Supporting Information

The enhancement in kinetics of oxygen reduction reaction on a nitrogen-doped carbon catalyst by introduction of iron via electrochemical methods

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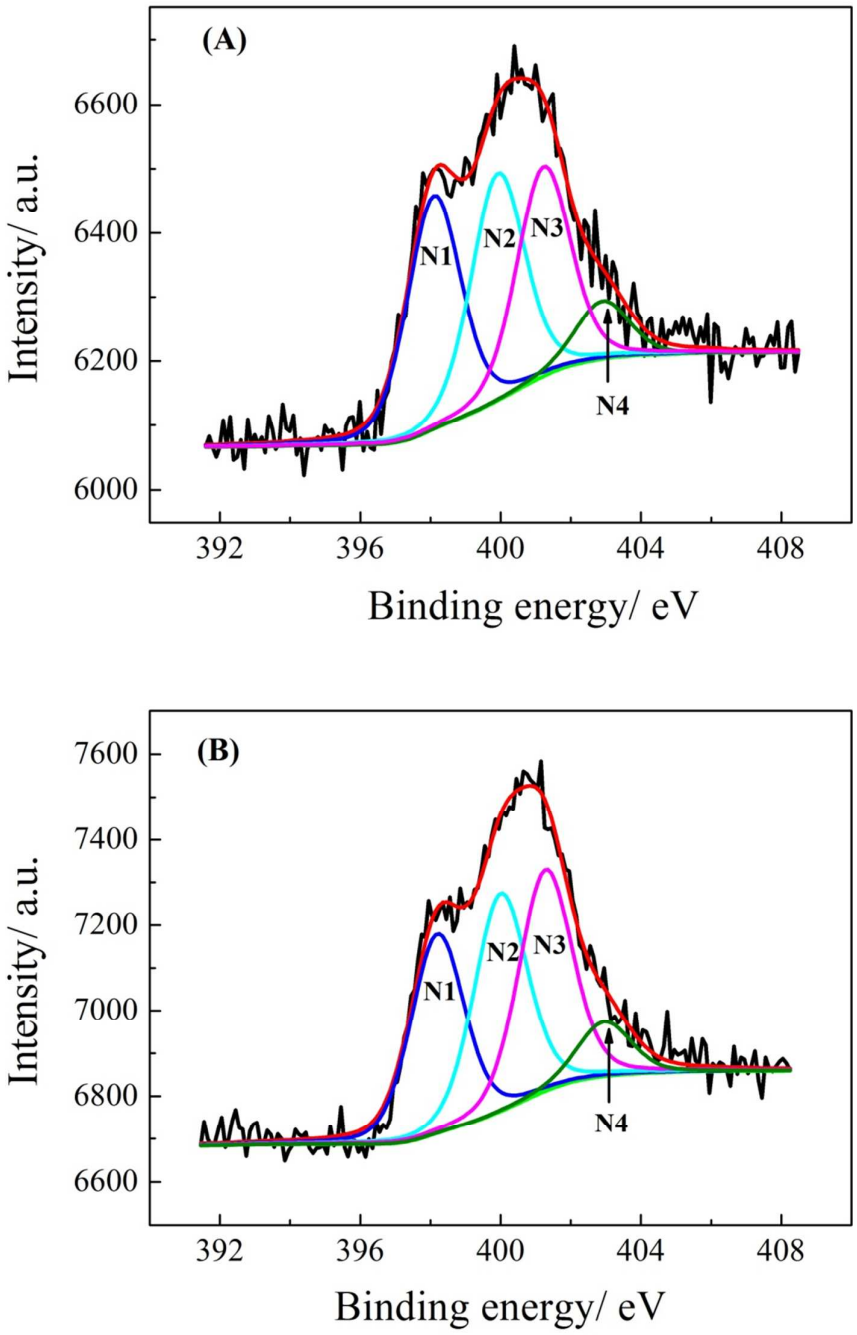


Figure S1. XPS N1s spectra for different P-PI/GC electrodes (A: without treatment, b: with the electrochemical treatment in 0.5 M Na_2SO_4 containing 0.1 M $FeSO_4$). The deconvoluted peaks correspond to pyridinic (N1), pyrrolic (N2), quaternary nitrogen (N3), and nitrogen oxide (N4), respectively. XPS measurements were carried out on a Shimadzu ESCA3400 spectrometer with Mg Kα radiation.

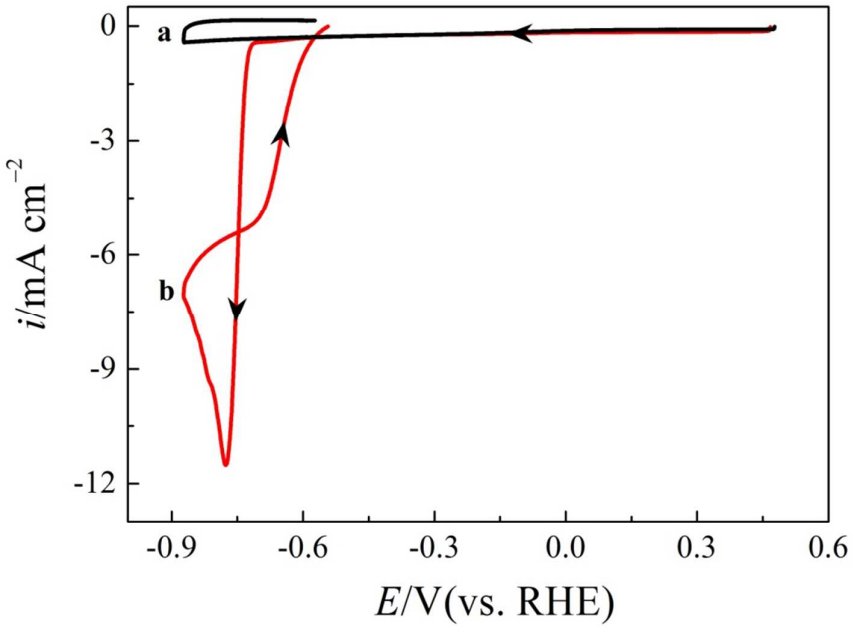


Figure S2. CVs recorded at P-PI/GC electrodes in Ar-sat. 0.5 M Na_2SO_4 containing no $FeSO_4$ (a) and 0.1 M $FeSO_4$ (b). Scan rate: 5 mV s^{-1}.

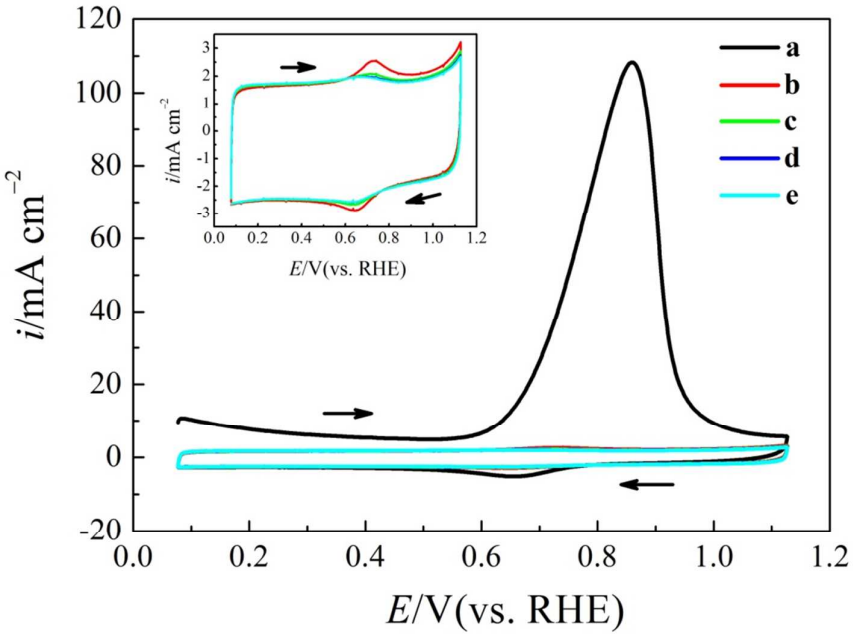


Figure S3. CVs for successive 5 potential cycles on the Fe-electrodeposited P-PI/GC electrode in Ar-sat. 0.5 M H_2SO_4. Curves a to e stand for the first to fifth cycle, respectively. The inset gives an enlarged view on and after the second cycle. Scan rate: 50 mV s^{-1}.

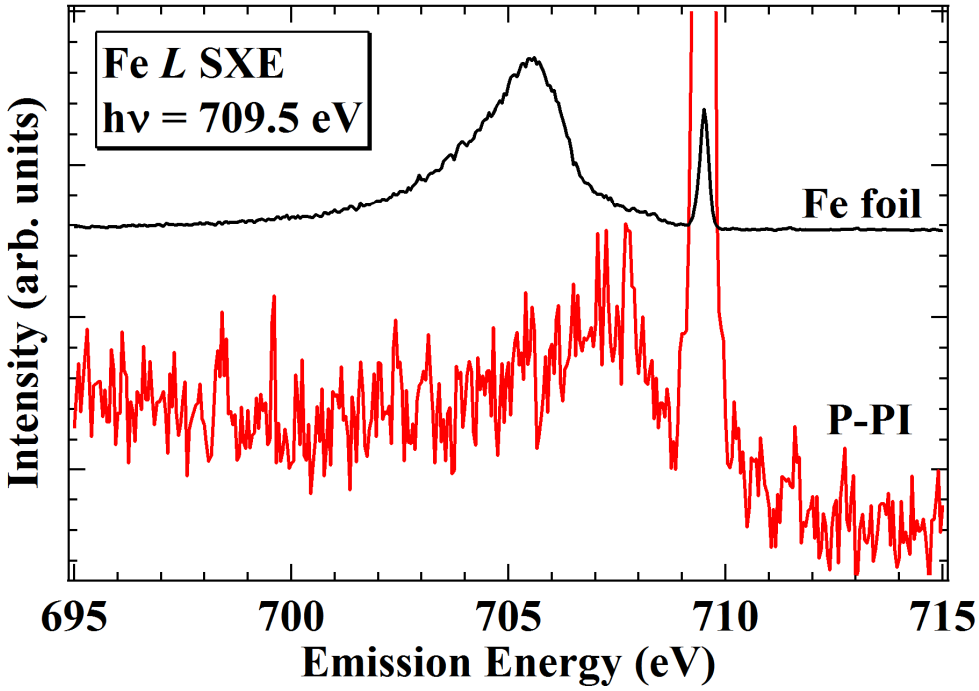


Figure S4. Fe L soft X-ray emission spectroscopy spectra of Fe foil and the P-PI with the electrochemical treatment in 0.5 M Na_2SO_4 containing 0.1 M $FeSO_4$.

Soft X-ray emission spectroscopy

Soft X-ray emission (SXE) spectroscopy measurements were performed at BL07LSU of SPring- 8 using an ultrahigh resolution SXE spectrometer [S1]. The energy resolution was better than 260 meV at 710.0 eV. SXE measurements were performed at room temperature. The base pressure was under 5×10^{-6} Pa. The whole one side of Au coated SiN substrate instead of GC due to the experimental setup was modified with P-PI, followed by the electrochemical treatment mentioned in the manuscript.

As can be seen from Figure S4, the peak profile of the P-PI catalyst is completely different from that of Fe foil, indicating absence of metallic compounds after the electrochemical treatment. The appearance of the *dd* excitation peak around 2 eV

below the elastic peak is characteristic for iron species with nitrogen coordination, rather than typical iron oxides having larger *dd* excitation peaks [S2]. In fact, the peak position of the *dd* excitation is similar to a metal-containing NDC catalyst with high ORR activity synthesized by the multi-step pyrolysis [S3]. The absence of Fe metallic compounds and oxides, and the presence of the Fe-N_x sites are consistent with the XAFS measurements.

[S1] Harada, Y.; Kobayashi, M.; Niwa, H.; Senba, Y.; Ohashi, H.; Tokushima, T.; Horikawa, Y.; Shin, S.; Oshima, M. Ultrahigh resolution soft x-ray emission spectrometer at BL07LSU in SPring-8. *Rev. Sci. Instrum.* **2012**, *83*, 013116.

[S2] Yang, W.; Sorini, a.; Chen, C.-C.; Moritz, B.; Lee, W.-S.; Vernay, F.; Olalde-Velasco, P.; Denlinger, J.; Delley, B.; Chu, J.-H.; Analytis, J.; Fisher, I.; Ren, Z.; Yang, J.; Lu, W.; Zhao, Z.; van den Brink, J.; Hussain, Z.; Shen, Z.-X.; Devereaux, T. Evidence for weak electronic correlations in iron pnictides. *Phys. Rev. B* **2009**, *80*, 014508.

[S3] Niwa, H.; Kiuchi, H.; Miyawaki, J.; Harada, Y.; Oshima, M.; Nabae, Y.; Aoki, T. Operando soft X-ray emission spectroscopy of iron phthalocyanine-based oxygen reduction catalysts. *Electrochem. commun.* **2013**, *35*, 57–60.

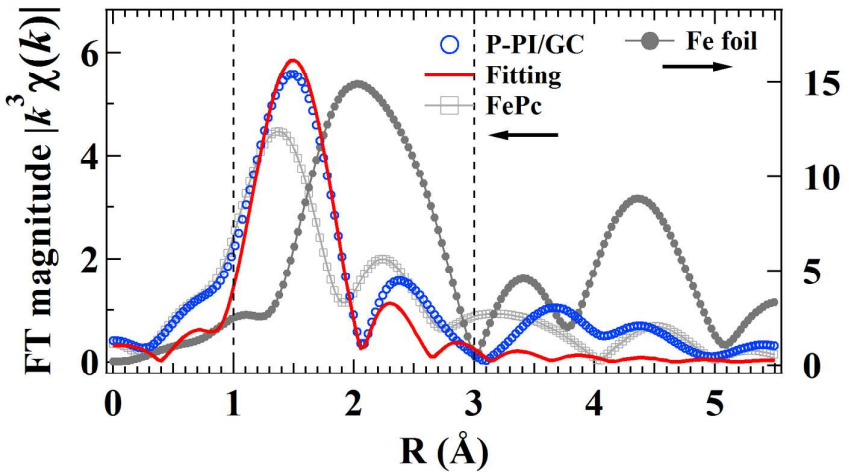
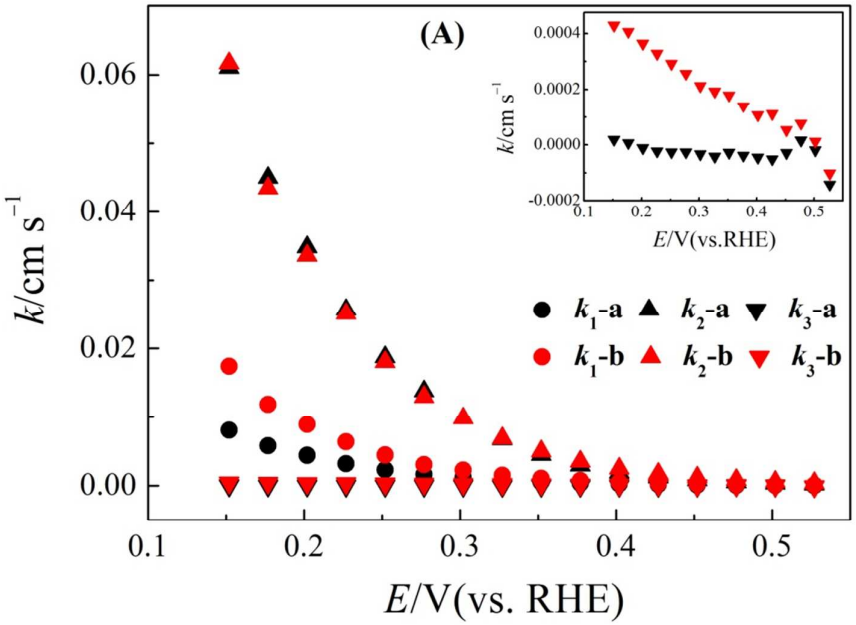
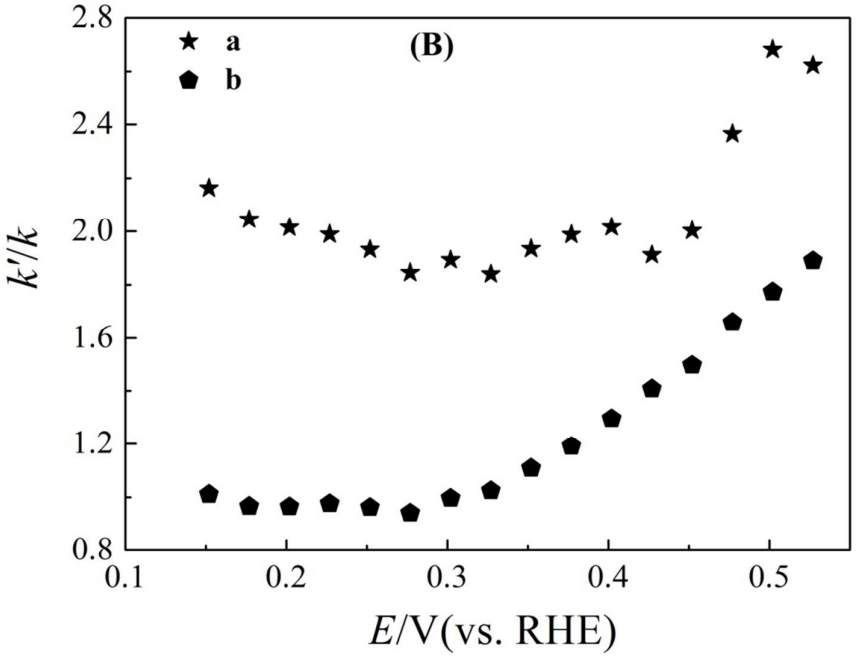


Figure S5. FT EXAFS spectra of the P-PI/GC with the electrochemical treatment in 0.5 M Na_2SO_4 containing 0.1 M $FeSO_4$, FePc and Fe foil. The curve-fitting of treated P-PI/GC is also shown. The fitting range is between the vertical dashed lines (1 to 3 Å).


(A)
0.06
0.04
0.02
0.00
k/cm s-1
0.1
0.2
0.3
0.4
0.5
E/V(vs. RHE)
k1-a
k2-a
k3-a
k1-b
k2-b
k3-b
0.0004
0.0002
0.0000
-0.0002
k/cm s-1
E/V(vs.RHE)


(B)
a
b
2.8
2.4
2.0
1.6
1.2
0.8
k'/k
0.1
0.2
0.3
0.4
0.5
E/V(vs. RHE)

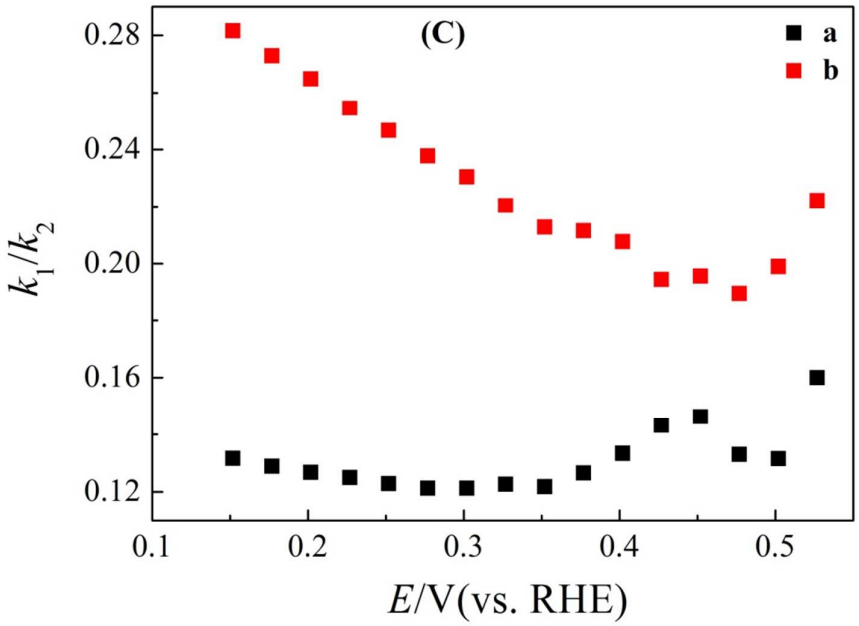
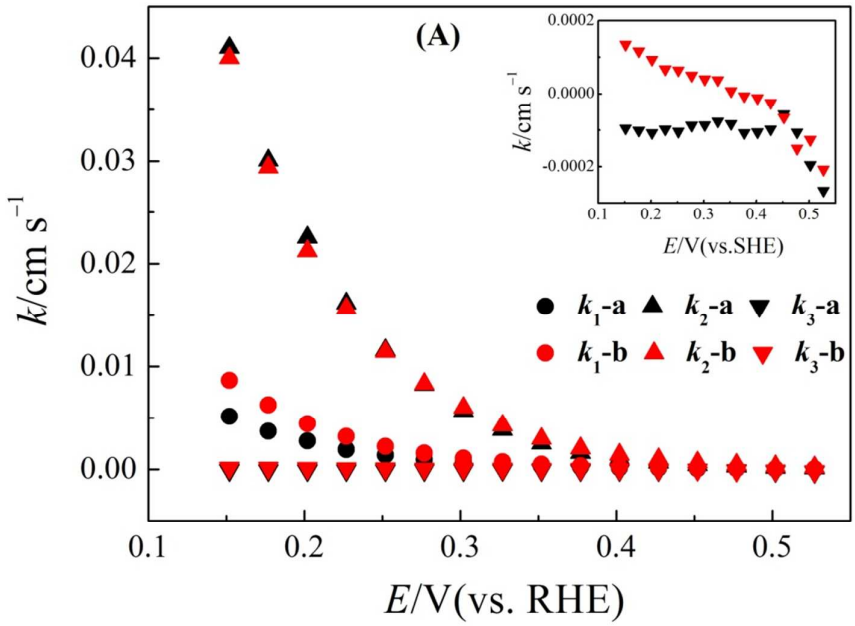
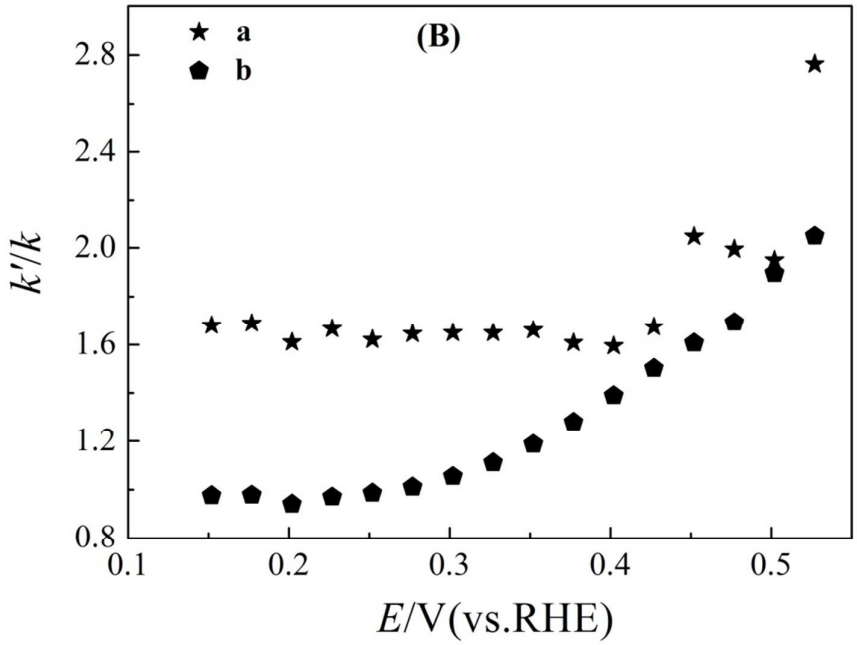


Figure S6. Dependency of k (A) and k_1/k_2 (C) on potential at different P-PI/GC electrodes (a: without treatment, b: with the electrochemical treatment in 0.5 M Na_2SO_4 containing 0.1 M $FeSO_4$). The inset of (A) shows the enlarged plots on k_3. (B) Changes in k_1 (a) and k_2 (b) induced by the electrochemical treatment. The symbols of k and k' represent rate constants before and after the treatment, respectively. The loading density of P-PI is 100 μg cm^{-2}.


(A)
0.04
0.03
0.02
0.01
0.00
k/cm s-1
0.1
0.2
0.3
0.4
0.5
E/V(vs. RHE)
k1-a
k2-a
k3-a
k1-b
k2-b
k3-b
0.0002
0.0000
-0.0002
k/cm s-1
0.1
0.2
0.3
0.4
0.5
E/V(vs.SHE)


(B)
a
b
2.8
2.4
2.0
1.6
1.2
0.8
k'/k
0.1
0.2
0.3
0.4
0.5
E/V(vs.RHE)

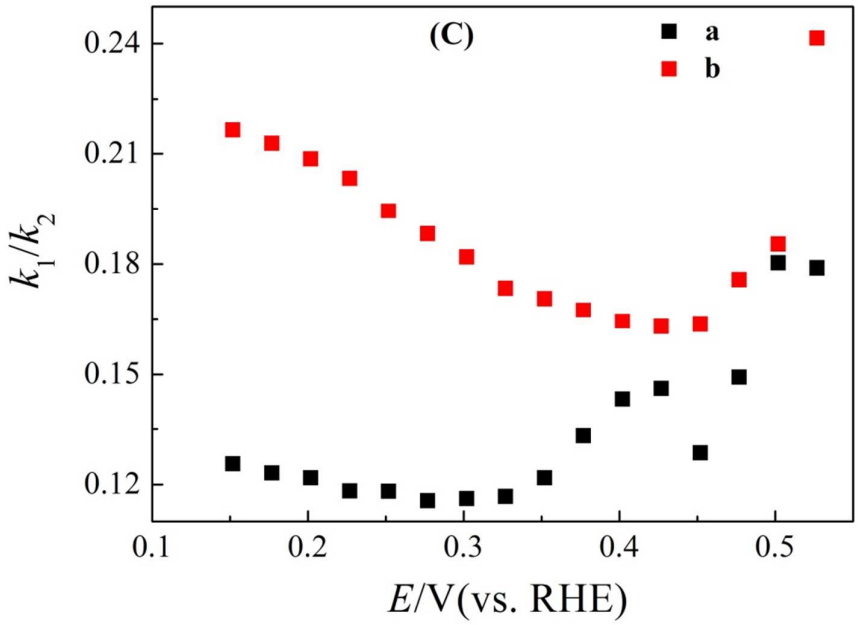


Figure S7. Plots similar to those in Figure S6 with a loading density of 50 μg cm^{-2} for the P-PI.