

**Nanocage-oriented Induction for Highly Ion-selective Sub-1-Nanometer Channels of Membranes**

Lei Hu<sup>a</sup>, Li Gao<sup>a</sup>, Mengting Di<sup>a</sup>, Xiaoming Yan<sup>a,\*</sup>, Xiaobin Jiang<sup>a</sup>, Xuemei Wu<sup>a</sup>, Gaohong He<sup>a,\*</sup>,  
Xianfeng Li<sup>b,\*</sup>

*<sup>a</sup> State Key Laboratory of Fine Chemicals, R&D Center of Membrane Science and Technology, School of Chemical Engineering, Dalian University of Technology, 2 Linggong Road, Dalian, LN 116024, China*

*<sup>b</sup> Division of Energy Storage, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, China*

\*Corresponding author: yanxiaoming@dlut.edu.cn (X. Yan); lixianfeng@dicp.ac.cn (X. Li); hgaohong@dlut.edu.cn (G. He)

## 1. Experimental section

### 1.1 Materials

Polybenzimidazole (PBI) has a molecular weight of 14000 g mol<sup>-1</sup>, which is supplied by Shanghai Shengjun Plastics Technology Co., Ltd. 1-Bromo-4-chlorobutane (99%, Energy Chemical), 3-aminopropyltriethoxysilane (99.5%, APTES, Energy Chemical), sodium hydride (NaH, 60 wt% in mineral oil, Macklin), hydrochloric acid (AR, Damao Chemical Reagent Factory), DMSO (AR, Tianjin Fuyu Fine Chemical Co., Ltd) and DMAc (AR, Tianjin Komi Chemical Reagent Co., Ltd) were used as received.

### 1.2 Synthesis of chloroalkane-substituted PBI (CPBI)

CPBI was synthesized by the reaction between PBI and 1-bromo-4-chlorobutane. PBI (1.0 g) was mixed with DMAc (50 mL) at room temperature to form a homogeneous solution. NaH (0.2 g) were added into the solution under magnetic stirring and then the reaction was carried out for 24 h. After cooling to 0 °C, 1-bromo-4-chlorobutane (0.145 mL) was added into the solution. The reaction was carried out at 0 °C for 12 h. Then, the solution was poured into ice water to form a precipitate, followed by washing with deionized water and ethanol, and drying to yield solid CPBI.

### 1.3 Preparation of octa-aminopropyl polyhedral oligomeric silsesquioxane (A<sub>8</sub>T<sub>8</sub>)

A<sub>8</sub>T<sub>8</sub> is synthesized according to the literature. APTES (5 mL) were dissolved in methanol (40 mL) at room temperature and then stirred for 3 min (Fig. S1). Then, 6.75 mL of hydrochloric acid (36.5%, m/v) is slowly dropped into the mixture. Under vigorous magnetic stirring, the reaction was carried out at room temperature for 7 days and white precipitate was obtained. The precipitate was collected by washing with methanol and drying under vacuum.

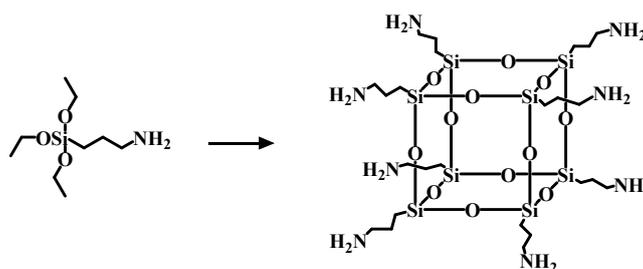


Figure S1. Synthesis strategy of A<sub>8</sub>T<sub>8</sub>

#### 1.4 Preparation of CPBI–A<sub>8</sub>T<sub>8</sub>-x membranes

CPBI–A<sub>8</sub>T<sub>8</sub>-x membrane was prepared via the reaction between amine groups in A<sub>8</sub>T<sub>8</sub> and chloroalkane in CPBI, where x (x=30, 40, and 50) represent the mass ratio of A<sub>8</sub>T<sub>8</sub> to total mass. CPBI was mixed with DMSO to form 3 wt% homogeneous solution A. In the meantime, A<sub>8</sub>T<sub>8</sub> was mixed with DMSO to form 3 wt% homogeneous solution B. After that, solution A and B were homogeneously mixed at RT, followed by casting into a clean glass dish and be placed into an oven at 80 °C for 24 h to achieve reaction. The membrane samples were removed out from glass plate and the thicknesses of the resulting membranes were 25–30 μm.

#### 1.5 Structural characterization

<sup>1</sup>H NMR, C NMR and Si NMR spectra of polymers were recorded on a Bruker (AVANCEIIIHD 500 MHz) with DMSO-*d*<sub>6</sub>. FT-IR spectra of polymer membranes with different mass ratios of CPBI to A<sub>8</sub>T<sub>8</sub> were recorded by using a Thermo Scientific Nexus 670 FT-IR spectrophotometer with 500–4000 cm<sup>-1</sup>. Before FT-IR tests, the membranes were each treated with 3.0 M H<sub>2</sub>SO<sub>4</sub> solution and deionized water.

#### 1.6 Swelling ratio and liquid uptake

By immersing the sample in a liquid (bulk water or 3 M H<sub>2</sub>SO<sub>4</sub>) at ambient temperature for 24 h, the swelling ratio and water or acid uptake were calculated from the wet weight ( $W_{\text{wet}}$ ), dry weight ( $W_{\text{dry}}$ ), wet length ( $L_{\text{wet}}$ ) and dry length ( $L_{\text{dry}}$ ).

#### 1.7 Morphology and contact angle

The photograph of prepared membrane was taken by a digital camera. Scanning electron microscope (SEM) and the cross-section energy-dispersive X-ray spectroscopy (EDS) element mapping of membranes was observed through Nova NanoSEM 450. Transmission electron microscope (TEM) of membrane was tested by FEI Tecnai G<sup>2</sup> F30. The membranes were dyed by 1 M KI, and dried after washed with deionized water. The contact angle was observed through a Contact Angle Goniometer (SL200KB, Kino Industry, USA) on a dry membrane surface at room temperature.

### 1.8 Area resistance

A conductive cell measurement method was used to measure the area resistances. All of the membranes (effective area,  $S= 1.766 \text{ cm}^2$ ) were sandwiched between two compartments filled with 3.0 M  $\text{H}_2\text{SO}_4$  solution. The resistances ( $R_1$  and  $R_2$  with and without a membrane) were obtained from an Ivium Technologies Impedance Analyzer and the area resistances were calculated as:

$$\text{Area resistance } (\Omega \text{ cm}^2) = S \cdot (R_1 - R_2)$$

### 1.9 $\text{VO}^{2+}$ permeability

A diffusion device sandwiching a  $7.065 \text{ cm}^2$  membrane was adopted to detect  $\text{VO}^{2+}$  permeability. A 100 mL 1.5 M  $\text{VOSO}_4$  in 3.0M  $\text{H}_2\text{SO}_4$  solution and an equivalent amount of 1.5M  $\text{MgSO}_4$  in 3.0 M  $\text{H}_2\text{SO}_4$  solution were filled on two sides, respectively. The  $\text{VO}^{2+}$  concentration of the  $\text{MgSO}_4$  solution side was detected with a UV-vis spectrometer (SDPTOP) at certain intervals at 760 nm.

### 1.10 Cell performance

Cell performances were investigated by sandwiching a  $3 \times 3 \text{ cm}^2$  (effective area) membrane with carbon felt electrodes and graphite plates. The carbon felt electrodes had a nominal thickness of 5 mm, which was provided by Gansu Hongwei Carbon Ltd, China. The carbon felt electrode was oxidized in an air atmosphere at  $400 \text{ }^\circ\text{C}$  for 8 h to improve electrochemical activity and hydrophilicity. For vanadium flow battery, 50 mL 1.5 M  $\text{VO}^{2+}/\text{VO}_2^+$  solutions in 3.0 M  $\text{H}_2\text{SO}_4$  and an equivalent amount of 1.5 M  $\text{V}^{2+}/\text{V}^{3+}$  solutions in 3.0 M  $\text{H}_2\text{SO}_4$  were cyclically pumped to evaluate the electrochemical performance. Charge–discharge measurements were conducted using a LANHE battery tester (CT2001A, 5 V/3 A) with voltages from 1.0 V to 1.55 V for the charge–discharge process. The voltages under open-circuit conditions were recorded.

### 1.11 Molecular simulation

The polymers which involved in the simulation were constructed via Material studio software version 2019. The construction of small molecules and polymers are produced using the amorphous cell module, the periodic box size:  $60 \times 45 \times 45 \text{ \AA}$ . The molecular dynamic simulation was performed via Forcite modle of Material studio with a COMPASS force field. The Periodic box size is  $60 \times 45 \times 45 \text{ \AA}$ , and NPT ensembles were employed to maintain the temperature at 298.15 K and the

pressure at 0.1 Mpa with a Nose temperature coupling. The stepsize of this simulation is 0.2 fs and cutoff distance is 1.2 nm, the van der Waals interactions and electrostatic interaction were calculated via particle-mesh Ewald method.

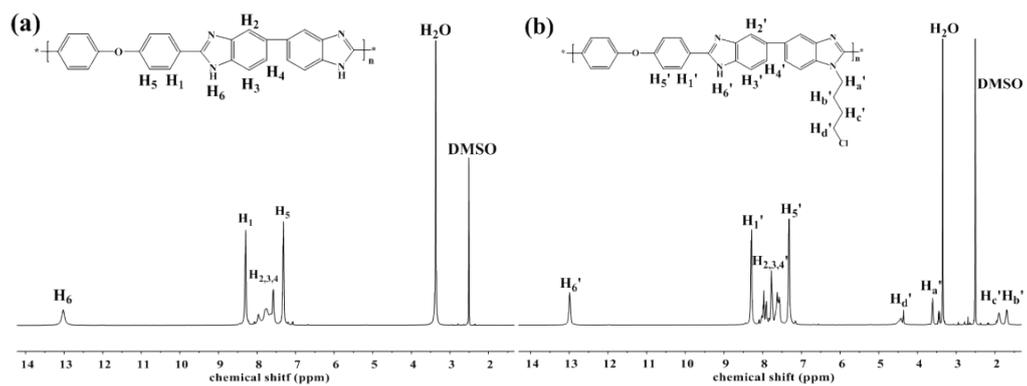


Fig. S2. <sup>1</sup>H NMR spectra of (a) PBI and (b) CPBI

The chemical shifts at 8.25 ppm ( $H_a$ ), 2.80 ppm ( $H_b$ ), 1.74 ppm ( $H_c$ ), and 0.74 ppm ( $H_d$ ) correspond to the protons in the side chain of  $A_8T_8$  in  $^1H$  NMR spectrum, respectively (Figure S2).

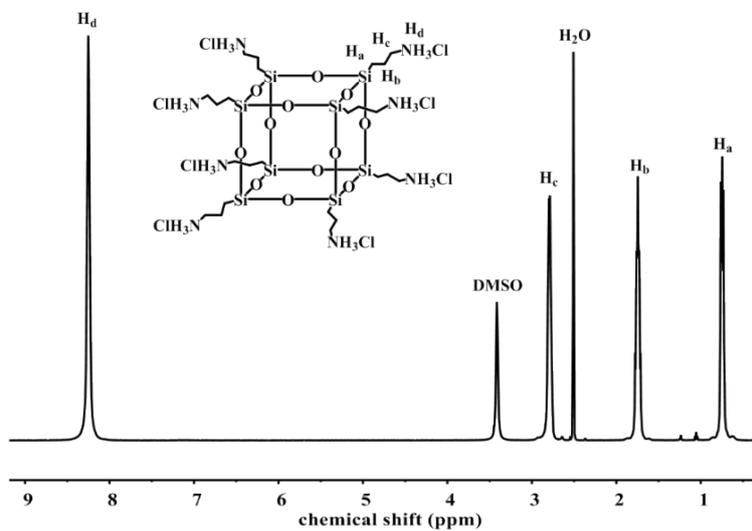


Figure S3.  $^1H$  NMR spectrum of  $A_8T_8$

The characteristic peaks at 8.87, 21.05, and 41.45 ppm are ascribed to  $-\text{CH}_2\text{Si}$ ,  $-\text{CH}_2-$ , and  $-\text{CH}_2\text{NH}_3\text{Cl}$  of  $\text{A}_8\text{T}_8$  in  $^{13}\text{C}$  NMR spectrum, respectively (Figure S3).

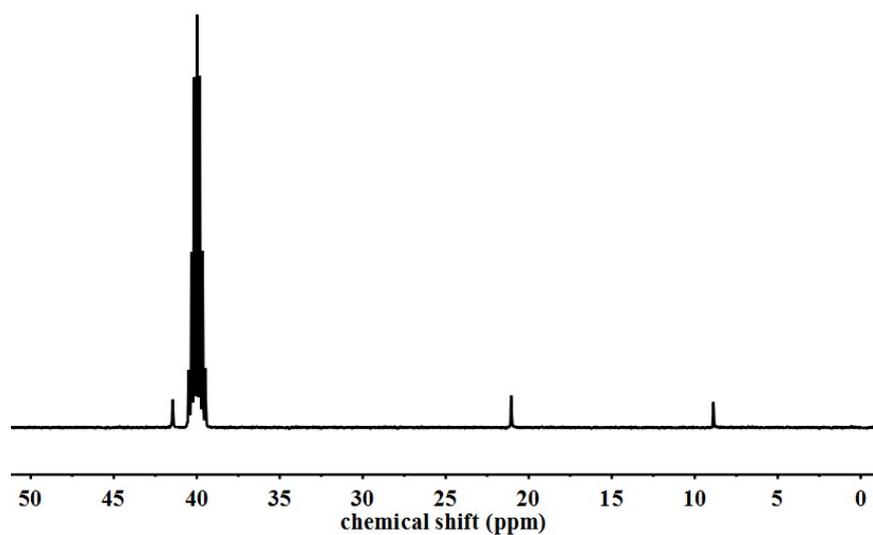


Figure S4.  $^{13}\text{C}$  NMR spectrum of  $\text{A}_8\text{T}_8$

A sharp solo peak at  $-66.5$  ppm in  $^{29}\text{Si}$  NMR spectrum is attributed to Si atom on the inorganic cubic core of  $\text{A}_8\text{T}_8$ , reflecting that Si–O–Si structure has been formed via hydrolytic condensation (Figure S4).

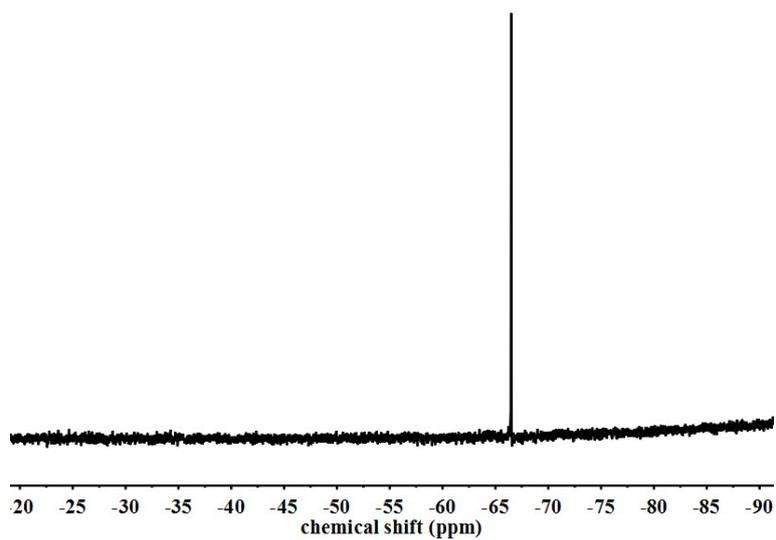


Figure S5.  $^{29}\text{Si}$  NMR spectrum of  $\text{A}_8\text{T}_8$

The absorption bands at 3432 and 1600  $\text{cm}^{-1}$  assigned to  $-\text{NH}_2$  in the FT-IR spectra illustrated the formation of  $\text{A}_8\text{T}_8$  (Figure S5). The characteristic absorptions attributed to the asymmetric stretching vibrations of Si–O–Si are clearly identified at 1120 and 1049  $\text{cm}^{-1}$ , and the bending vibration of Si–O–Si at 548  $\text{cm}^{-1}$  were observed related to  $\text{A}_8\text{T}_8$  nanocage, which confirmed the formation of  $\text{A}_8\text{T}_8$ .

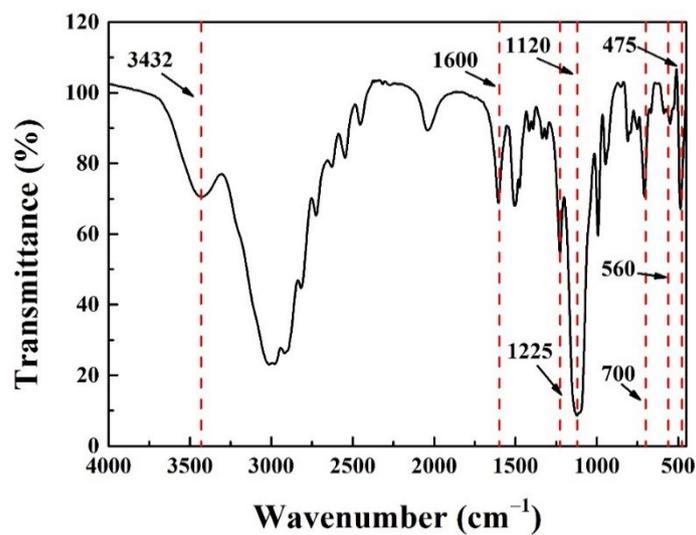


Figure S6. FT-IR spectra of  $\text{A}_8\text{T}_8$

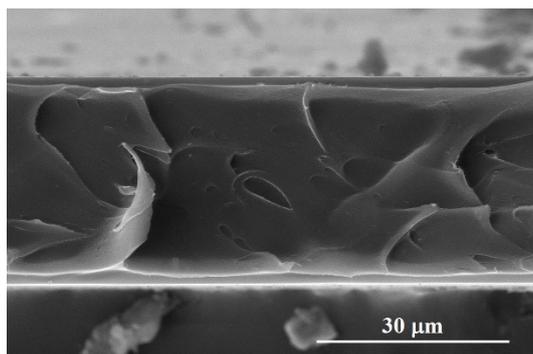


Fig. S7 cross-sectional SEM image of PBI

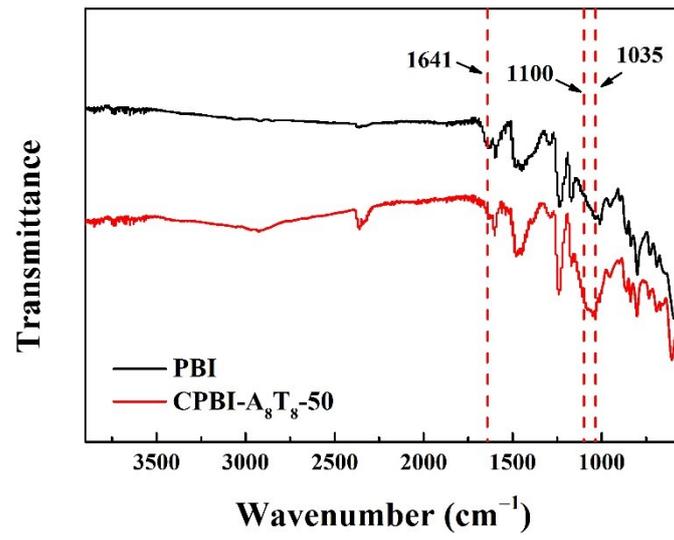


Figure S8. FT-IR spectra of CPBI and CPBI-A<sub>8</sub>T<sub>8</sub>-50 membrane

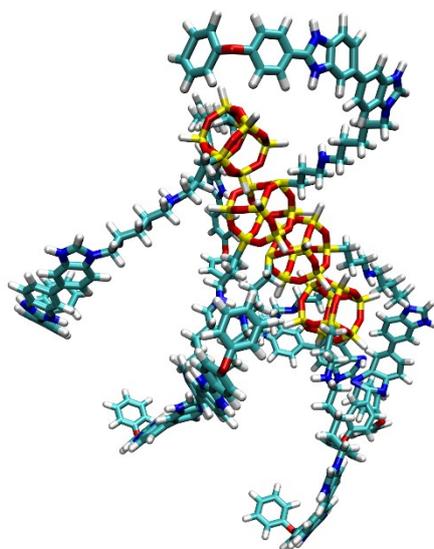


Figure S9. Molecular structure of CPBI-A<sub>8</sub>T<sub>8</sub>-50 membrane

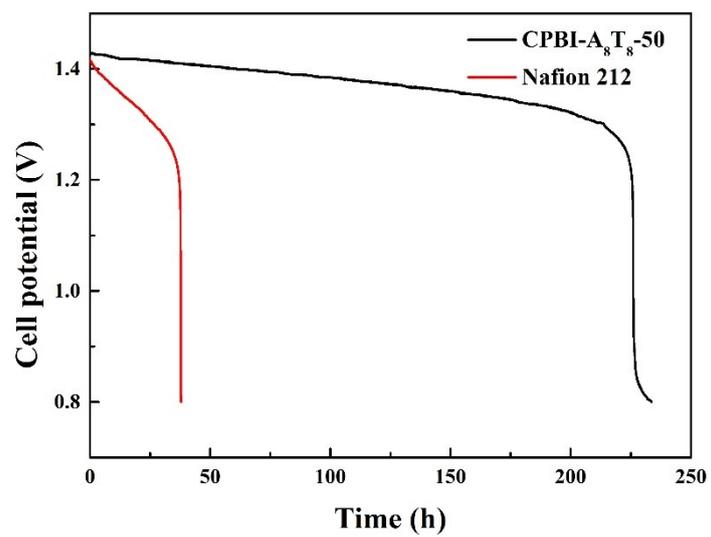


Figure S10. The self-discharge curves using CPBI-A<sub>8</sub>T<sub>8</sub>-50 and Nafion 212 membranes.

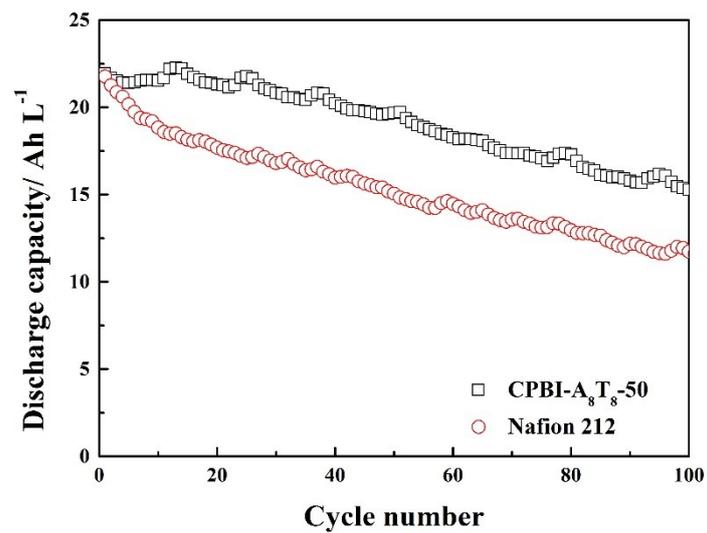


Figure S11. Discharge capacity retentions at 120 mA cm<sup>-2</sup> of CPBI-A<sub>8</sub>T<sub>8</sub>-50 and Nafion 212 membranes

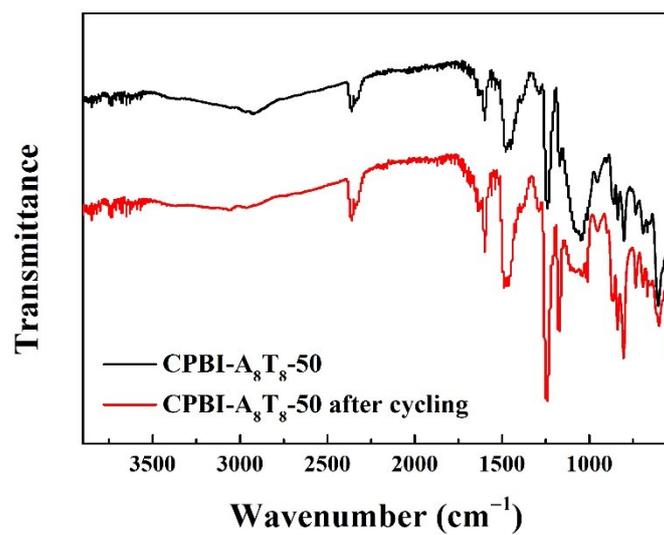


Figure S12. The FT-IR spectra of CPBI-A<sub>8</sub>T<sub>8</sub>-50 membranes before and after 7000 charge-discharge cycle at 120 mA cm<sup>-2</sup>