Electronic Supplementary Information Electrochemical

Electrochemical Properties of a Ferrocene-Containing Poly(vinyl alcohol)-Based Redox Hydrogel and Its Application as a Matrix for Electrochromic Devices

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The results of ATR-FTIR Spectroscopy

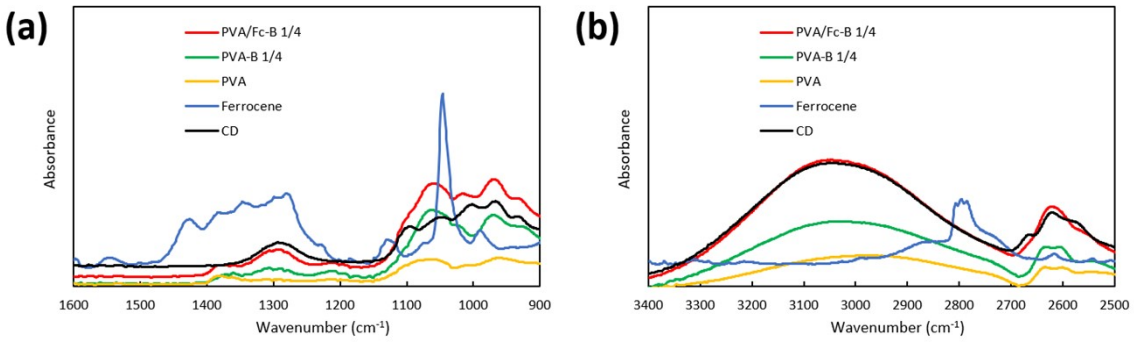

Fig. S1 Results of ATR-FTIR measurements of hydrogels: (a) region of 900 cm^{-1} – 1600 cm^{-1}, (b) region of 2500 cm^{-1} – 3400 cm^{-1}.

Explanation of Nicholson's equation[1]

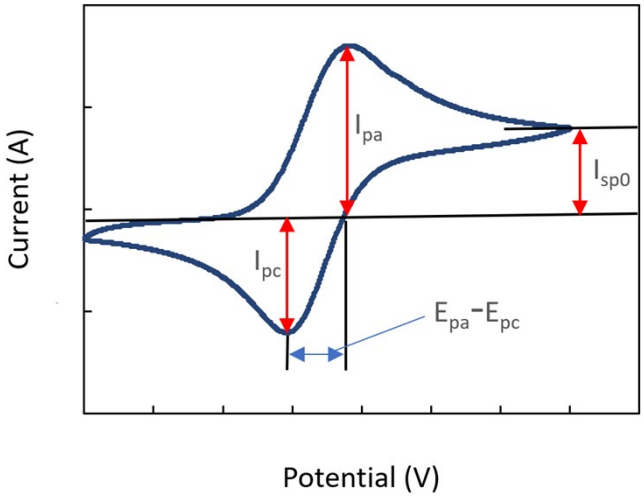

Fig. S2 Cyclic voltammogram of one-electron electrochemical process for explanation of Nicholson's equation. I_{pa}: Peak current at first-oxidation potential in anodic oxidation process. I_{pc}: Peak current at first-reduction potential in anodic oxidation process. I_{sp0}: Current at switching potential of the direction of scan on first wave in anodic oxidation process.

For one-electron oxidation, modified Nicholson's equation is described as,[1]

$I_{pc} / I_{pa} = (I_{pc} - I_{sp0}) / I_{pa} + 0.485\ I_{sp0} / I_{pa} + 0.086$.

Tables S1– S6

Table S1 Electrochemical data for **Fc/CD** aq. (CV, Fig. 5a).

	Anodic process	Cathodic process		Anodic process	Cathodic process		
Scan rate /V s^{-1}	E_{pa}/V	E_{pc}/V	E_{pa}-E_{pc}/mV	I_{pa}/μA	I_{pc}/μA	I_{sp0}/μA	I_{pc}/I_{pa}
0.5	0.443	0.268	175	87.6	87.8	59.4	1.42
0.4	0.431	0.27	161	80.8	79.6	52.0	1.38
0.3	0.417	0.275	142	73.4	69.6	45.0	1.33
0.2	0.405	0.279	126	62.9	58.0	35.8	1.28
0.1	0.393	0.286	107	48.5	41.4	26.3	1.20
0.05	0.392	0.287	105	33.8	28.9	17.6	1.19
0.01	0.382	0.292	90	16.1	12.1	7.97	1.08

I_{pc}/I_{pa} was estimated by Nicholson's equation.

Table S2 Electrochemical data for **PVA/Fc-B-N** 1/4 (CV, Fig. 5b).

	Anodic process	Cathodic process		Anodic process	Cathodic process		
Scan rate /V s^{-1}	E_{pa}/V	E_{pc}/V	E_{pa}-E_{pc}/mV	I_{pa}/μA	I_{pc}/μA	I_{sp0}/μA	I_{pc}/I_{pa}
0.5	0.351	0.252	99	22.2	23.5	15.7	1.49
0.4	0.341	0.255	86	20.1	20.9	13.5	1.45
0.3	0.337	0.254	83	17.2	18.1	11.4	1.46
0.2	0.339	0.255	84	14.7	15.3	9.17	1.43
0.1	0.339	0.255	84	10.6	10.8	6.25	1.39
0.05	0.337	0.259	78	7.91	7.61	4.50	1.32
0.01	0.335	0.26	75	3.78	3.15	1.46	1.11

I_{pc}/I_{pa} was estimated by Nicholson's equation.

Table S3 Electrochemical data for **PVA**/**Fc-B-N** 1/6 (CV, Fig. 5c).

	Anodic process	Cathodic process		Anodic process	Cathodic process		
Scan rate /V s^{-1}	E_{pa}/V	E_{pc}/V	E_{pa}-E_{pc}/mV	I_{pa}/μA	I_{pc}/μA	I_{sp0}/μA	I_{pc}/I_{pa}
0.5	0.35	0.236	114	23.2	25.2	23.0	1.65
0.4	0.338	0.239	99	17.4	18.4	16.1	1.59
0.3	0.338	0.239	99	17.4	18.4	16.1	1.59
0.2	0.338	0.238	100	13.8	14.7	12.5	1.59
0.1	0.335	0.242	93	10.0	9.89	8.39	1.48
0.05	0.337	0.251	86	7.08	6.51	5.39	1.37
0.01	0.327	0.256	71	4.34	2.29	2.76	0.92

I_{pc}/I_{pa} was estimated by Nicholson's equation.

Table S4 Electrochemical data for **PVA**/**Fc-B-N** 1/8 (CV, Fig. 5d).

	Anodic process	Cathodic process		Anodic process	Cathodic process		
Scan rate /V s^{-1}	E_{pa}/V	E_{pc}/V	E_{pa}-E_{pc}/mV	I_{pa}/μA	I_{pc}/μA	I_{sp0}/μA	I_{pc}/I_{pa}
0.5	0.332	0.201	131	11.2	1.89	22.3	2.74
0.4	0.328	0.196	132	9.89	1.68	19.4	2.74
0.3	0.331	0.198	133	8.44	1.51	15.9	2.79
0.2	0.333	0.205	128	8.17	1.23	12.4	2.33
0.1	0.337	0.216	121	4.75	8.94	7.67	2.75
0.05	0.315	0.223	92	3.43	6.30	5.56	2.71
0.01	0.335	0.25	85	3.60	2.61	1.46	1.01

I_{pc}/I_{pa} was estimated by Nicholson's equation.

Table S5 Electrochemical data for **PVA**/**Fc-B-N** 1/16 (CV, Fig. 5e).

	Anodic process	Cathodic process		Anodic process	Cathodic process		
Scan rate/V s^{-1}	E_{pa}/V	E_{pc}/V	E_{pa}-E_{pc}/mV	I_{pa}/μA	I_{pc}/μA	I_{sp0}/μA	I_{pc}/I_{pa}
0.5	*	*	*	*	*	*	*
0.4	*	*	*	*	*	*	*
0.3	*	*	*	*	*	*	*
0.2	*	*	*	*	*	*	*
0.1	*	*	*	*	*	*	*
0.05	*	*	*	*	*	*	*
0.01	0.355	0.272	83	3.28	5.60	4.42	1.86

*: Only the data obtained at a scan rate of 0.01 V/s could be extracted from the electrochemical measurements.

I_{pc}/I_{pa} was estimated by Nicholson's equation.

Table S6 Electrochemical data for **PVA**/**Fc-B** 1/4 (CV, Fig. 5f).

	Anodic process	Cathodic process		Anodic process	Cathodic process		
Scan rate/V s^{-1}	E_{pa}/V	E_{pc}/V	E_{pa}-E_{pc}/mV	I_{pa}/μA	I_{pc}/μA	I_{sp0}/μA	I_{pc}/I_{pa}
0.5	*	*	*	*	*	*	*
0.4	*	*	*	*	*	*	*
0.3	*	*	*	*	*	*	*
0.2	*	*	*	*		*	*
0.1	*	*	*	*	*	*	*
0.05	*	*	*	*	*	*	*
0.01	0.383	0.214	169	4.57	3.45	2.46	1.10

*: Only the data obtained at a scan rate of 0.01 V/s could be extracted from the electrochemical measurements.

I_{pc}/I_{pa} was estimated by Nicholson's equation.

Fig. S3

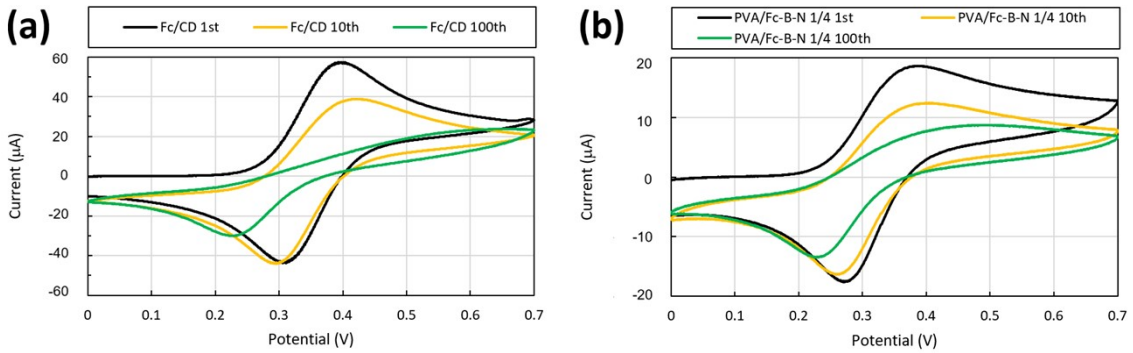

Fig. S3 Cyclic voltammograms of one-electron electrochemical process for (a) **Fc/CD** aqueous solution with 1 M NaCl and (b) **PVA/Fc-B-N** 1/4.

Fig. S4

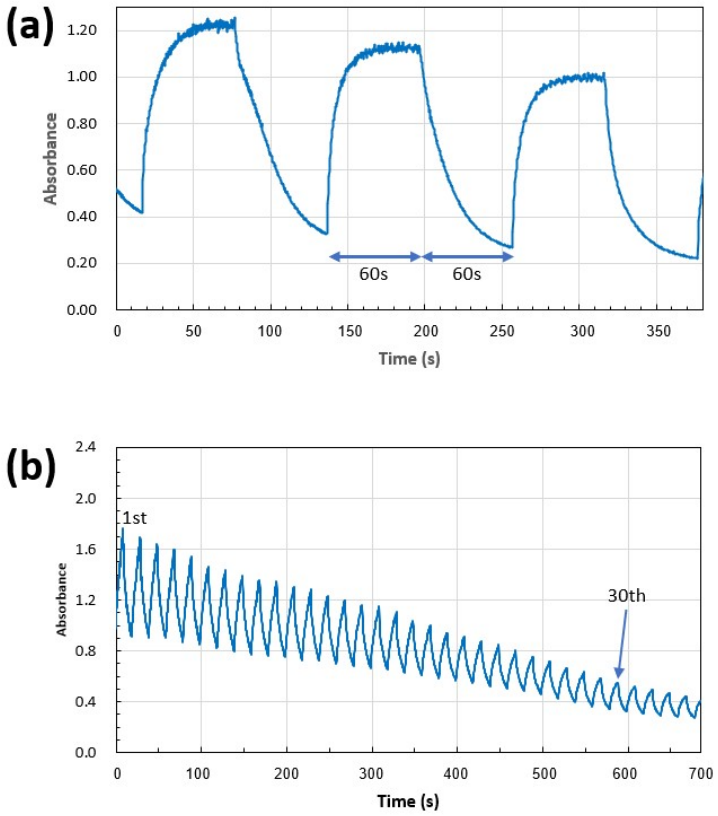

Fig. S4 Electrochemical responses of PVA/Fc-B 1/4/NaCl/EB.(a) Response to square-wave potentials alternating between –1.9 V and 0 V every 60 seconds, (b) Response to square-wave potentials alternating between –1.9 V and 0 V every 10 seconds, monitored at 550 nm.

Reference

1 A. J. Bard, L. R. Faulkner and H. S. White, *Electrochemical Methods: Fundamentals and Applications, 3rd Edition*, chapter 7, Wiley, 2022.