulk)

V^{5+}/V^{4+} (200 mM, equimolar solution)	Nafion-free	0.08
V^{5+}/V^{4+} (200 mM, equimolar solution)	Nafion-containing	0.272
BQ/BQH_2 (5 mM, equimolar solution)	Nafion-free	0.001
BQ/BQH_2 (5 mM, equimolar solution)	Nafion-containing	0.029
$AQDS/AQDSH_2$ (5 mM)	Nafion-free	0.007
$AQDS/AQDSH_2$ (5 mM)	Nafion-containing	0.021

Fitting parameters of $AQDS/AQDSH_2$ on Nafion-free and Nafion-containing carbon-modified GCD

Table ST12 Parameters obtained by fitting the EIS pattern recorded at equilibrium potential (~195 mV) on Nafion-free and Nafion-containing carbon-modified GCD in 5 mM of $AQDSH_2$ dissolved in 1 M H_2SO_4.

Electrode	Parameter	Obtained fitting value	Relative standard error (%)	χ^2 (Chi-square)	Relative error of the measured impedance
Nafion-free	R_s (Ω cm^2)	1.82	5.09	0.0003	1.82
	R_1 (Ω cm^2)	1.47	6.06		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.0001	5.02		
	ϕ_1	0.774	8.67		

	R_3 (Ω cm^2)	24.46	4.77		
	Q_3 (F cm^{-2} $s^{\phi-1}$)	0.005	4.57		
	ϕ_3	0.783	1.16		
	W(Ω cm^2 $s^{-1/2}$)	0.0009	1.89		
Nafion-containing	R_s (Ω cm^2)	1.97	1.86	0.0007	2.17
	R_1 (Ω cm^2)	4.24	3.2		
	Q_1 (F cm^{-2} $s^{\phi-1}$)	0.0003	4.35		
	ϕ_1	0.768	6.48		
	R_3 (Ω cm^2)	43.39	4.45		
	Q_3 (F cm^{-2} $s^{\phi-1}$)	0.00061	9.48		
	ϕ_3	0.769	2.89		
	W (Ω cm^2 $s^{-1/2}$)	0.00054	2.47		

Bode plots of AQDS/$AQDSH_2$ on Nafion-free and Nafion-containing carbon-modified GCD

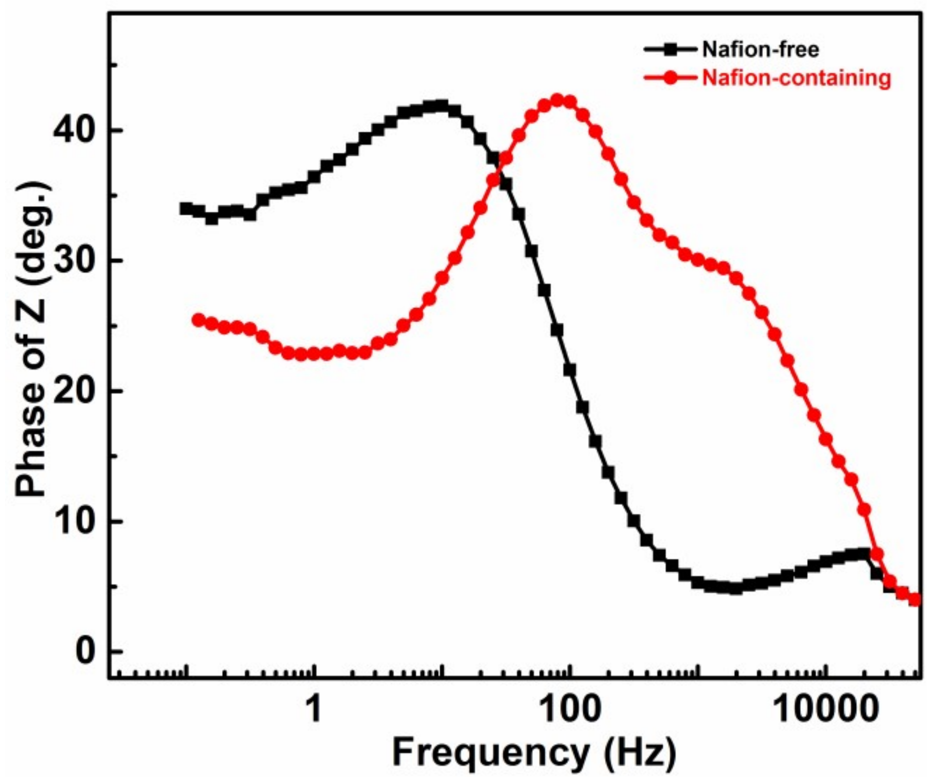


Figure S10 Bode plots of 5 mM $AQDSH_2$ dissolved in 1 M H_2SO_4 on Nafion-free and Nafion-containing GCD recorded at equilibrium potential (~195 mV).

Equivalent circuit fitting parameters of AQDS/$AQDSH_2$ on Nafion-free and Nafion-containing electrodes recorded at various rotation rates

Table ST13 Parameters obtained by fitting the EIS pattern recorded at equilibrium potential (~195 mV) for various rotation rates on Nafion-free carbon-modified GCD in 5 mM of $AQDSH_2$ dissolved in 1 M H_2SO_4.

Rotation speed of the electrode	Parameter	Obtained fitting value	Relative standard error (%)	χ^2(Chi-square)	Relative error of the measured impedance

(rpm)					
400	R_s (Ω cm^2)	1.76	4.07	0.0002	1.41
	R_1 (Ω cm^2)	1.47	2.34		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.0002	7.4		
	ϕ_1	0.91	6.9		
	R_3 (Ω cm^2)	11.05	3.43		
	Q_3 (F cm^{-2} s$^{\phi-1}$)	0.005	2.75		
	ϕ_3	0.793	1.1		
	R_4 (Ω cm^2)	35.4	4.16		
	Q_4 (F cm^{-2} s$^{\phi-1}$)	0.013	4.57		
	ϕ_4	0.76	2.09		
800	R_s (Ω cm^2)	1.78	4.07	0.0001	1.125
	R_1 (Ω cm^2)	1.47	7.34		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.0003	7.4		
	ϕ_1	0.89	6.9		
	R_3 (Ω cm^2)	11.05	3.43		
	Q_3 (F cm^{-2} s$^{\phi-1}$)	0.006	3.95		
	ϕ_3	0.79	1.23		
	R_4 (Ω cm^2)	27.9	3.96		
	Q_4 (F cm^{-2} s$^{\phi-1}$)	0.008	3.95		
	ϕ_4	0.97	1.75		
1200	R_s (Ω cm^2)	1.81	5.75		
	R_1 (Ω cm^2)	1.51	1.79		

	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.0003	4.18	0.00009	0.94
	ϕ_1	0.87	5.6		
	R_3 (Ω cm^2)	11.22	7.6		
	Q_3 (F cm^{-2} s$^{\phi-1}$)	0.005	4.18		
	ϕ_3	0.80	1.39		
	R_4 (Ω cm^2)	24.6	3.8		
	Q_4 (F cm^{-2} s$^{\phi-1}$)	0.007	3.85		
	ϕ_4	0.94	1.4		
1600	R_s (Ω cm^2)	1.81	3.52	0.00007	0.847
	R_1 (Ω cm^2)	1.51	2.79		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.0003	4.18		
	ϕ_1	0.87	5.6		
	R_3 (Ω cm^2)	11.22	7.6		
	Q_3 (F cm^{-2} s$^{\phi-1}$)	0.005	4.18		
	ϕ_3	0.80	1.39		
	R_4 (Ω cm^2)	22.7	3.91		
	Q_4 (F cm^{-2} s$^{\phi-1}$)	0.005	3.81		
	ϕ_4	0.91	1.37		
2000	R_s (Ω cm^2)	1.76	4.07	0.0001	1.13
	R_1 (Ω cm^2)	1.47	2.34		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.0002	7.4		
	ϕ_1	0.91	6.9		
	R_3 (Ω cm^2)	11.05	3.43		

	Q_3 (F cm^{-2} s$^{\phi-1}$)	0.005	2.75		
	ϕ_3	0.793	1.1		
	R_4 (Ω cm^2)	22	4.45		
	Q_4 (F cm^{-2} s$^{\phi-1}$)	0.005	4.52		
	ϕ_4	0.88	1.73		
2400	R_s (Ω cm^2)	1.76	4.07	0.0001	1.27
	R_1 (Ω cm^2)	1.47	2.34		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.0002	7.4		
	ϕ_1	0.91	6.9		
	R_3 (Ω cm^2)	11.05	3.43		
	Q_3 (F cm^{-2} s$^{\phi-1}$)	0.005	2.75		
	ϕ_3	0.793	1.1		
	R_4 (Ω cm^2)	21.7	5.69		
	Q_4 (F cm^{-2} s$^{\phi-1}$)	0.004	5.66		
	ϕ_4	0.88	2.02		

Table ST14 Parameters obtained by fitting the EIS pattern recorded at equilibrium potential (~195 mV) for various rotation rates on Nafion-containing carbon-modified GCD in 5 mM of $AQDSH_2$ dissolved in 1 M H_2SO_4.

Rotation speed of	Parameter	Obtained fitting value	Relative standard error	χ^2(Chi-	Relative error of the

the electrode (rpm)			(%)	square)	measured impedance
400	R_s (Ω cm^2)	2.04	1.19	0.0003	1.83
	R_1 (Ω cm^2)	4.23	2.34		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.0004	6.71		
	ϕ_1	0.74	4.08		
	R_3 (Ω cm^2)	26.22	4.15		
	Q_3 (F cm^{-2} s$^{\phi-1}$)	0.0007	1.05		
	ϕ_3	0.784	3.02		
	R_4 (Ω cm^2)	55.07	4.47		
	Q_4 (F cm^{-2} s$^{\phi-1}$)	0.005	4.47		
	ϕ_4	0.86	2.93		
800	R_s (Ω cm^2)	2.04	1.19	0.0002	1.63
	R_1 (Ω cm^2)	4.23	1.25		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.0004	2.71		
	ϕ_1	0.72	3.38		
	R_3 (Ω cm^2)	26.22	8.15		
	Q_3 (F cm^{-2} s$^{\phi-1}$)	0.0007	1.05		
	ϕ_3	0.824	3.05		
	R_4 (Ω cm^2)	40.5	6.08		
	Q_4 (F cm^{-2} s$^{\phi-1}$)	0.004	5.7		
	ϕ_4	0.89	3.29		

1200	R_s (Ω cm^2)	2.04	1.19	0.0002	1.54
	R_1 (Ω cm^2)	4.24	1.35		
	Q_1 (F cm^{-2} $s^{\phi-1}$)	0.0004	2.47		
	ϕ_1	0.72	2.94		
	R_3 (Ω cm^2)	26.2	7.54		
	Q_3 (F cm^{-2} $s^{\phi-1}$)	0.0007	3.23		
	ϕ_3	0.864	3.05		
	R_4 (Ω cm^2)	35.8	7.01		
	Q_4 (F cm^{-2} $s^{\phi-1}$)	0.003	6.9		
	ϕ_4	0.898	3.35		
1600	R_s (Ω cm^2)	2.04	1.19	0.0002	1.49
	R_1 (Ω cm^2)	4.29	1.39		
	Q_1 (F cm^{-2} $s^{\phi-1}$)	0.0004	1.89		
	ϕ_1	0.72	2.94		
	R_3 (Ω cm^2)	26.2	7.54		
	Q_3 (F cm^{-2} $s^{\phi-1}$)	0.0007	3.03		
	ϕ_3	0.864	3.05		
	R_4 (Ω cm^2)	33.9	1.14		
	Q_4 (F cm^{-2} $s^{\phi-1}$)	0.002	8.13		
	ϕ_4	0.89	3.41		
2000	R_s (Ω cm^2)	2.04	1.19		
	R_1 (Ω cm^2)	4.24	1.35		
	Q_1 (F cm^{-2} $s^{\phi-1}$)	0.0004	2.47		

	ϕ_1	0.72	2.94		
	R_3 (Ω cm^2)	26.22	7.54	0.0002	1.42
	Q_3 (F cm^{-2} s$^{\phi-1}$)	0.0007	3.23		
	ϕ_3	0.864	3.05		
	R_4 (Ω cm^2)	31.25	7.95		
	Q_4 (F cm^{-2} s$^{\phi-1}$)	0.002	8.9		
	ϕ_4	0.90	3.62		
2400	R_s (Ω cm^2)	2.04	1.19		
	R_1 (Ω cm^2)	4.24	1.35		
	Q_1 (F cm^{-2} s$^{\phi-1}$)	0.0004	2.47		
	ϕ_1	0.72	2.94		
	R_3 (Ω cm^2)	26.22	7.54	0.0002	1.49
	Q_3 (F cm^{-2} s$^{\phi-1}$)	0.0007	3.23		
	ϕ_3	0.864	3.11		
	R_4 (Ω cm^2)	26.5	1.82		
	Q_4 (F cm^{-2} s$^{\phi-1}$)	0.002	1.98		
	ϕ_4	0.894	3.85		

IR compensation

IR compensation for solution resistance (R_s): From the fitting parameters of the EIS pattern, solution resistance is obtained. The IR drop due to the solution resistance (R_s) is calculated, and subtracted this drop from the applied potential. By plotting this corrected voltage and the current, IR_s drop corrected LSV is obtained. Similarly, the same procedure is applied for resistance to the transport process (R_2), internal mass-transport resistance (R_3), and external mass-transport resistance (R_4), to obtain their respective resistance corrected LSVs.