EIS Investigation of Organic Redox Reactions (p-Benzoquinone/Hydroquinone couple) - Implications to Organic Redox Flow Batteries

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Supporting Information (SI)

Activation of N (10) electrode in 0.1 M KOH

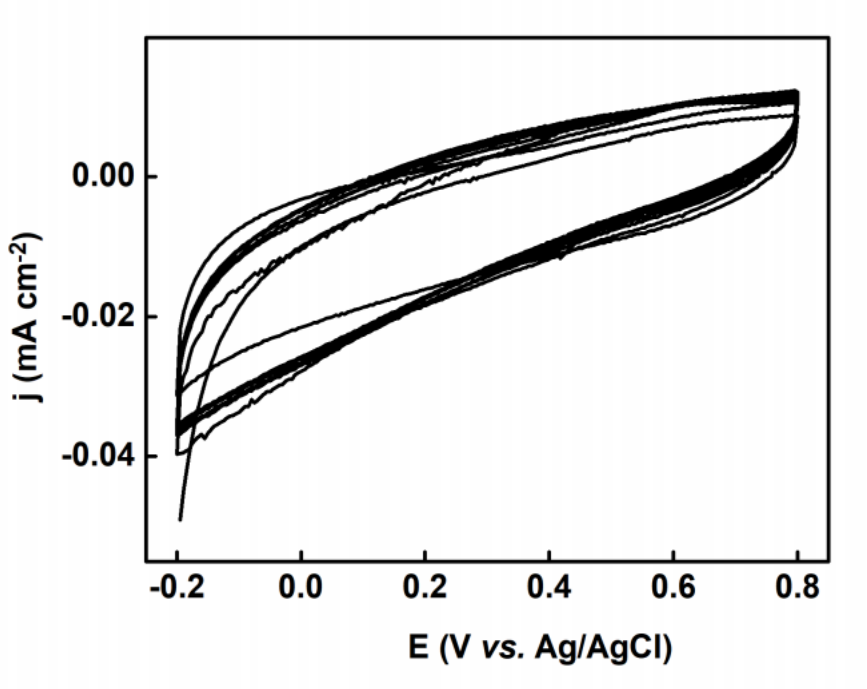

Figure S1 Voltammogram of N (10) electrode recorded in argon-saturated 0.1 M KOH at 20 mV s^{-1} scan rate (loading 17 µg cm^{-2}).

CV of V^{4+}/V^{5+} on N (0) and N (20) electrodes

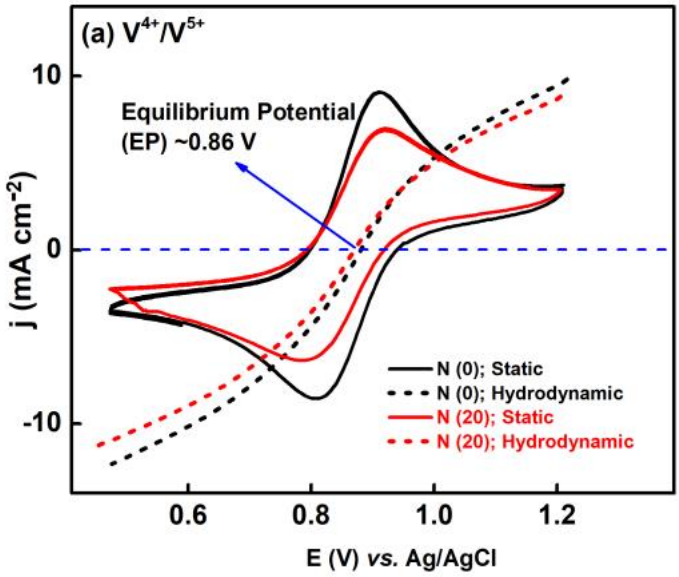

Figure S2 Voltammograms and LSV at 1600 rpm of equimolar solution of 200 mM V^{4+}/V^{5+} in 3 M H_2SO_4 on N (0) and N (20) electrodes. (the current values in the LSV (dashed lines) are divided by a factor of 2.5 to enclose in the figure frame).

EIS of BQ/BQH_2 and V^{4+}/V^{5+} on N (0) electrode

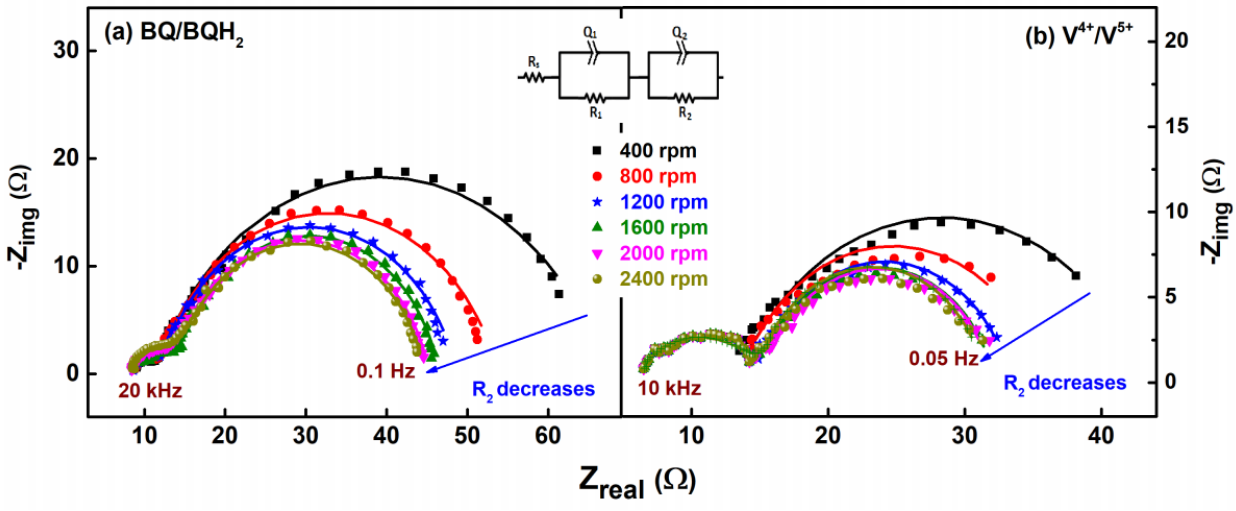

Figure S3 Nyquist plots (recorded at equilibrium potential) of equimolar solution of (a) 5 mM BQ/BQH_2 in 1 M H_2SO_4 (b) 200 mM V^{4+}/V^{5+} in 3 M H_2SO_4 on N (0) electrode for different hydrodynamic conditions. The EC is shown in the inset, symbols and solid lines show the experimental and fitted data, respectively.

Equivalent circuit fitting parameters of BQ/BQH_2 and V^{4+}/V^{5+} on N (0) electrode recorded at various rotation rates

Table S1 Parameters obtained by fitting the EIS pattern recorded at equilibrium potential on N (0) electrode in equimolar solution of 5 mM BQ/BQH_2 in 1 M H_2SO_4.

Rotation Rate (rpm)	R_s (Ω)	R_1 (Ω)	Q_1 (S sec^ϕ)	ϕ_1	R_2 (Ω)	Q_2 (S sec^ϕ)	ϕ_2	χ^2(Chi-square)
400	9.5	2.8	0.00031	0.753	55.81	0.00465	0.738	0.00047
800	9.7	3.1	0.00026	0.786	42.15	0.00354	0.784	0.000439
1200	9.3	3.79	0.00030	0.75	36.56	0.00286	0.81	0.000375
1600	9.6	5.86	0.00077	0.62	31.86	0.00238	0.85	0.00054
2000	9.3	5.81	0.00046	0.71	31.3	0.00217	0.84	0.00025
2400	9.2	6.2	0.000368	0.753	30.28	0.00198	0.85	0.000264

Table S2 Parameters obtained by fitting the EIS pattern recorded at equilibrium potential on N (0) electrode in equimolar solution (200 mM) of V^{4+}/V^{5+} in 3 M H_2SO_4.

Rotation Rate (rpm)	R_s (Ω)	R_1 (Ω)	Q_1 (S sec^ϕ)	ϕ_1	R_2 (Ω)	Q_2 (S sec^ϕ)	ϕ_2	χ^2(Chi-square)
400	6.5	9.5	0.000314	0.74	29.47	0.0224	0.738	0.000068
800	6.6	9.3	0.000318	0.745	21.96	0.0173	0.798	0.000051
1200	6.9	9.6	0.0006	0.616	17.95	0.0168	0.841	0.000034
1600	6.7	9.4	0.00055	0.644	16.62	0.0152	0.857	0.000040
2000	6.5	9.3	0.00064	0.617	16.02	0.0136	0.869	0.000050
2400	6.8	9.1	0.00061	0.608	15.88	0.0128	0.872	0.000061

Equivalent circuit fitting parameters of BQ/BQH_2 and V^{4+}/V^{5+} on N (10) electrode recorded at various rotation rates

Table S3 Parameters obtained by fitting the EIS pattern recorded at equilibrium potential (~0.5 V) on N (10) electrode in equimolar solution (5 mM) of BQ/BQH_2 in 1 M H_2SO_4.

Rotation Rate (rpm)	R_s (Ω)	R_1 (Ω)	Q_1 (S sec^ϕ)	ϕ_1	R_2 (Ω)	Q_2 (S sec^ϕ)	ϕ_2	χ^2(Chi-square)
400	10.11	13.39	0.000053	0.9258	87.2	0.003812	0.4856	0.000948
800	9.98	18.9	0.000065	0.8797	109.6	0.001181	0.632	0.000261
1200	9.89	24.8	0.000077	0.8463	112.8	0.000905	0.708	0.00013
1600	10.2	25.83	0.000070	0.8571	121.8	0.000765	0.733	0.000129
2000	9.8	28.24	0.000072	0.8519	127.6	0.00070	0.752	0.000167
2400	10.3	35.26	0.000083	0.827	147	0.00070	0.783	0.00007

Table S4 Parameters obtained by fitting the EIS pattern recorded at equilibrium potential (~0.86 V) on N (10) electrode in equimolar solution (200 mM) of V^{4+}/V^{5+} in 1 M H_2SO_4.

Rotation Rate (rpm)	R_s (Ω)	R_1 (Ω)	Q_1 (S sec^ϕ)	ϕ_1	R_2 (Ω)	Q_2 (S sec^ϕ)	ϕ_2	χ^2(Chi-square)
400	4.17	6.9	0.00097	0.917	34.31	0.0165	0.692	0.00044
800	4.74	7.1	0.00118	0.873	25.87	0.0137	0.788	0.00048
1200	4.72	7.4	0.00112	0.874	22.43	0.0124	0.849	0.00033
1600	5.2	7.3	0.00107	0.881	20.67	0.0114	0.869	0.00017
2000	5.2	7.5	0.00103	0.886	19.51	0.0107	0.885	0.00013
2400	5.0	7.9	0.00110	0.907	18.56	0.0104	0.876	0.00019

Equivalent circuit fitting parameters of BQ/BQH_2 at static condition for carbon-modified electrodes of various Nafion contents

Table S5 Parameters obtained by fitting the EIS pattern recorded at equilibrium potential in equimolar solution (5 mM) of BQ/BQH_2 in 1 M H_2SO_4 on GCDs of various Nafion contents.

GCD	R_s (Ω)	R_1 (Ω)	Q_1 (S sec^ϕ)	ϕ_1	R_3 (Ω)	Q_3 (S sec^ϕ)	ϕ_3	W (Ω $s^{-1/2}$)	χ^2(Chi-square)
N (0)	8.9	1.15	0.000016	1	8.77	0.0143	0.85	0.0208	0.00056
N (5)	9.1	5.1	0.000033	0.99	19.6	0.0089	0.55	0.0267	0.00002
N (10)	9.4	8.3	0.000031	1	30.1	0.0032	0.51	0.0227	0.00007
N (15)	9.8	21.5	0.000093	0.81	43.6	0.0012	0.76	0.0218	0.00003
N (20)	10.3	29.6	0.000066	0.87	72.45	0.00092	0.73	0.0231	0.00009

Nyquist and bode plots for carbon-modified GCD containing various Nafion contents

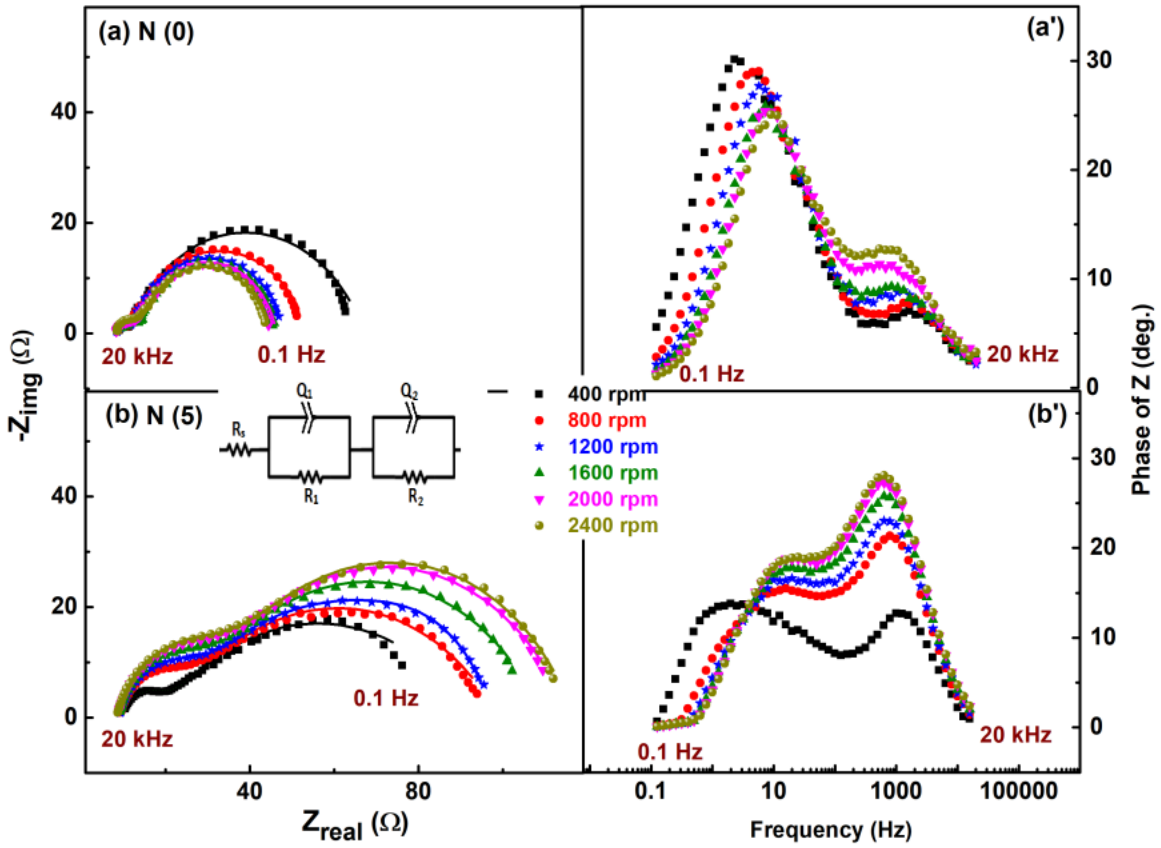

Figure S4 Nyquist ((a) and (b)) and Bode plots ((a') and (b')) of equimolar solution (5 mM) of BQ/BQH_2 in 1 M H_2SO_4 on N (0) and N (5) electrodes, respectively, under different hydrodynamic conditions of the GCD. The symbols and solid lines show the experimental and fitted data, respectively.

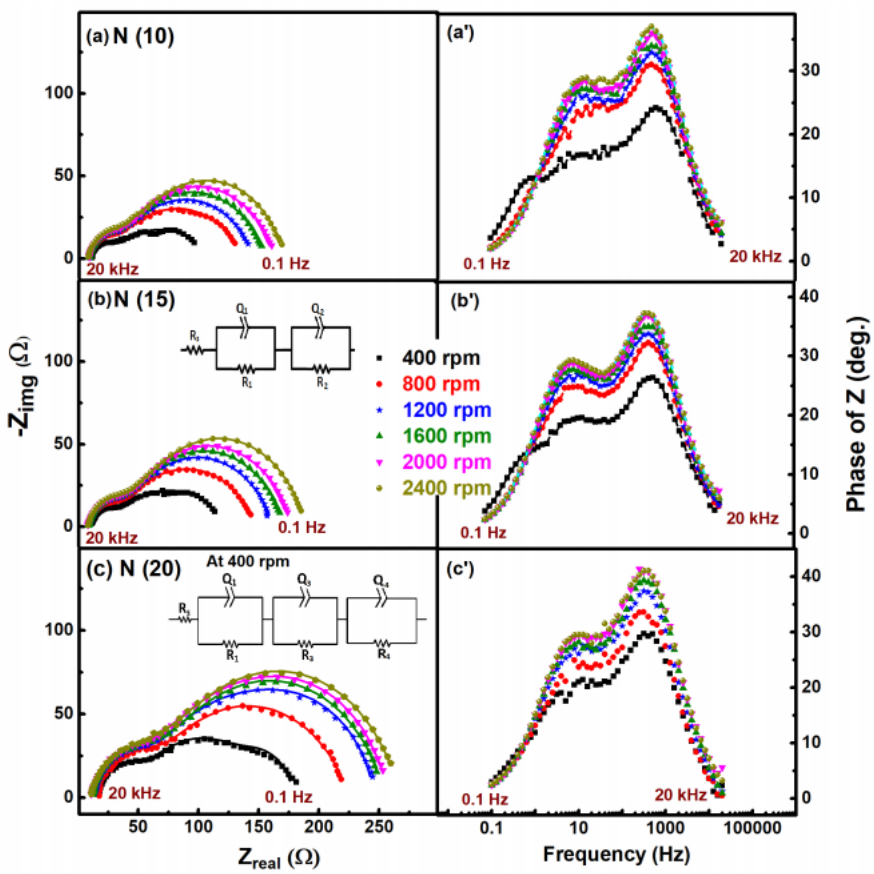

Figure S5 Nyquist ((a), (b) and (c)) and Bode plots ((a'), (b') and (c')) of equimolar solution (5 mM) of BQ/BQH_2 in 1 M H_2SO_4 on N (10), N (15) and N (20) electrodes, respectively, under different hydrodynamic conditions of the GCD. The symbols and solid lines show the experimental and fitted data, respectively.

Equivalent circuit fitting parameters of BQ/BQH$_2$ on N (5) and N (15) electrodes recorded at various rotation rates

Table S6 Parameters obtained by fitting the EIS pattern recorded at equilibrium potential (~0.5 V) on N (5) electrode in equimolar solution (5 mM) of BQ/BQH$_2$ in 1 M H_2SO_4.

Rotation Rate (rpm)	R_s (Ω)	R_1 (Ω)	Q_1 (S sec^ϕ)	ϕ_1	R_2 (Ω)	Q_2 (S sec^ϕ)	ϕ_2	χ^2(Chi-square)
400	9.31	9.91	0.00011	0.794	73.69	0.00572	0.549	0.00005
800	8.92	15.16	0.000085	0.837	74.84	0.00213	0.613	0.00026
1200	8.94	18.06	0.000078	0.839	74.16	0.00148	0.662	0.00010
1600	8.87	20.95	0.000076	0.84	79.51	0.00117	0.691	0.000091
2000	9.12	23.8	0.000078	0.833	82.79	0.00097	0.721	0.000067
2400	8.97	25.6	0.000080	0.829	83.21	0.00089	0.738	0.000079

Table S7 Parameters obtained by fitting the EIS pattern recorded at equilibrium potential (~0.5 V) on N (15) electrode in equimolar solution (5 mM) of BQ/BQH_2 in 1 M H_2SO_4.

Rotation Rate (rpm)	R_s (Ω)	R_1 (Ω)	Q_1 (S sec^ϕ)	ϕ_1	R_2 (Ω)	Q_2 (S sec^ϕ)	ϕ_2	χ^2(Chi-square)
400	10.1	14.52	0.000064	0.902	102.4	0.00274	0.515	0.000407
800	9.73	24.41	0.000075	0.852	114.7	0.00113	0.689	0.00015
1200	9.69	29.91	0.000082	0.833	123.2	0.00087	0.751	0.000114
1600	8.98	32.09	0.000085	0.823	131.4	0.000806	0.764	0.000086
2000	9.12	34.02	0.000086	0.822	136.4	0.000751	0.780	0.000073
2400	9.59	35.26	0.000083	0.827	147	0.000702	0.783	0.000076

F-test for the EC of EIS patterns recorded under hydrodynamic conditions on N (20) electrode

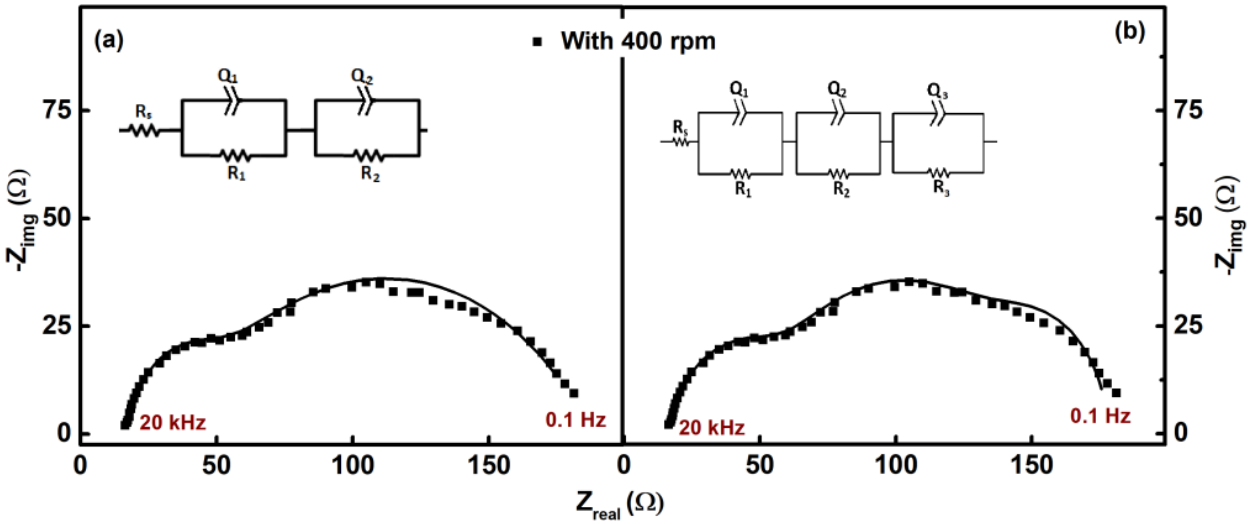

Figure S6 Nyquist plots recorded at equilibrium potential on N (20) electrode in equimolar solution of 5 mM BQ/BQH_2 (1:1) in 1 M H_2SO_4. The respective equivalent circuits are shown in the inset.

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, as shown in Figure S2 (a) and (b). The fitting of mid-frequency and low-frequency features in the Nyquist plots are different in both the cases. The x^2 (Chi-square) is lower when the equivalent circuit consists of three (R, Q) elements. Further clarification is obtained from F-test.

Table S8 Parameters obtained by fitting the EIS pattern recorded at equilibrium potential on N (20) 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 Figure S6(a).

Parameter	Obtained fitting value	Relative standard error (%)	χ^2(Chi-square)	Relative error of the measured impedance
R_s (Ω)	10.67	2.391	0.0006377	2.52
R_1 (Ω)	29.69	4.17		
Q_1 (S sec^ϕ)	0.0000366	2.999		
ϕ_1	0.96	5.661		
R_2 (Ω)	148.7	4.887		
Q_2 (S sec^ϕ)	0.001203	4.687		
ϕ_2	0.537	4.705		

Table S9 Parameters obtained by fitting the EIS pattern recorded at equilibrium potential on N (20) 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 Figure S6(b).

Parameter	Obtained fitting value	Relative standard error (%)	χ^2(Chi-square)	Relative error of the measured impedance
R_s (Ω)	10.4	1.267	0.0004931	2.221
R_1 (Ω)	33.81	1.61		
Q_1 (S sec^ϕ)	0.0000562	1.688		
ϕ_1	0.8598	3.548		
R_2 (Ω)	39.28	2.5		
Q_2 (S sec^ϕ)	0.009859	3.1		
ϕ_2	0.92	1.71		
R_3 (Ω)	89.09	2.67		
Q_3 (S sec^ϕ)	0.0006978	2.56		
ϕ_3	0.7735	1.236		

F (α, k, 2N-m-k) = 2.68869

Where, k=3, m=7 and N=59, α = 0.05

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

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 higher Nafion-concentration.

Equivalent circuit fitting parameters of BQ/BQH_2 on N (20) electrode recorded at various rotation rates

Table S10 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 S4.

Rotation Rate (rpm)	R_s (Ω)	R_1 (Ω)	Q_1 (S sec^ϕ)	ϕ_1	R_2 (Ω)	Q_2 (S sec^ϕ)	ϕ_2	χ^2(Chi-square)
800	10.4	43.54	0.000049	0.885	166.2	0.000689	0.725	0.00083
1200	10.9	46.49	0.000053	0.871	192.3	0.000595	0.749	0.00019
1600	10.4	50.94	0.000064	0.845	201.1	0.000561	0.784	0.00019
2000	10.1	53.06	0.000065	0.853	205.6	0.000536	0.782	0.00009
2400	10.8	56.4	0.000069	0.844	207.6	0.000535	0.779	0.00001

Adsorption voltammograms

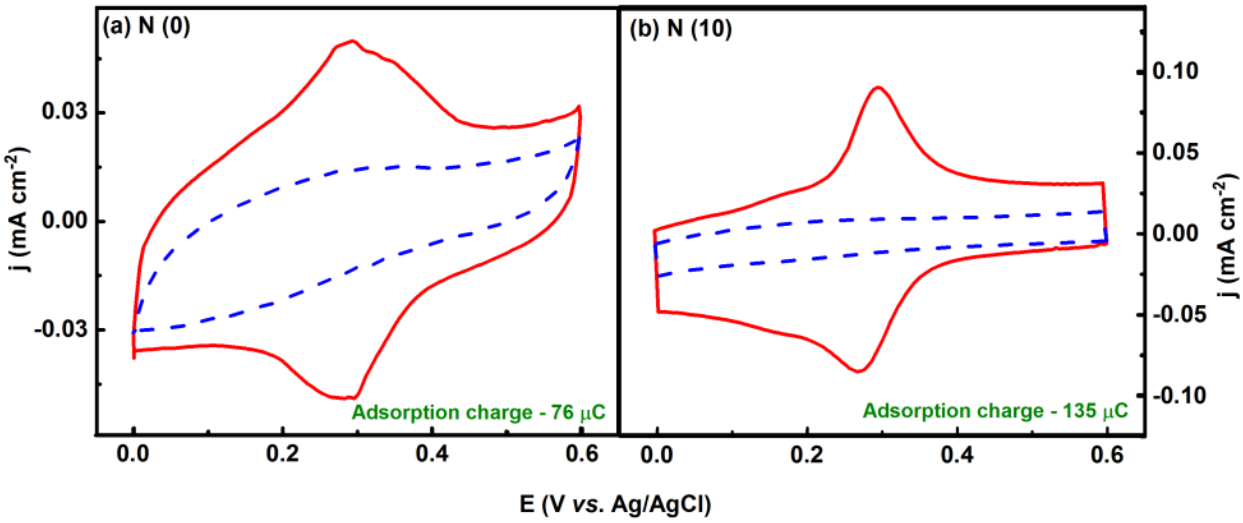

Figure S7 Voltammograms of equimolar solution (5 mM) of BQ/BQH_2 adsorbed on (a) N (0) and (b) N (10) electrode surfaces in argon-saturated 1 M H_2SO_4.

EIS recorded at OCP for single species

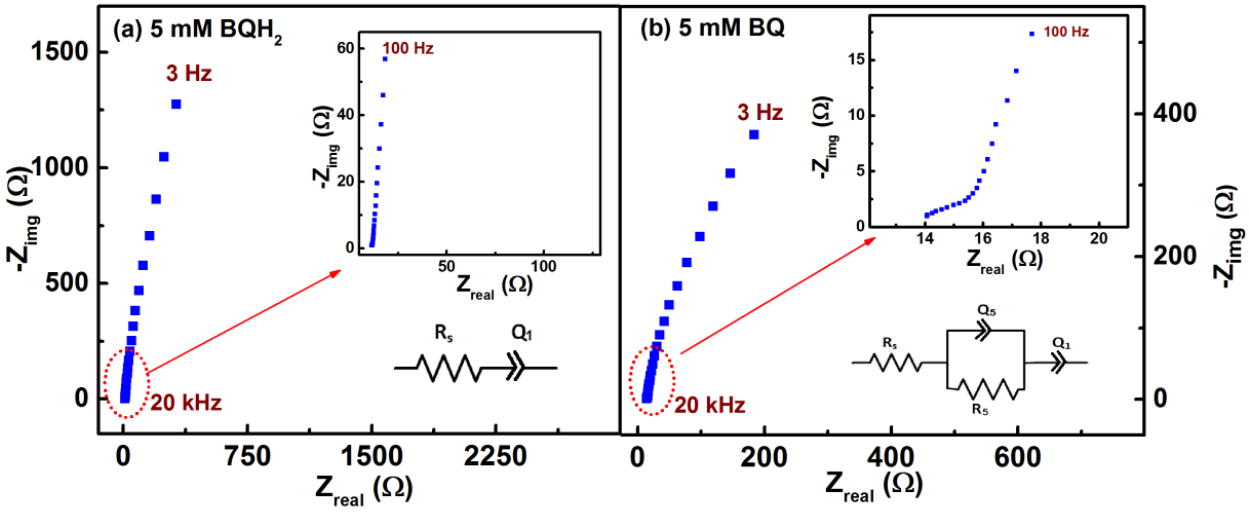

Figure S8 EIS recorded at OCP (Open circuit potential) under the static condition of the GCD for the frequency range 20 kHz – 3 Hz for (a) 5 mM BQH_2 and (b) 5 mM BQ in 1 M H_2SO_4 on N (10) electrode.

Time-dependent nature of adsorption on single species

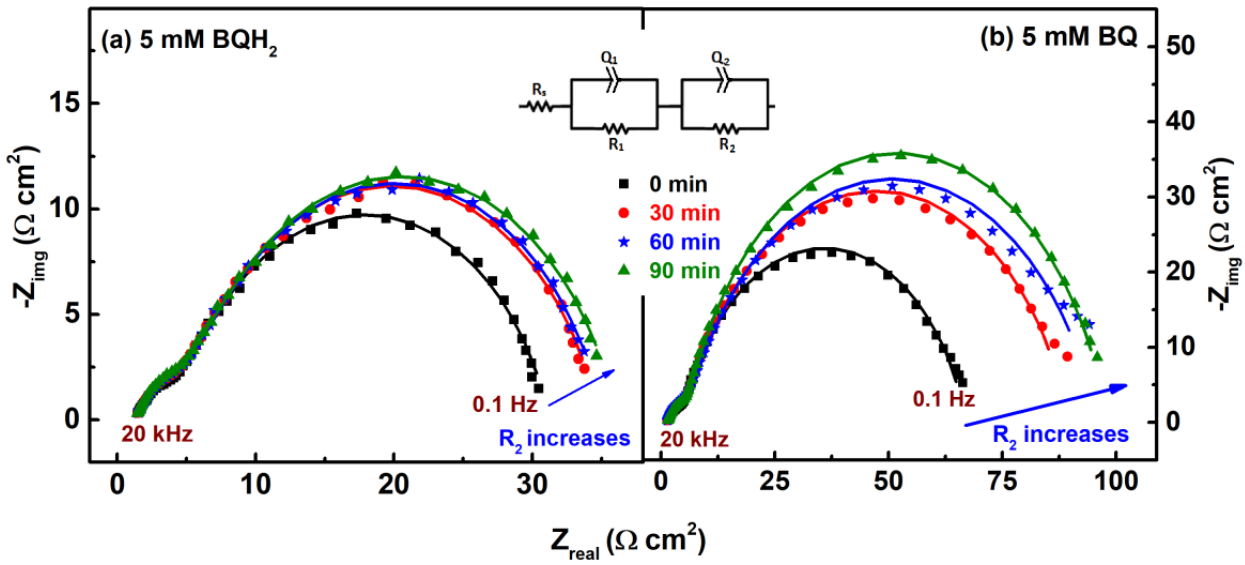

Figure S9 EIS patterns of 5 mM (a) BQH_2 (b) BQ in 1 M H_2SO_4 recorded at equilibrium potential (~0.5 V) on N (10) electrode for various time intervals. ECs are given in the inset. The symbols and solid lines show experimental and fitted data, respectively.

Interaction between Nafion and BQ

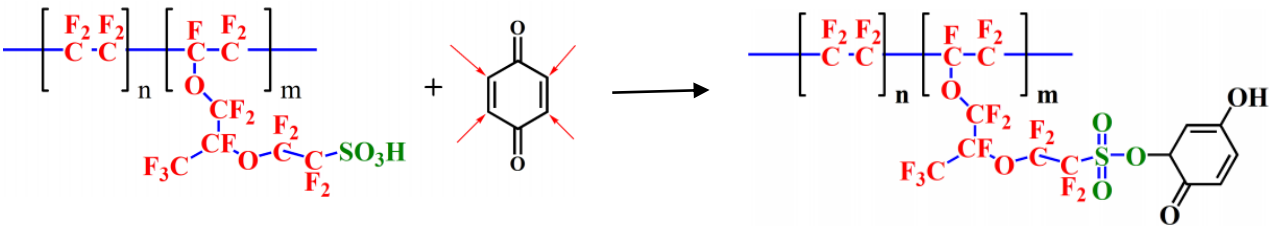

Figure S10 Schematic of Nafion interaction with BQ

^{1}H NMR Spectra

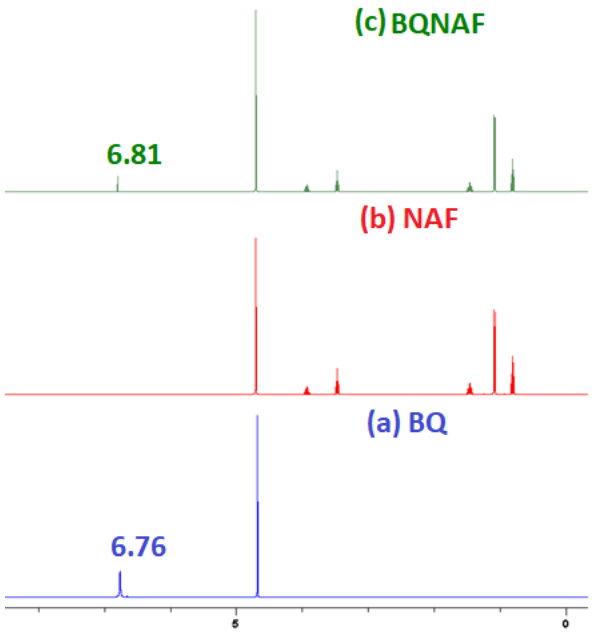

Figure S11 ^{1}H NMR spectra recorded for (a) pure BQ, (b) Nafion and (c) BQ Nafion uniform solution in D_2O.

Flow cell studies

Table S11 Parameters obtained by fitting the EIS pattern recorded in a flow cell at equilibrium potential in equimolar solution (5 mM) of BQ/BQH_2 in 1 M H_2SO_4.

Time (min)	R_s (Ω)	R_1 (Ω)	Q_1 (S sec^ϕ)	ϕ_1	R_2 (Ω)	Q_2 (S sec^ϕ)	ϕ_2	χ^2(Chi-square)
0	0.176	0.295	0.0601	0.673	0.209	10.06	1	0.00087
60	0.191	0.419	0.0625	0.682	0.246	9.44	1	0.00062
120	0.185	0.536	0.090	0.621	0.339	6.99	1	0.00101
180	0.173	0.589	0.087	0.614	0.517	4.71	1	0.00102

Table S12 Parameters obtained by fitting the EIS pattern recorded in a flow cell at equilibrium potential in equimolar solution (200 mM) of V^{4+}/V^{5+} in 3 M H_2SO_4.

Time (min)	R_s (Ω)	R_1 (Ω)	Q_1 (S sec^ϕ)	ϕ_1	χ^2(Chi-square)
0	0.157	1.09	0.0071	0.907	0.00084
60	0.155	1.09	0.0070	0.909	0.0009
120	0.155	1.1	0.00709	0.908	0.00083
180	0.154	1.1	0.0069	0.912	0.00097

Table S13 Parameters obtained by fitting the EIS pattern recorded in a flow cell at equilibrium potential in equimolar solution (200 mM) of V^{2+}/V^{3+} in 3 M H_2SO_4.

Time (min)	R_s (Ω)	R_1 (Ω)	Q_1 (S sec^ϕ)	ϕ_1	χ^2(Chi-square)
0	0.131	0.901	0.0058	0.891	0.00054
60	0.133	0.901	0.0058	0.891	0.00051
120	0.131	0.90	0.00579	0.89	0.0006
180	0.128	0.90	0.00578	0.89	0.00064

Table S14 Parameters obtained by fitting the EIS pattern recorded in a flow cell at equilibrium potential in equimolar solution (200 mM) of V^{2+}/V^{3+} in 3 M H_2SO_4 in the anolyte compartment and 100 mM BQ/BQH_2 in the catholyte compartment.

Time (min)	R_s (Ω)	R_1 (Ω)	Q_1 (S sec^ϕ)	ϕ_1	χ^2(Chi-square)
0	0.0925	0.791	0.0604	0.803	0.0035
60	0.0957	1.051	0.0437	0.821	0.0032
120	0.103	1.193	0.0466	0.811	0.0053
180	0.11	1.34	0.0351	0.849	0.0013

Polarization and power density curves

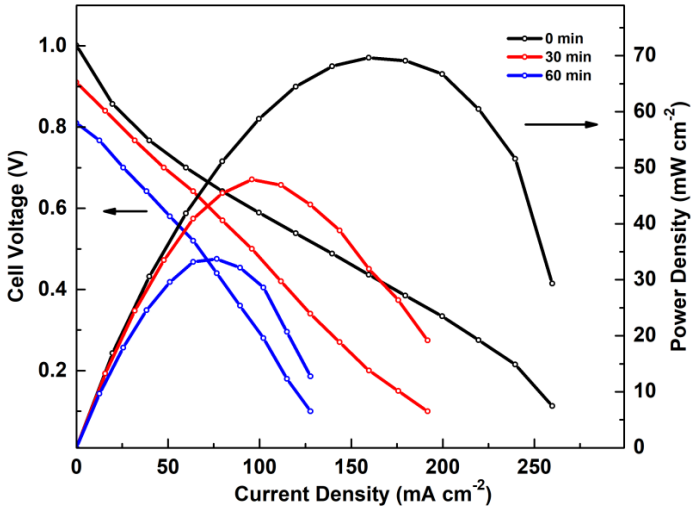

Figure S12 Polarization and power density curve obtained for V^{2+}/BQ flow cell recorded with Carbon felt electrodes and Nafion 117 membrane. Flow cell is operated at 20 mL min^{-1}.

Table S15

Flow cell	Anolyte	Catholyte	Impedance with time
BQ/BQH_2	BQ/BQH_2 equimolar solution	BQ/BQH_2 equimolar solution	Increases
V^{4+}/V^{5+}	V^{4+}/V^{5+} equimolar solution	V^{4+}/V^{5+} equimolar solution	Constant
V^{2+}/V^{3+}	V^{2+}/V^{3+} equimolar solution	V^{2+}/V^{3+} equimolar solution	Constant
V^{2+}/BQ	V^{2+}	BQ	Increases

Raman Spectra of Nafion 117 membrane

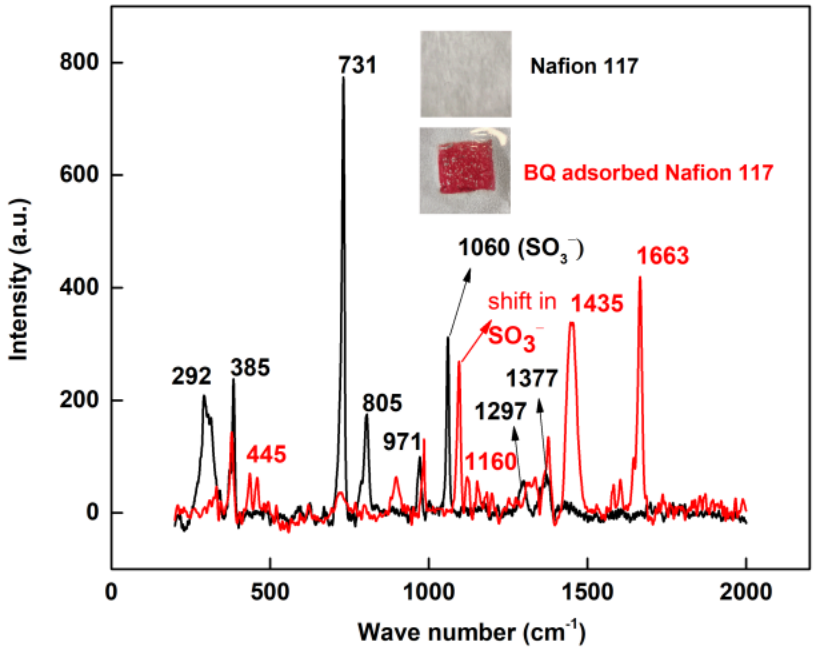

Figure S13 Raman spectra of Nafion 117 (black line) and Nafion 117 obtained from the V^{2+}/BQ cell (red line).