

Supporting information

Redox Targeting-Based Aqueous Redox Flow Lithium Battery

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Experimental section

Materials synthesis: All the chemicals were purchased from Sigma Aldrich without further purification. Carbon-coated $\text{LiTi}_2(\text{PO}_4)_3$ was synthesized by solid-state reactions. In detail, 0.476 g Li_2CO_3 (99.0%), 2.060 g TiO_2 (99.5%), 5.108 g $(\text{NH}_4)_2\text{HPO}_4$ (99.0%) and 1.000 g sugar (carbon source) were mixed with stirring in deionized water at 80°C. After water totally evaporated, a white precursor was obtained. The precursor was then put into a tube furnace and sintered at 900°C in nitrogen atmosphere for 12 h, from which around 5.000 g carbon-coated $\text{LiTi}_2(\text{PO}_4)_3$ powder can be obtained. The crystal structure and morphology of the obtained powder were verified by X-ray diffraction (Bruker D8) and scanning electron microscopy (Zeiss). The LiFePO_4 and $\text{LiTi}_2(\text{PO}_4)_3$ granules were made by a granulation machine (Caleva Muti Lab) with 10 wt.% Methyl cellulose (MCC) as binder.

Electrochemical measurements: LiFePO_4 and $\text{LiTi}_2(\text{PO}_4)_3$ electrodes were prepared for cyclic voltammetry tests. In detail, carbon-coated LiFePO_4 (Li-cell Co.) was mixed with carbon black (CB) and polyvinylidene fluoride (PVDF) with N-methyl pyrrolidone (NMP) as solvent to make a slurry (LiFePO_4 : CB: PVDF=8: 1: 1). The slurry was coated onto a piece of glassy carbon and dried in a vacuum oven at 80°C. Electrodes of homemade carbon-coated $\text{LiTi}_2(\text{PO}_4)_3$ were prepared similarly. To

catalyze the reaction of S^{2-}/S_2^{2-} , carbon felt electrode was coated with Cu_2S slurry with methyl cellulose as the binder. Cu_2S was made by immersing Cu foam into 1 M Li_2S_2 solution. Cyclic voltammogram (CV) of $LiFePO_4$ and $LiTi_2(PO_4)_3$ were measured with three-electrode cells. Pt plate and Hg/HgO were used as the counter and reference electrode, respectively. The supporting electrolyte for $LiFePO_4$ was 0.1 M LiOH in water and TEGDME mixed solvent, and that for $LiTi_2(PO_4)_3$ was 0.1 M LiOH in water. Experiments were conducted on an electrochemical station (AUTOLAB PGSTAT30) at a scan rate of 5 mV s^{-1} .

Catholytes for CV tests were prepared by dissolving 10 mM $K_4[Fe(CN)_6]$ and 0.1 M LiOH in water and TEGDME (0%, 10%, 20%, 30%, 40% in volume) mixed solvents. Anolytes were prepared by dissolving Li_2S and S (molar ratio of 1:1) in deionized water to form 10 mM Li_2S_2 solution, and 0.1 M LiOH was used as supporting electrolyte. CVs of both catholyte and anolyte were measured using three-electrode cells with Pt disk and Hg/HgO as the counter and reference electrode, respectively. The working electrodes were glassy carbon and Cu_2S -coated carbon felt for the measurement of catholyte and anolyte, respectively. The scan rate was 5 mV s^{-1} .

Characterization of redox targeting reactions: The reversible redox targeting reactions between $LiFePO_4$ and $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ were characterized by immersing 2 g $LiFePO_4$ powder in 80 mL 0.3 M $K_3Fe(CN)_6$ solution for 12 h. The

powder was then collected by centrifuge and half of the products was sent for XRD and FTIR measurements. The other half was immersed in 80 mL 0.3 M $\text{K}_4\text{Fe}(\text{CN})_6$ solution for another 12 h before centrifuged for XRD and FTIR measurements.

The reversible redox targeting reactions between $\text{LiTi}_2(\text{PO}_4)_3$ and $\text{S}^{2-}/\text{S}_2^{2-}$ were studied by immersing 1 g homemade carbon-coated $\text{LiTi}_2(\text{PO}_4)_3$ in 10 mL 1 M Li_2S solution for 12 h. The powder was then collected by centrifuge and half of the products was sealed in N_2 atmosphere for XPS and Raman measurements. The other half was immersed in 10 mL 1 M Li_2S_2 solution for another 12 h before centrifuged for XPS and Raman measurements.

Redox flow battery fabrication and testing: Catholyte symmetric cells were constructed by using 10 mL 0.3 M $\text{K}_4\text{Fe}(\text{CN})_6$ on one side and 30 mL 0.3 M $\text{K}_3\text{Fe}(\text{CN})_6$ on the other side. 0.9 g LiFePO_4 granules were added into the capacity-limiting side after 3 cycles. Anolyte symmetric cells were constructed by using 10 mL 0.3 M Li_2S on one side and 7 mL 0.1 M Li_2S_2 on the other side. 1.0 g $\text{LiTi}_2(\text{PO}_4)_3$ granules were added into the capacity-limiting tank after 9 cycles. The SMRT-based full cells were fabricated by using 10 mL 0.3 M $\text{K}_4\text{Fe}(\text{CN})_6$ catholyte and an excess amount of 1 M Li_2S_2 anolyte. 0.9 g LiFePO_4 granules were added into the cathodic tank after 3 cycles. The electrode area for all the above cells is 4 cm^2 . Supporting electrolyte of catholyte and anolyte is 0.1 M LiOH in mixed solvent (TEGDME, 30

vol%) and 0.1 M LiOH in H₂O, respectively. The cathodic and anodic electrode for all the cells are carbon felt and Cu₂S coated carbon felt, respectively, and Nafion 117 was used as separation membrane

The performance of the cells was measured with an Arbin battery tester. Constant currents of 20, 10 and 5 mA were applied for catholyte and anolyte symmetric cells, respectively. The cutoff voltages for the catholyte and anolyte symmetric cells were set to be 0.5 to -0.5 V and 0.2 to -0.2 V, respectively. The measurement of SMRT-based flow cells was conducted at a constant current of 20 mA and cutoff voltage of 0.4 to 1.3 V. The power performance of the cells was measured with the ramp procedure of Arbin with a current increment of 1 mA s⁻¹.

Thermodynamic basis of the SMRT reactions: The single molecule redox targeting (SMRT) reaction of battery material is thermodynamically favorable. This could be understood in terms of the equilibrium potential changes of redox mediator relative to the paired battery material, which generates the driving force for the forward reaction during the charging process and backward reaction during the discharging process. Firstly, the redox potentials of LiFePO₄ and LiTi₂(PO₄)₃ are dependent on the activity (a_{Li^+}) of Li⁺ in the electrolyte, as described by the Nernst equations (1) and (2):

$$E_{LFP} = E_{LFP}^{\theta} + \frac{RT}{F} \ln a_{Li^+} \quad (1)$$

$$E_{LTP} = E_{LTP}^{\theta} + \frac{RT}{2F} \ln a_{Li^{+}} \quad (2)$$

Here with Li^{+} as the charge balancing ion, its concentration is supposedly unchanged throughout the charge/discharge process. Thus, the redox potentials of $LiFePO_4$ and $LiTi_2(PO_4)_3$ are considered to be broadly constant.

In contrast, as a starting point while $K_4Fe(CN)_6$ and Li_2S_2 share identical equilibrium potentials with the above materials, these values vary with state-of-charge (discharge) as stated by the Nernst equation (3) and (4).

$$E_{KFCN} = E_{KFCN}^{\theta} + \frac{RT}{F} \ln \frac{a_{[Fe(CN)_6]^{3-}}}{a_{[Fe(CN)_6]^{4-}}} \quad (3)$$

$$E_{LS} = E_{LS}^{\theta} + \frac{RT}{2F} \ln \frac{a_{S_2^{2-}}}{a_{S^{2-}}^2} \quad (4)$$

Upon charging, more oxidized species relative to reduced species are formed in the catholyte, with which the activities of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ will change in the direction favoring the increase of equilibrium potential of the redox mediator according to the Nernst equation (3). As a result, a potential difference between the redox mediator and $LiFePO_4$ is generated to drive the oxidation of the latter by $[Fe(CN)_6]^{3-}$. Meanwhile, more reduced species relative to oxidized species are formed in the anolyte upon the charging process. According to the Nernst equation (4), the equilibrium potential of S^{2-}/S_2^{2-} would become lower than $LiTi_2(PO_4)_3$,

which thus promotes the reduction of the material by S^{2-} . Upon discharging, an opposite Nernstian potential difference prevails in both the cathodic and anodic compartments, with which the redox targeting reactions take place conversely.

Evaluation of the volumetric capacity of polysulfide-based anolyte: To evaluate the maximum volumetric capacity of polysulfide-based anolyte, the solubility of Li_2S in 1 M $LiOH$ solution was firstly examined, which is around 2.63 M determined by dissolving saturated Li_2S into 1 M $LiOH$ solution. Thereafter, elemental S was added into the above saturated Li_2S solution until the polysulfide solution reached new saturation condition. The quantity of S in Li_2S solution was determined to be around 8.25 M, which broadly corresponds to a composition of Li_2S_4 and higher order polysulfides. For the SMRT reaction between $LiTi_2(PO_4)_3$ and S^{2-}/S_2^{2-} , the maximum volumetric capacity is thus limited by the solubility of Li_2S . As the reaction of S^{2-} to S_2^{2-} involves 2 electrons, the maximum volumetric capacity of the anolyte can be determined to be 141 Ah L^{-1} .

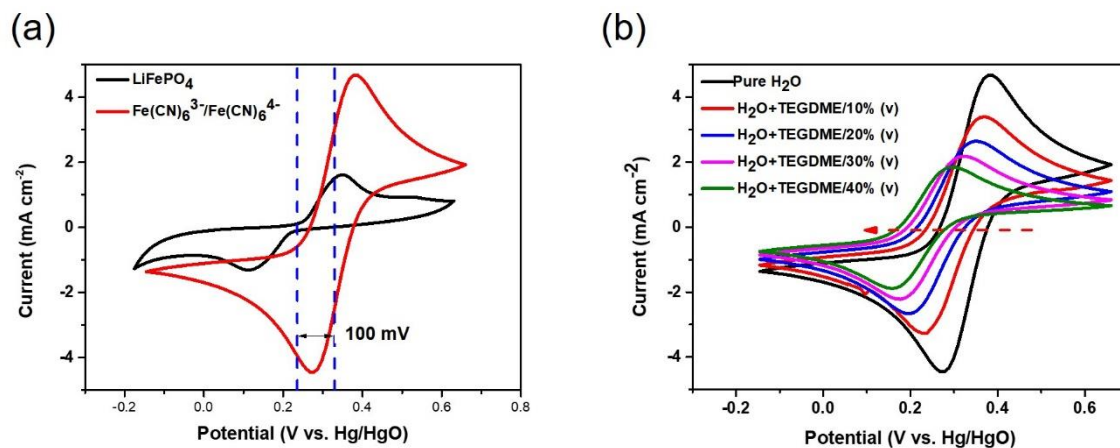


Figure S1. Redox potential of LiFePO_4 and $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ in different solvents. (a) CV curves of LiFePO_4 and $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ in 0.1 M LiOH aqueous solution at a scan rate of 5 mV s^{-1} . (b) CV curves of $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ in 0.1 M LiOH aqueous solution in the presence of 10%, 20%, 30%, 40% volume percentage of TEGDME as a co-solvent. The scan rate was 5 mV s^{-1} .

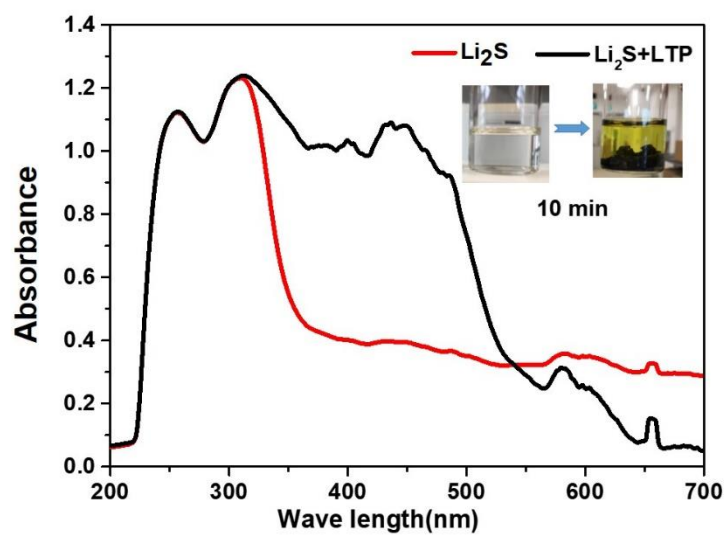


Figure S2. UV-Vis spectra and photographs of Li_2S solution before and after adding $\text{LiTi}_2(\text{PO}_4)_3$ for 10 min.

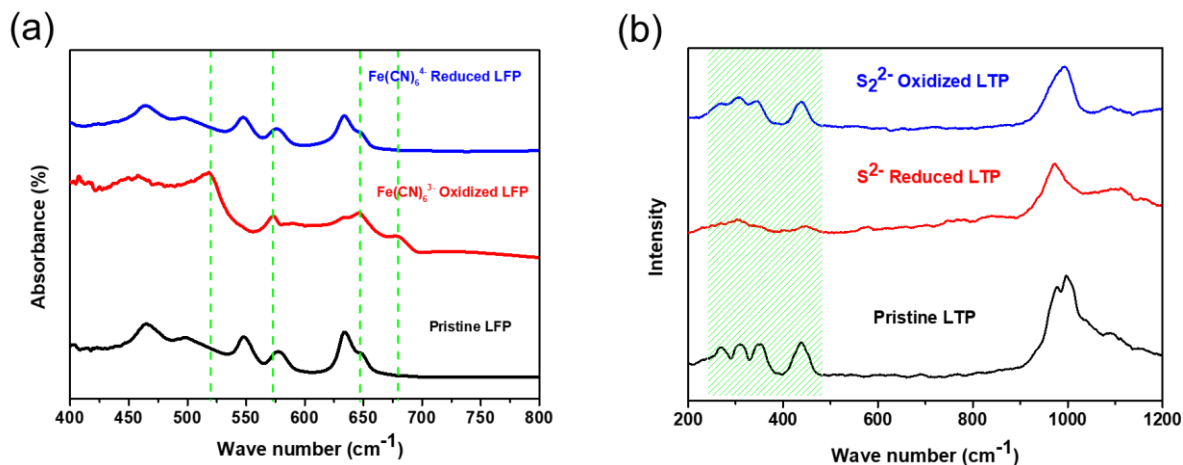


Figure S3. FTIR spectra of LiFePO_4 and Raman spectra of $\text{LiTi}_2(\text{PO}_4)_3$ at different stages of redox targeting reactions with the paired redox mediators. (a) FTIR spectra of pristine, oxidized, reduced LiFePO_4 by $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ in 0.1 M LiOH aqueous solution with 30% (v) TEGDME as co-solvent. (b) Raman spectra of pristine, reduced, oxidized $\text{LiTi}_2(\text{PO}_4)_3$ by $\text{S}^{2-}/\text{S}_2^{2-}$ in 1 M LiOH aqueous solution. The typical reaction duration for these experiments is 12 h.

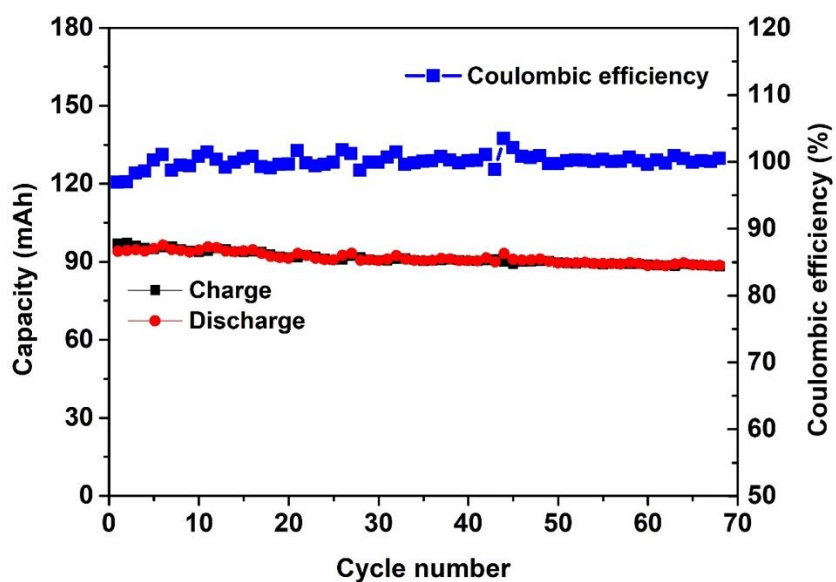


Figure S4. Cycling performance of a catholyte symmetric flow cell. 0.9 g LiFePO_4 granules were loaded into one side of the electrolyte tank containing 10 mL 0.3 M $\text{K}_4\text{Fe}(\text{CN})_6$. The electrolyte on the other side consists of 30 mL 0.3 M $\text{K}_3\text{Fe}(\text{CN})_6$. The current density was 10 mA cm^{-2} with carbon felt (4 cm^2) as the electrode.

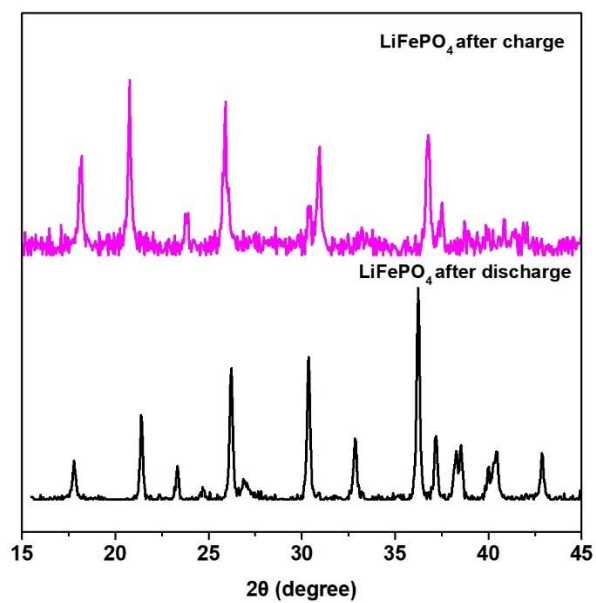


Figure S5. XRD patterns of LiFePO_4 after fully charge and discharge.

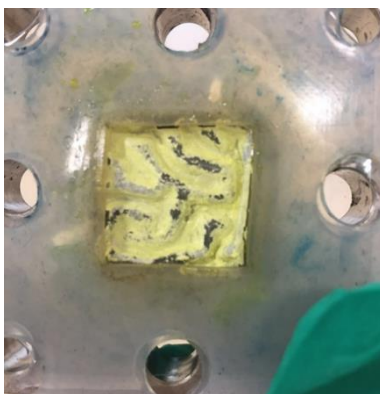


Figure S6. Photograph of a membrane faced to catholyte after 30 cycles.

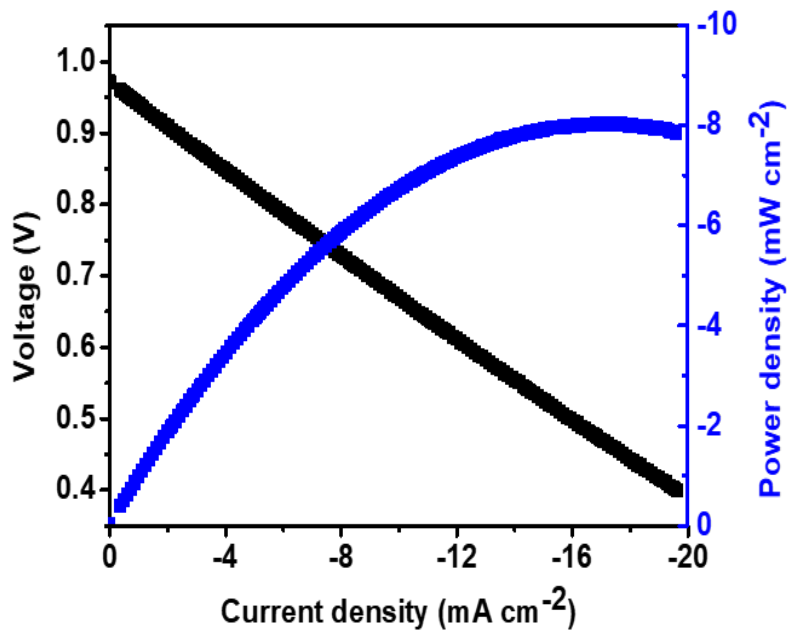


Figure S7. Power performance of a SMRT-based aqueous RFLB cell. J-V curve and the power performance of the cell with 7 mL 0.3 M $\text{K}_4\text{Fe}(\text{CN})_6$ catholyte and 4 mL 1 M Li_2S_2 anolyte in the cell in conjunction with 0.9 g LiFePO_4 and 1.0 g $\text{LiTi}_2(\text{PO}_4)_3$ granules in the cathodic and anodic tanks, respectively. The measurement was conducted at 100% SOC.

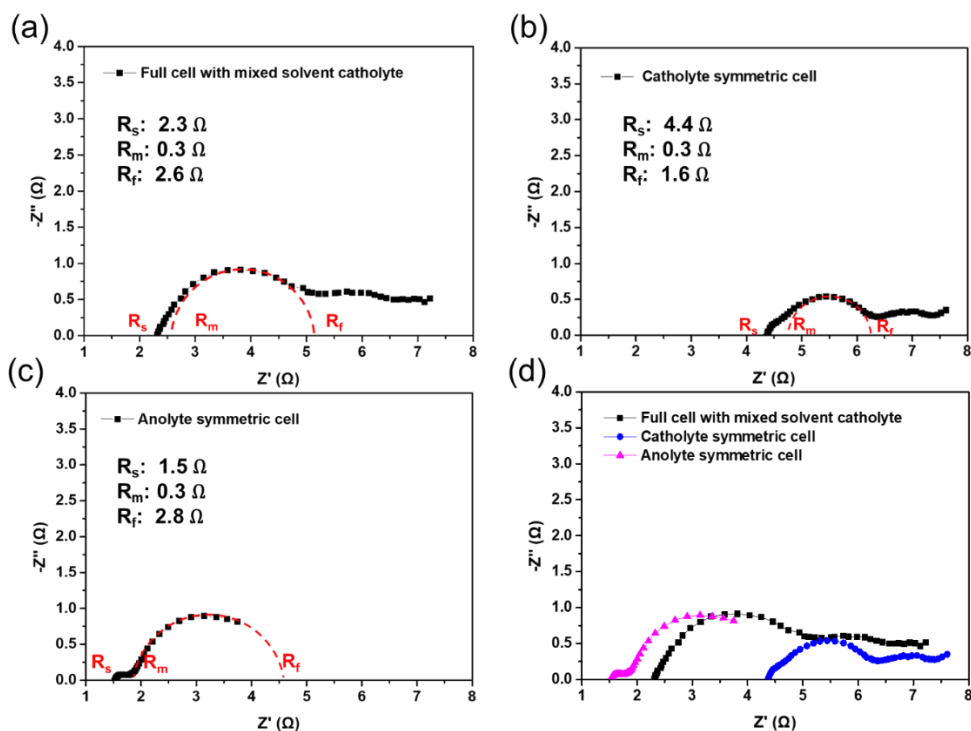


Figure S8. Electrochemical impedance spectroscopic analysis. (a) Full cell with 0.3 M $\text{K}_4\text{Fe}(\text{CN})_6$ in mixed water and TEGDME solvent as catholyte and 1 M Li_2S in water as anolyte. (b) Catholyte symmetric cell with 0.3 M $\text{K}_4\text{Fe}(\text{CN})_6$ in mixed water and TEGDME solvent in both compartments. (c) Anolyte symmetric cell with 1 M Li_2S in water in both compartments. (d) Comparison of full cell, catholyte and anolyte symmetric cells. The supporting electrolyte for the catholyte and anolyte was 0.1 M LiOH and 1 M LiOH , respectively. The thickness and area of electrode (carbon felt) is 0.4 cm and 4 cm^2 , respectively. All the experiments were conducted on an electrochemical station (Autolab PGSTAT30) with a frequency range of 0.1 to 10^6 Hz. R_s , R_m and R_f are resistances of solution, membrane and charge transfer, respectively.