

Investigating dendrites and side reactions in sodium-oxygen batteries for improved cycle lives

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Supplementary Information

Experimental section

1. Materials and batteries assembly

A sodium metal slice (Fisher Scientific, labgrade) was used as the metal anode and P50 (AvCarb®) was used as the air electrode. The electrolytes were 1,2-dimethoxyethane (DME, Novolyte Tech.) or bis (2-methoxyethyl) ether (diglyme, Sigma-Aldrich, 99.5%) containing 0.5 M sodium trifluoromethanesulfonate (sodium triflate, Sigma-Aldrich, 98%). Both solvents and oxygen gas (99.993%, UHP) were dried with 3 Å molecular sieves (Sigma-Aldrich) before use.

Purchased Nafion® 211 membranes (25 µm thickness, DuPont) were stirred in a solution of 1 M NaOH in dimethyl sulfoxide (DMSO) (>99.9%, Sigma-Aldrich) and water with 1:1 volume ratio at 65 °C for 2 h to exchange protons to sodium ions. Then the Nafion-Na⁺ membranes were washed by stirring in distilled water at 90 °C for 2 h and dried in a vacuum oven at 100 °C for 20 h. After pretreatment, dry Nafion-Na⁺ membranes were transferred into a glove box and stored under high purity Argon for future use. Before characterizations and battery tests, Nafion-Na⁺ membranes were immersed in electrolytes for 48 h. The water contents in electrolytes were tested by using a Mettler Toledo C20 Karl Fischer Coulometer.

In the sodium-oxygen batteries with Nafion-Na⁺ membranes, the thickness of separators was well controlled. Without the Nafion-Na⁺ membrane, one piece of glass fiber (Whatman, 600 µm thickness) was used as the separator soaked with saturated electrolytes (0.5 M sodium triflate in DME or diglyme). With the Nafion-Na⁺ membrane, it was sandwiched by two pieces of glass fiber separators (Whatman, 300 µm thickness, 600 µm thickness in total). All the cells were assembled in the glove box and stayed in 1 atm oxygen atmosphere for 2 h to reach equilibrium. The battery performance tests were performed by a Maccor testing station (model: 4304). The testing voltage window was 1.6 V-3.4 V (vs. Na⁺/Na) and the current density was set to 0.16 mA cm⁻² based on the area of 0.64 cm². Six-hour discharge was set in the battery performance tests.

2. Characterization

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were performed by a FEI/Philips Sirion Field Emission SEM. When transferring the air sensitive sample, a glove bag filled with Argon was used to transfer the sample. X-ray diffraction (XRD) was performed by a Bruker D8 advance X-ray powder diffractometer on flat plate mode with an air-tight holder. Nuclear magnetic resonance (NMR) spectroscopy was used to investigate the electrolyte decomposition products in sodium-oxygen batteries. The separator samples with electrolyte were put in D₂O solvent (99.9%, Sigma-Aldrich). After dissolving in D₂O solvent, the electrolyte sample was transferred to an NMR test tube and ¹H-NMR and ¹⁹F-NMR spectra were tested by a 400 MHz NMR spectrometer (Bruker, Avance III). The battery products and surface layer components on both electrodes were characterized by Raman spectrometer (inVia, Renishaw) with an air-tight holder at an excitation wavelength of

633 nm (laser power 6 mW). X-ray photoelectron spectroscopy (XPS) was tested with an airtight chamber module by a Kratos Axis Ultra XPS spectrometer. The XPS spectra were collected using monochromatic Al K α radiation. In XPS analysis, all spectra were calibrated by referencing the binding energy of carbon-carbon bond at 284.8 eV.

3. EIS measurements and battery performance tests

Ionic conductivity of Nafion-Na⁺ membrane was determined by a two-electrode AC impedance method using an EIS600 potentiostat. The frequency range was set from 10⁶ Hz to 1 Hz at 21 °C (room temperature). Before the measurement, the Nafion-Na⁺ membrane was taken out from the electrolyte and sandwiched by two blocking electrodes made by platinum coated conductive fluorine-doped tin oxide (Pt-FTO) glass. Filter paper was used to remove the extra electrolyte. DC bias was 0 V vs. open circuit potential and the AC amplitude was 10 mV. EIS data were fitted by Gamry Echem Analyst software. The ionic conductivity of electrolyte in glass fiber was tested by the same method.

Results and discussions

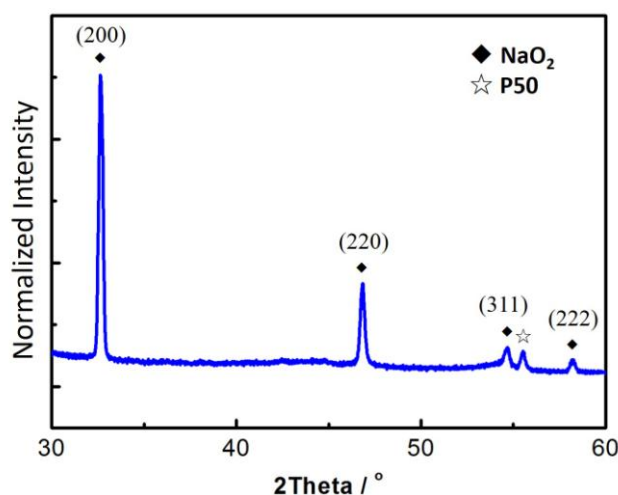


Figure S1. XRD patterns of P50 cathode after 20 h discharge in 0.5 M Na triflate DME electrolyte.

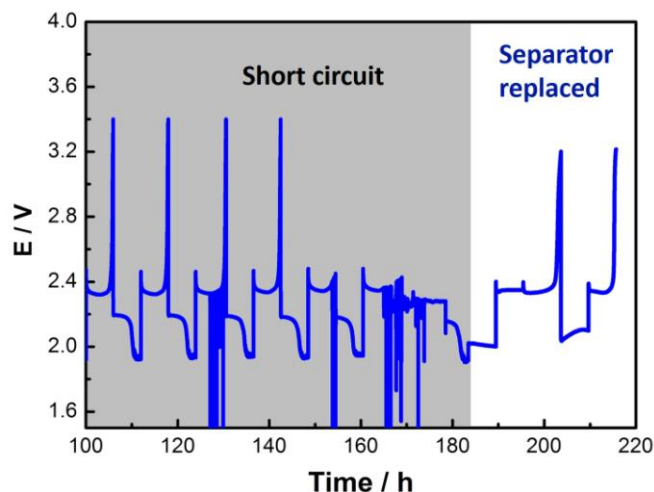


Figure S2. The discharge/charge profiles of the Na-O₂ battery after replacing the GF separator.

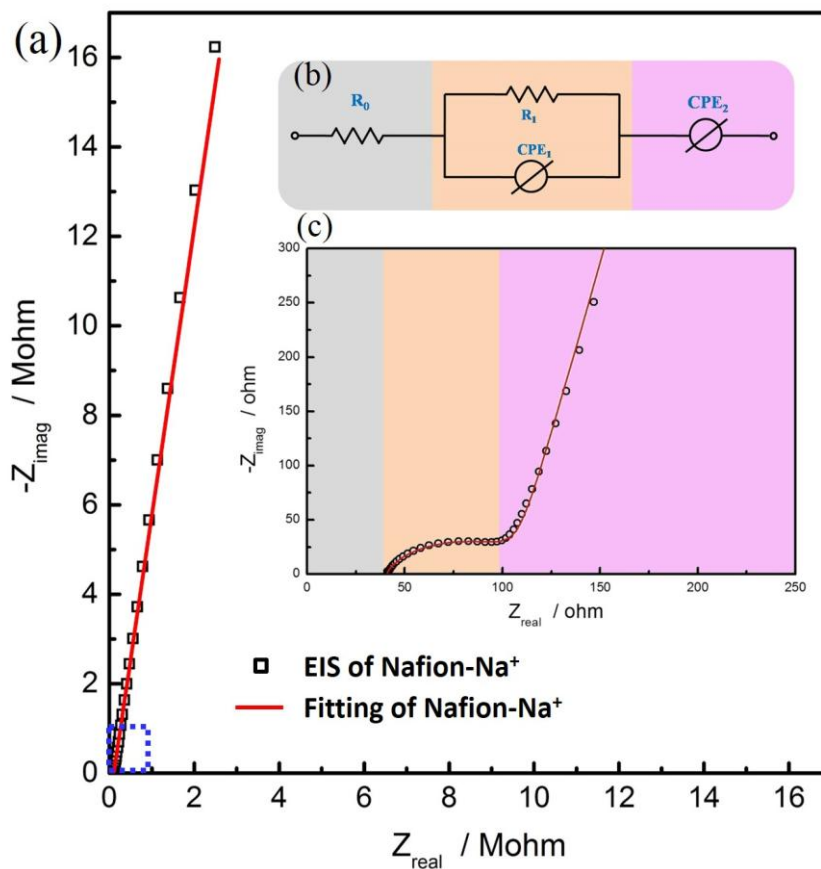


Figure S3. (a) Nyquist plot and (b) Equivalent circuit of Nafion-Na⁺ membrane in device. (c) Amplified Nyquist plot of the blue square in (a).

Ionic conductivity was determined by a two-electrode AC electrochemical impedance spectroscopy (EIS) method. A simplified equivalent circuit¹ and Nyquist plots are shown in Figure S3. In the system, there is no Faradic charge across the membrane/electrode interface, so the interface is merely capacitive, which is represented by a constant-phase element (CPE_2). was used to model the capacitance of the two interfaces, shown in Figure S3b. The bulk resistance and bulk capacitance of the membrane are represented by a parallel combination of an RC circuit (R_1 and CPE_1). R_0 represents the series resistance of the device that can result from the sheet resistance of FTO and the circuit contacts.

From the Nyquist plot (Figure S3c), the intersection point at Z_{real} axis gives the value of R_0 . The semicircle at high frequencies corresponds to the ionic resistance (R_1) and capacitance (CPE_1) of the Nafion-Na⁺ membrane. At low frequencies, the straight curve with an angle of 82° represents the non-ideal capacitance (CPE_2) of two Pt-FTO/membrane interfaces. R_1 is the bulk resistance of the membrane and is used to calculate the ionic conductivity.

The equation to calculate ionic conductivity is shown as follows:

$$\sigma = \frac{L}{R \cdot A}$$

where σ is the ionic conductivity, R is the bulk resistance, L is the thickness and A is the area of Nafion- Na^+ membrane.

Table S1. Measurements of ionic conductivity of Nafion- Na^+ membranes

Samples (#)	R (Ω)	A (cm^2)	L (cm)	σ (S/cm)
1	242.1	0.42	2.5e-3	2.46e-5
2	65.32	1.54	2.5e-3	2.49e-5
3	66.49	1.54	2.5e-3	2.44e-5
4	381.5	0.27	2.5e-3	2.43e-5

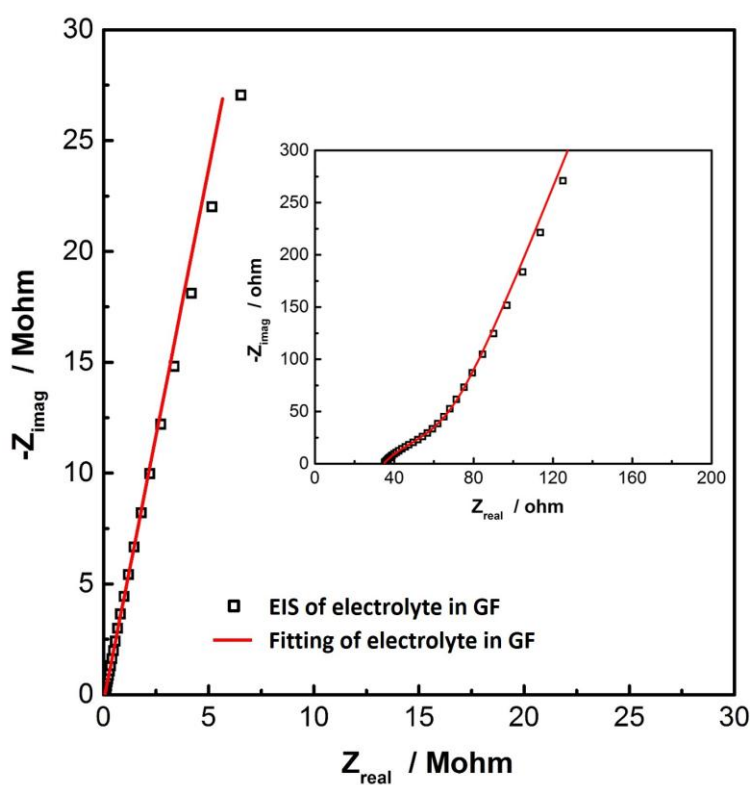


Figure S4. Nyquist plots and fitting data of the DME based electrolyte in GF separator.

Table S2. Measurements of ionic conductivity of the DME based electrolyte in GF separator.

Samples (#)	R (Ω)	A (cm^2)	L (cm)	σ (S/cm)
1	32.89	1.33	4.0e-2	4.58e-4

2	32.40	1.33	4.0e-2	4.65e-4
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Table S3. Calculated Ohmic loss from the total separator.

Samples in battery	Average σ (S/cm)	A (cm ²)	L (cm)	R (Ω)	I (mA cm ⁻²)	Ohmic loss (mV)
Nafion-Na⁺	2.46e-5	0.636	2.50e-3	1.60e2	0.100	16.0
Glass Fibers	4.62e-4	0.636	4.00e-2	1.35e2	0.100	13.5

Table S4. Water contents of electrolytes before and after immersion of Nafion-Na⁺ membrane.

Water content (ppm)				
Electrolytes	Trial 1	Trial 2	Trial 3	Average
Before immersion	23.7	24.8	24.1	24.2
After immersion	24.8	22.9	25.4	24.4

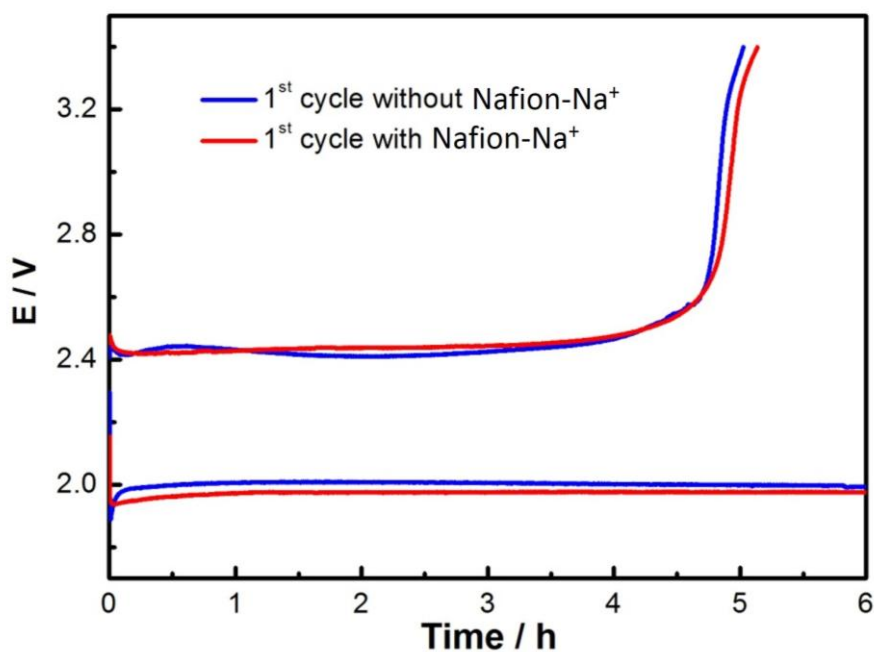


Figure S5. The comparison of voltage profiles with and without Nafion-Na⁺ membrane in 0.5 M Na triflate DME electrolyte.

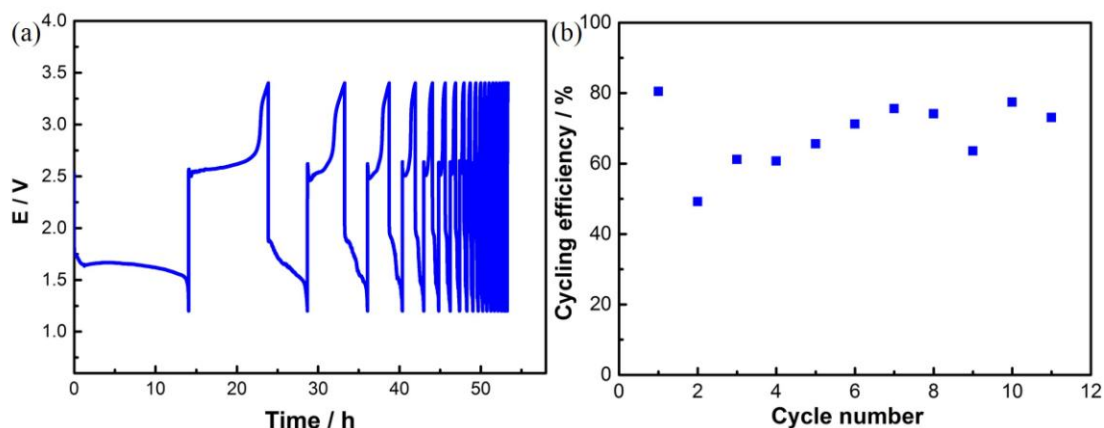


Figure S6. (a) The voltage profiles and (b) The cycling efficiency of each cycle in a Na-O₂ battery with limited Na in the anode.

Cycling efficiency for the metal anode is a very important factor to represent the anode performance of metal air batteries. In the battery assembly, the anode used small amount of Na (1.5 mg) corresponding to 17.5 h discharge (1.75 mAh based on the current of 0.1 mA). The separator was glass fiber/Nafion-Na⁺/glass fiber composite and the cathode was P50 carbon fiber paper. The electrolyte was 0.5 M Na triflate in DME and the battery operated in 1 atm oxygen atmosphere with current of 0.1 mA. The voltage window was set to 1.2-3.4 V with no discharge time limit. In this case, the end of discharge indicates the depletion of Na in the anode and the charge capacity shows how many Na is obtained from the decomposition of NaO₂. The cycling efficiency of the first cycle is determined by the first discharge capacity divided by the theoretical capacity. The cycling efficiency of the second cycle was determined by the second discharge capacity (Na consumed) divided by the first charge capacity (Na formed). The cycling efficiency for each cycle ranges from 60%-80% which indicates Na metal undergoes a severe decay in the anode. Errors could lead to an underestimate of the cycling efficiency. Since limited Na was used in the anode, the ion diffusion is more difficult than the large amount of Na used in the anode, resulting in larger overpotentials in the cell.

¹ T. Soboleva, Z. Xie, Z. Shi, E. Tsang, T. Navessin and S. Holdcroft, *Journal of Electroanalytical Chemistry*, 2008, **622**, 145.