Pseudocapacitive Slurry Electrodes Using Redox-Active Quinone for High-Performance Flow Capacitors: An Atomic-Level Understanding on Pore Texture and Capacitance Enhancement

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Supporting information:

1. N_2 adsorption/desorption isotherms and pore size distribution of the highly porous carbon spheres.
2. XPS analysis of the double-layer capacitive and pseudocapacitive (w/ 0.3 M HQ) slurry electrodes.
3. Adsorption structures and energies of an HQ molecule on a carbon surface via π–π interaction and chemical bonding.
4. The effect on capacitance and rate performance with various concentrations of HQ redox mediator.
5. A possible HQ cluster structure at a micropore entrance.
6. Cycle life test of the pseudocapacitive slurry electrode (w/ 0.3 M HQ).
7. Electrochemical impedance spectroscopy (EIS) fitting parameters from the equivalent circuit fitting.

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1. N_2 adsorption/desorption isotherms and pore size distribution of the highly porous carbon spheres.

The amount of nitrogen adsorbed onto the AC8K30 porous carbon spheres was used to calculate the specific surface area by BET (Brunauer-Emmett-Teller) method. The primitive carbon spheres exhibited BET surface areas of 3634 m^2g^{-1}. Pore size distribution (PSD) was determined by the non-local density functional theory (NLDFT) method.

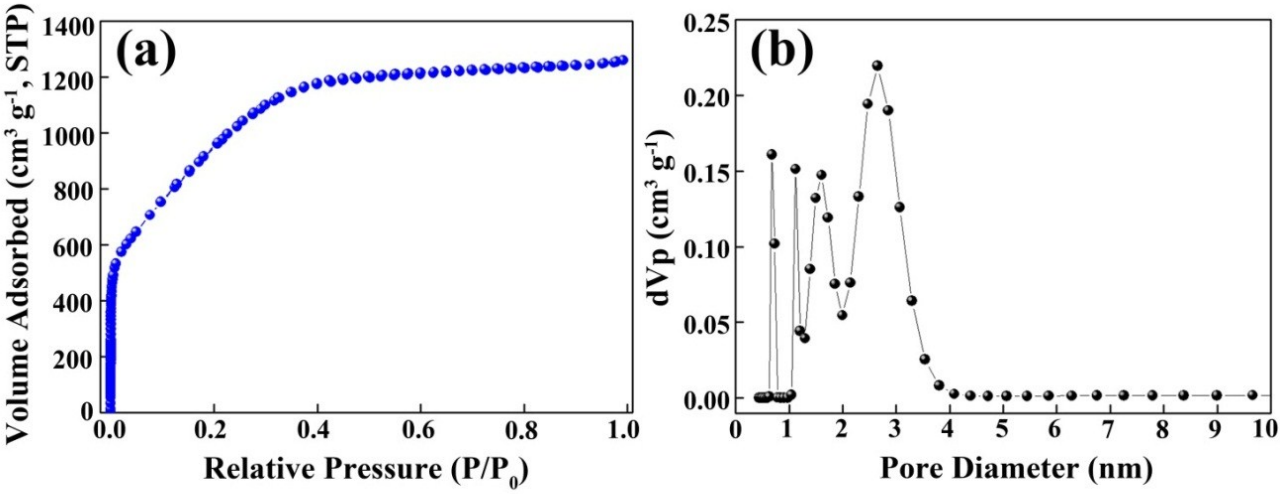


Fig. S1 (a) N_2 adsorption/desorption isotherms, and (b) the pore size distribution of the AC8K30 highly porous carbon spheres.

2. XPS analysis of the double-layer capacitive and pseudocapacitive (w/ 0.3 M HQ) slurry electrodes.

To gain insight into HQ-based slurry electrode, unmodified (double-layer capacitive slurries) and HQ adsorbed (pseudocapacitive (w/ 0.3 M HQ) slurries) carbon slurry electrodes were characterized by XPS. As shown in Fig. S2, the survey spectra clearly show the presence of C 1s (285 eV) and O 1s (532 eV) peaks for both samples.

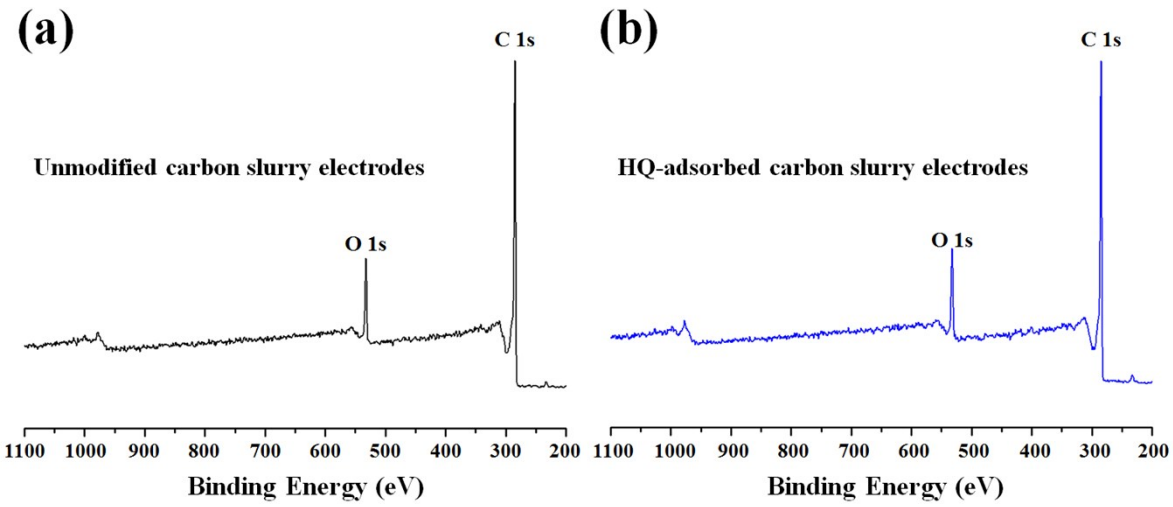


Fig. S2 XPS survey spectra of (a) unmodified (double-layer capacitive slurries) and (b) HQ-adsorbed (pseudocapacitive (w/ 0.3 M HQ) slurries) carbon slurry electrodes.

To confirm the difference between two samples and the successful adsorption of HQ on carbon, we normalized and overlaid the high-resolution XPS spectra for C 1s and O 1s (Fig. S3). While it is hard to identify differences in O 1s spectrum, there is a peak intensity increase at ~286 eV in C 1s spectrum after the modification with HQ. Based on these results, we further analyzed the high-resolution C 1s spectra by using the deconvolution process (Fig. S4). The C 1s spectrum of unmodified carbon exhibits a main peak at 284.7 eV, which is attributed to sp^2 C–C

bonds in a graphite-like carbon.[S1,S2] In addition, there are characteristic peaks at 285.8 eV, 286.5 eV, and 287.4 eV that represent β–carbon,[S3] C–OH or C–O–C,[S4] and C=O,[S4] respectively. β–carbons are those that are attached to oxidized carbons. From the high-resolution C 1s spectrum after the surface modification with HQ, we examined the area near 286 eV where the peak intensity increased in the normalized survey spectra. The C 1s spectrum of HQ-adsorbed carbon shows the peak at 285.6 eV in addition to the peaks from the unmodified carbon. We thought that the peak at 285.6 eV could be induced by HQ, and further analyzed HQ by XPS. The high-resolution C 1s spectrum of HQ represents two peaks at 284.2 eV and 285.6 eV after deconvolution (Fig. S5). This result is consistent with the previous study, which reported two main peaks for HQ.[S5] As the spectrum curve near ~284 eV is relatively linear, compared with other areas, we could not identify a peak at 284.2 eV in the high-resolution C 1s spectrum of HQ-adsorbed carbon, even after deconvolution. This is also consistent with the lack of any large difference in the region from the overlaid C 1s spectra of unmodified and HQ-absorbed carbons. Taking these results together, it is concluded that HQ successfully adsorbed onto carbon.

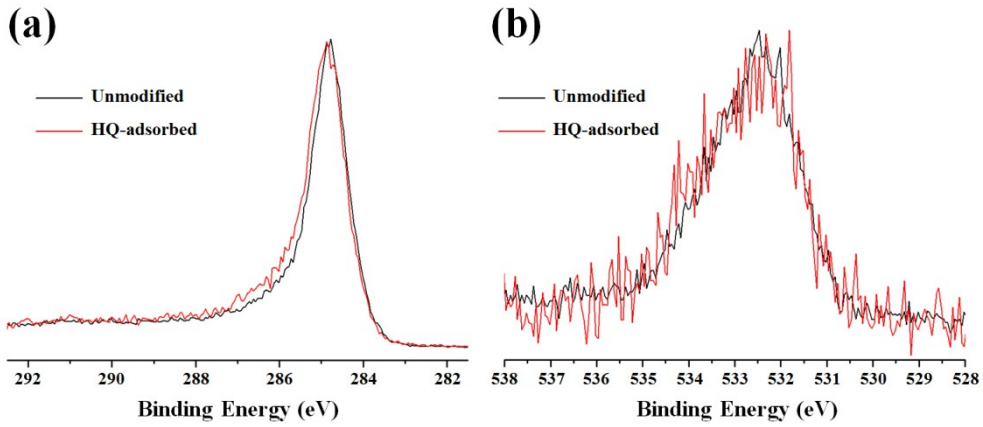


Fig. S3 (a) C 1s and (b) O 1s high-resolution XPS spectra of unmodified (black line) and HQ-adsorbed (red line) carbon slurry electrodes. Unmodified and HQ-adsorbed spectra are normalized according to the maximum intensity of unmodified spectrum.

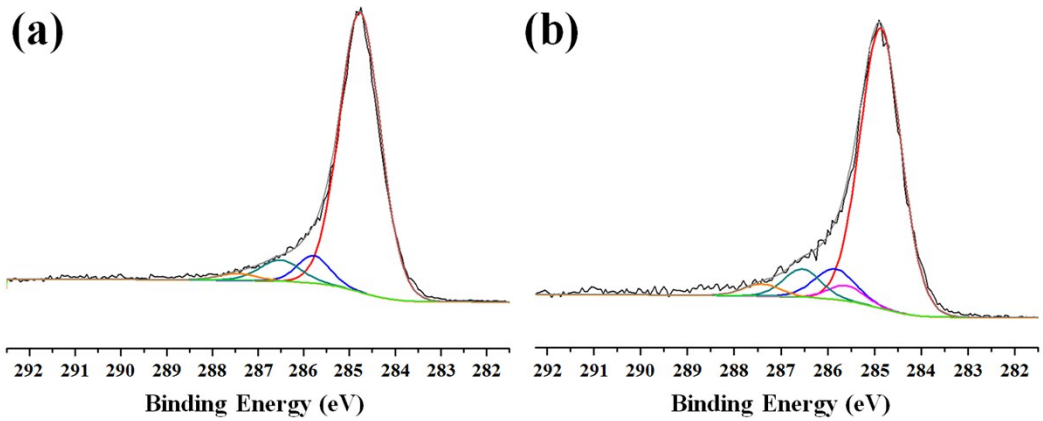


Fig. S4 Deconvoluted C 1s high-resolution XPS spectra of (a) unmodified and (b) HQ-adsorbed carbon slurry electrodes.

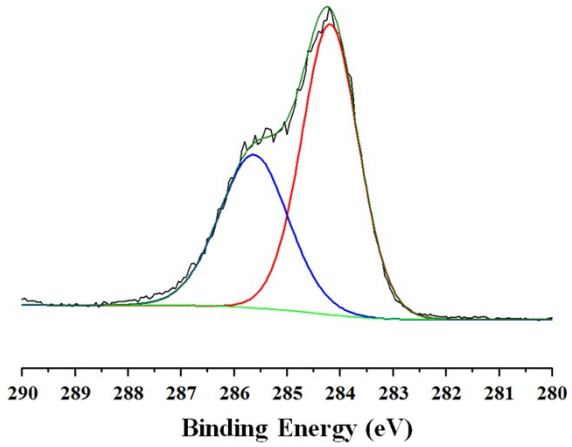


Fig. S5 Deconvoluted C 1s high-resolution XPS spectrum of HQ.

[S1] I. Palchan, M. Crespin, H. Estrade-Szwarckopf, B. Rousseau, *Chem. Phys. Lett.*, 1989, **157**, 321.

[S2] K. Shilbagaki, S. Motojima, *Carbon*, 2000, **38**, 2087.

[S3] A. Le Comte, D. Chhin, A. Gagnon, R. Retoux, T. Brousse, D. Bélanger, *J. Mater. Chem. A.*, 2015, **3**, 6146.

[S4] P. Burg, P. Fydrych, D. Cagniant, G. Nanse, J. Bimer, A. Jankowska, *Carbon*, 2002, **40**, 1521.

[S5] T. Ohta, M. Yamada, H. Kuroda, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 1158.

3. Adsorption structures and energies of an HQ molecule on a carbon surface via π–π interaction and chemical bonding.

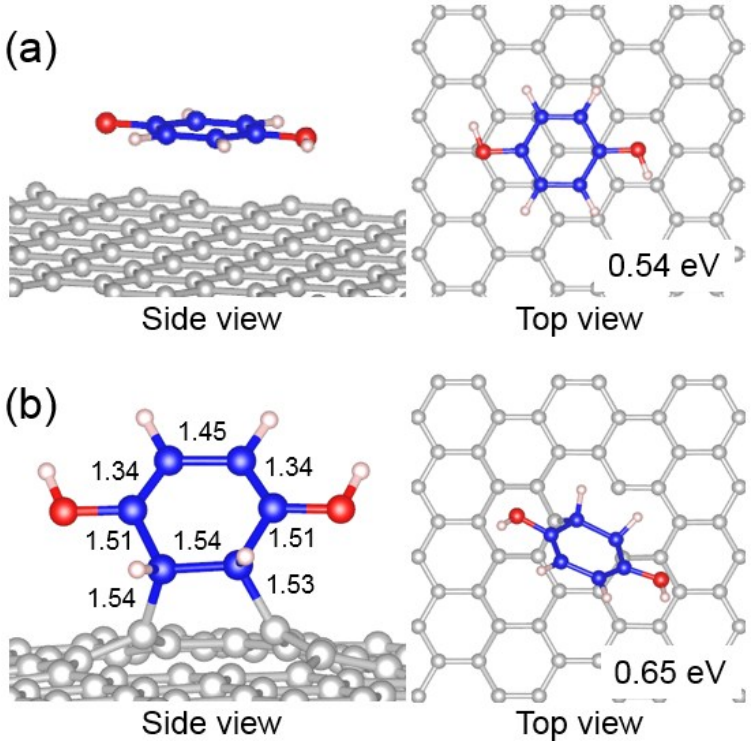
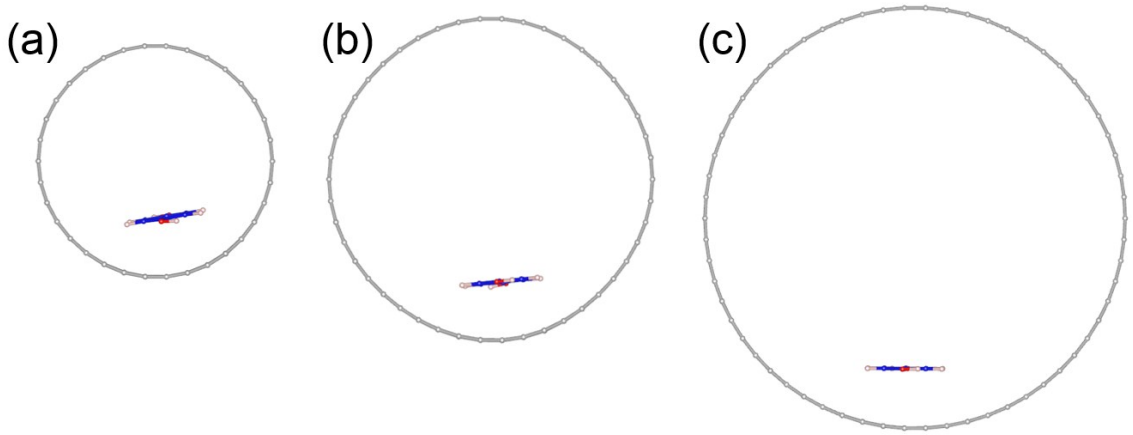


Fig. S6 Adsorption structures and energies of an HQ molecule on a carbon surface via (a) π–π interaction and (b) chemical bonding. The C–C distances (in Å) of the chemically bonded HQ are given. Grey, red, and pink dots denote the C, O, and H atoms, respectively. The carbon atoms of the HQ are marked as blue.

We calculated the grafting of a HQ molecule via π–π interaction on the pore walls of different sizes. The calculated structures and energies are given in the figure below. The calculated adsorption energies of an HQ molecule on the (a) 1.34, (b) 1.78, and (c) 2.51 nm pores are 1.00, 0.95, and 0.75 eV, respectively, decreasing as the pore diameter increases. Grey, red, and pink dots denote the C, O, and H atoms, respectively. The carbon atoms of the grafted HQ are marked as blue.


(a)
(b)
(c)

4. The effect on capacitance and rate performance with various concentrations of HQ redox mediator.

The effect on capacitance and rate performance with various concentrations of HQ redox mediator in the slurry was studied as shown in Fig. S7. At a scan rate of 2 mV s^{-1}, the gravimetric capacitance values for 0.1, 0.2, 0.3, and 0.38 M HQ concentrations were 289, 362, 412, 513 F g^{-1}, respectively. The maximum capacitance obtained was 513 F g^{-1} (at 2 mV s^{-1}) for the pseudocapacitive slurry electrode (w/ 0.38 M HQ). However, the optimum HQ concentration for both rate performance and capacitance is 0.3 M HQ.

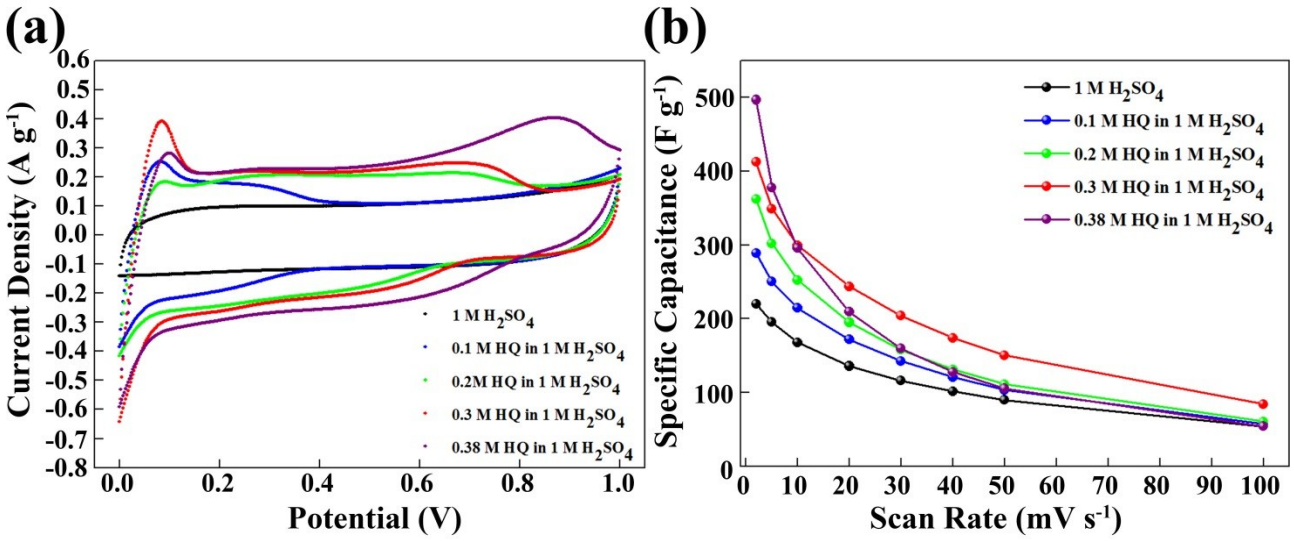


Fig. S7 (a) CVs for slurry electrodes with various concentrations of HQ added at 2 mV s^{-1}. (b) Rate performance of the corresponding slurry electrodes at various scan rates.

5. A possible HQ cluster structure at a micropore entrance.

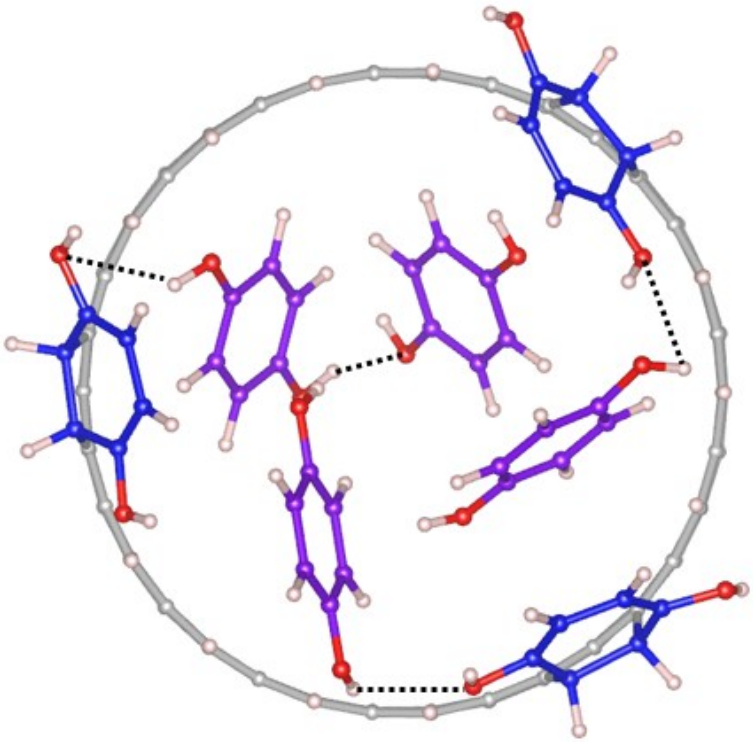


Fig. S8 A possible HQ cluster structure at the pore entrance of 1.34 nm micropore. The benzene rings of directly grafted HQs are marked as blue while those of indirectly grafted HQs are marked as purple. The dash line represents hydrogen bonds.

6. Cycle life test of the pseudocapacitive slurry electrode (w/ 0.3 M HQ).

In Fig. S9, the galvanostatic cycling performance of the pseudocapacitive slurry electrode was investigated at 20 mA (current density of 5 mA cm^{-2}) for 1000 cycles. After 1000 cycles, the decline in capacitance for the pseudocapacitive slurry electrode was about 40 %, whereas the decline was more than 50 % for the previously reported HQ modified slurry electrodes.

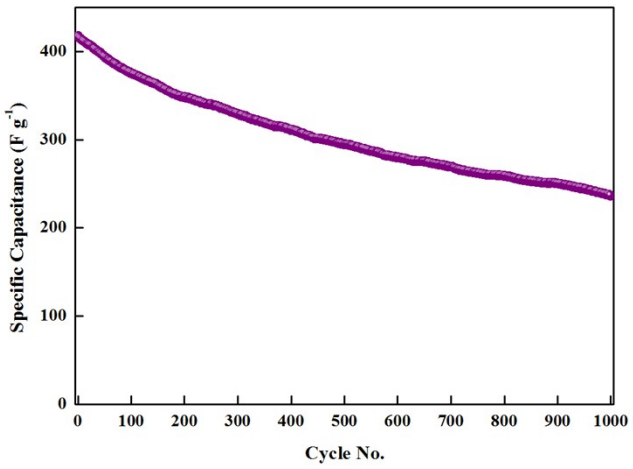


Fig. S9 Specific discharge capacitance as a function of cycle number.

7. Electrochemical impedance spectroscopy (EIS) fitting parameters from the equivalent circuit fitting.

Table S1 EIS fitting parameters for DL capacitive and pseudocapacitive (0.3 M HQ) slurries

	DL capacitive slurry	Pseudocapacitive slurry
L1(H)	3.24×10^{-7} ($\pm 3.49 \times 10^{-7}$)	2.96×10^{-7} ($\pm 3.55 \times 10^{-7}$)
R1 (Ω)	1.82×10^{-1} ($\pm 4.14 \times 10^{-3}$)	1.67×10^{-1} ($\pm 5.48 \times 10^{-3}$)
R2 (Ω)	1.76×10^{-1} ($\pm 1.30 \times 10^{-2}$)	1.66×10^{-1} ($\pm 1.57 \times 10^{-2}$)
Y1 ($\Omega^{-1} \cdot s^{-n}$)	2.72×10^{-4} ($\pm 1.15 \times 10^{-4}$)	1.28×10^{-3} ($\pm 6.63 \times 10^{-4}$)
n1	8.59×10^{-1} ($\pm 4.00 \times 10^{-2}$)	7.39×10^{-1} ($\pm 4.85 \times 10^{-2}$)
C1 (F)	5.30×10^{-5}	6.45×10^{-5}
R3 (Ω)	3.04×10^{-1} ($\pm 9.79 \times 10^{-3}$)	1.90×10^{-1} ($\pm 8.18 \times 10^{-3}$)
Y2 ($\Omega^{-1} \cdot s^{-n}$)	2.17×10^{-1} ($\pm 1.29 \times 10^{-2}$)	3.45×10^{-1} ($\pm 2.61 \times 10^{-2}$)
n2	4.76×10^{-1} ($\pm 1.24 \times 10^{-2}$)	4.90×10^{-1} ($\pm 1.76 \times 10^{-2}$)
C2 (F)	1.09×10^{-2}	2.03×10^{-2}
WO_R (Ω)	2.55 ($\pm 4.23 \times 10^{-2}$)	1.48 ($\pm 3.26 \times 10^{-2}$)
WO_T (s)	7.65 ($\pm 2.12 \times 10^{-2}$)	3.92 ($\pm 1.33 \times 10^{-2}$)
WO_P	0.5	0.5