

Dense monolithic MOF and carbon nanotube hybrid with enhanced volumetric and areal capacities for lithium-sulfur battery

Hui Zhang,¹ Wenqi Zhao,^{1,2} Yizeng Wu,¹ Yunsong Wang,¹ Mingchu Zou,¹ Anyuan Cao^{1*}

¹Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China

²Center for Composite Materials and Structures, Harbin Institute of Technology, Harbin 150080, China

* Corresponding author: anyuan@pku.edu.cn

Supporting Information

Experimental Section

Materials. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AR) and nitric acid (HNO_3 , AR) were ordered from Xilong Chemical Co., Ltd. Methanol (CH_3OH , GR) and 2-methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, $\geq 99\%$) were provided by Beijing Tongguang Fine Chemical Co. and Beijing Bailingwei Science and Technology Co., Ltd. respectively. Sublimed sulfur (AR, $\geq 99.5\%$) and carbon disulfide (CS_2 , ACS) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. All chemicals are analytical grade without further purification.

Fabrication of D-CNTs@ZIF-8 Hybrids. CNTs were obtained from the ultrasonication of CNT sponge, which was synthesized by our earlier reported chemical vapor deposition method utilizing ferrocene and 1,2-dichlorobenzene as catalyst and carbon precursor, respectively. Before grafting ZIF-8, CNTs were treated by concentrated nitric acid at $120\text{ }^\circ\text{C}$ for 12 h, and then washed with deionized water until neutral ($\text{pH} \sim 7$). After freeze-dried, the acidized CNTs were functionalized by oxidized carboxylic groups, facilitating *in-situ* growth of MOFs on CNTs. The densified hybrid of ZIF-8 and CNTs was fabricated by a solvothermal procedure using methanol as solvent. Particularly, CNTs (120 mg) were mixed with Hmim (0.649 g) methanol (20 ml) solution homogenously through repeated ultrasonication and stirring, which was then added by $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.239 g) methanol (20 ml) solution in dropwise manner. The mixture was stirred continuously for 15 min, and then placed in a 50 ml Teflon-line autoclave, heating to $90\text{ }^\circ\text{C}$ for 6 h. After the solvothermal reaction, the product labelled as CNTs@ZIF-8 was washed with methanol for three times. Different from previous heating-drying and freeze-drying method, we placed the washed hybrid under room temperature ($20 \pm 1\text{ }^\circ\text{C}$) overnight to densify the hybrid, achieving the densified CNTs@ZIF-8 hybrid (D-CNTs@ZIF-8) with the ZIF-8 content of 50 wt% finally. When increasing ZIF-8 precursor content by 1.22, 1.82, 2.33, 3 and 4 fold, different densified hybrids with corresponding ZIF-8 contents (55, 65, 70, 75, and 80 wt%) were obtained through the same procedure.

Fabrication of S@D-CNTs@ZIF-8. Before sulfur loading, the densified CNTs@ZIF-8 hybrids were activated at $120\text{ }^\circ\text{C}$ for 6 h. To guarantee sufficient sulfur solution impregnation, these hybrids were soaked into a sulfur/ CS_2 solution (25 mg ml^{-1}) for 3 days, and all of them were then dried at $40\text{ }^\circ\text{C}$. The obtained sulfur-contained hybrids were further treated at $155\text{ }^\circ\text{C}$ for 12 h in a sealed autoclave to obtain S@D-CNTs@ZIF-8.

Adsorption Test of Lithium Polysulfides. For the adsorption test, Li_2S_6 -contained electrolyte was synthesized by adding Li_2S and sulfur in amounts corresponding to the nominal stoichiometry of Li_2S_6 in 1,3-dioxolane and dimethoxyethane (1:1 in volume) under stirring at $60\text{ }^\circ\text{C}$ for 12 h. The obtained solution with a concentration of 2 mg mL^{-1} was used for the sulfide adsorption test.

Material Characterization. The morphology and structure of the prepared samples were analyzed by SEM (Hitachi S4800) and TEM (FEI Tecnai F20, 200 kV). The pore structure was determined by N₂ adsorption at 150 °C using an ASAP 2020 volumetric sorption analyzer. The specific surface area was calculated from the isotherm using the BET equation. The pore size distribution was calculated by NLDFT which could acquire the size distribution of micro and meso pores over the entire range precisely on the basis of the desorption branch. TGA curves were acquired from a thermogravimetric analyzer (TA instruments) at a heating rate of 10 °C min⁻¹ in nitrogen. X-ray photoelectron spectroscopy (XPS) analysis were performed on an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al K α radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation.

Cell assembly and Electrochemical Characterization. The obtained hybrids of S@D-CNTs@ZIF-8 were used as freestanding Li-S cathodes with a lithium metal foil as the counter-electrode and a polypropylene (PP) film (Celgard 2400) as the separator. The electrolyte contains 1M lithium bis(trifluoromethane sulfonyl) imide (LiTFSI) in a binary solvent of 1,3-dioxolane and dimethoxyethane (1:1 in volume) or with 1 wt% lithium nitrate as the additive. Coin-type (CR 2032) cells were assembled in an argon-filled glove box, and the electrodes with the area of 1×1=1 cm² and thickness of 20 μ m were permeated by electrolyte with the E/S ratio of 20 mL g⁻¹. This ratio is a reasonable value in our system because limited or excessive electrolyte will result in insufficient electrolyte permeation or decrease of battery energy density and cycling stability, respectively. A galvanostatic cycling test of the assembled cells was carried out on a Neware system in the potential range of 1.3–3.0 V at different discharge/charge current densities of 0.2 C to 1C. In order to guarantee sufficient electrolyte permeation, we tested the EISs after the Li-S cells had been discharged and charged for five cycles, state of charged (SOC). EIS measurement was performed on a CHI660E electrochemical workstation, and the curves were obtained by applying a sine wave with amplitude of 5 mV over the frequency range from 100 kHz to 0.01 Hz.

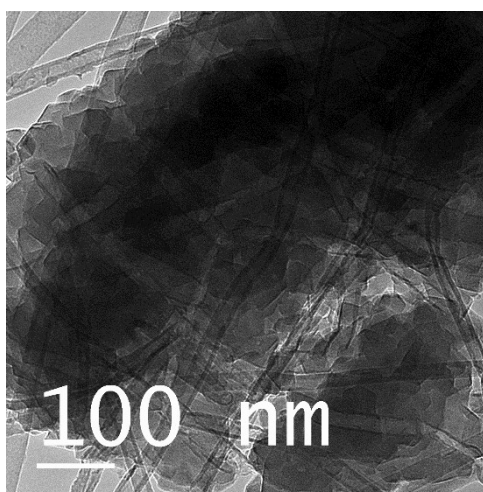


Figure S1. TEM image of the densified CNTs@ZIF-8 hybrid with the MOF content of 70 wt%.

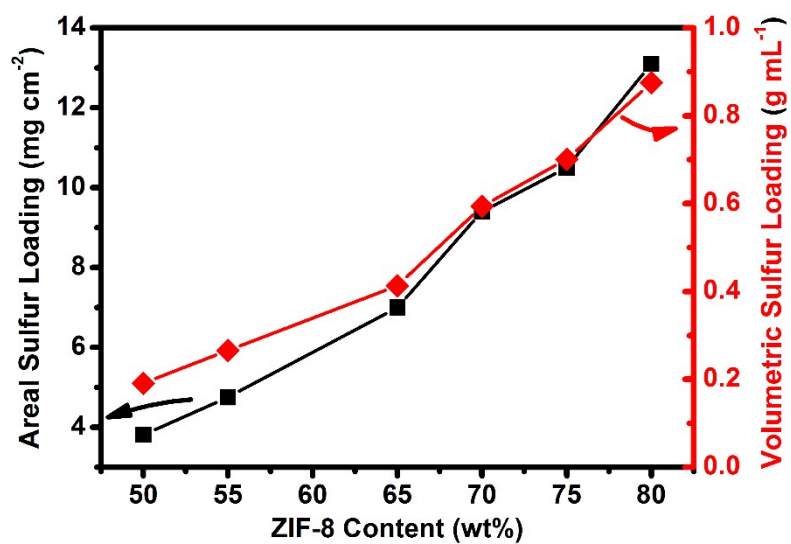


Figure S2. Areal (black line) and volumetric (red line) sulfur loadings of the densified CNTs@ZIF-8 hybrids with different MOF contents (50-80 wt%).

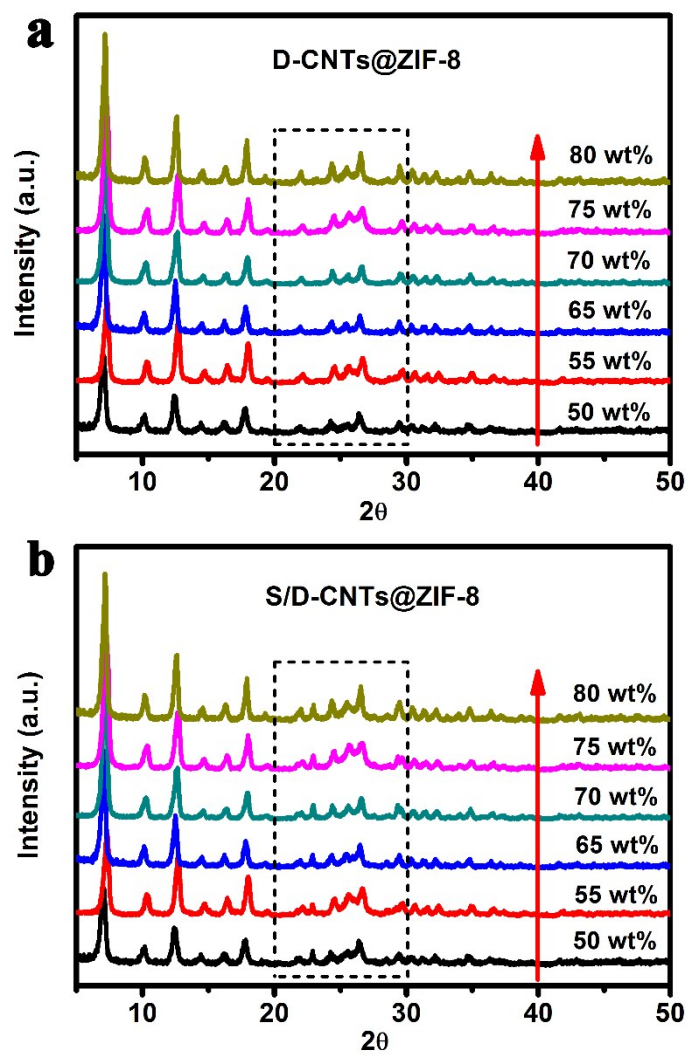


Figure S3. XRD patterns of all D-CNTs@ZIF-8 and S/D-CNTs@ZIF-8.

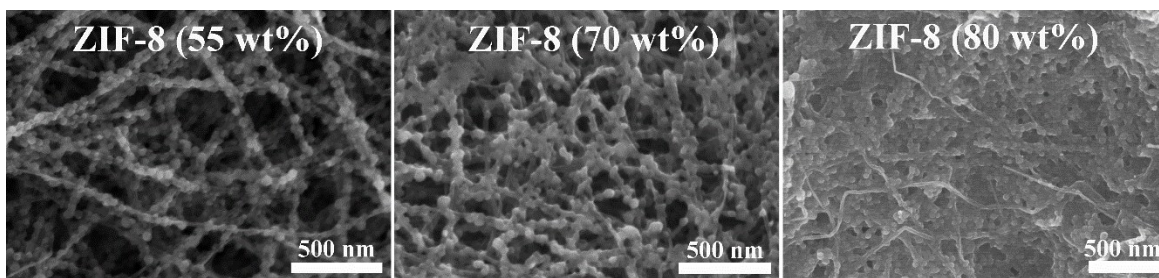


Figure S4. SEM images of D-CNTs@ZIF-8 (55, 70 and 80 wt%) after being loaded with sulfur.

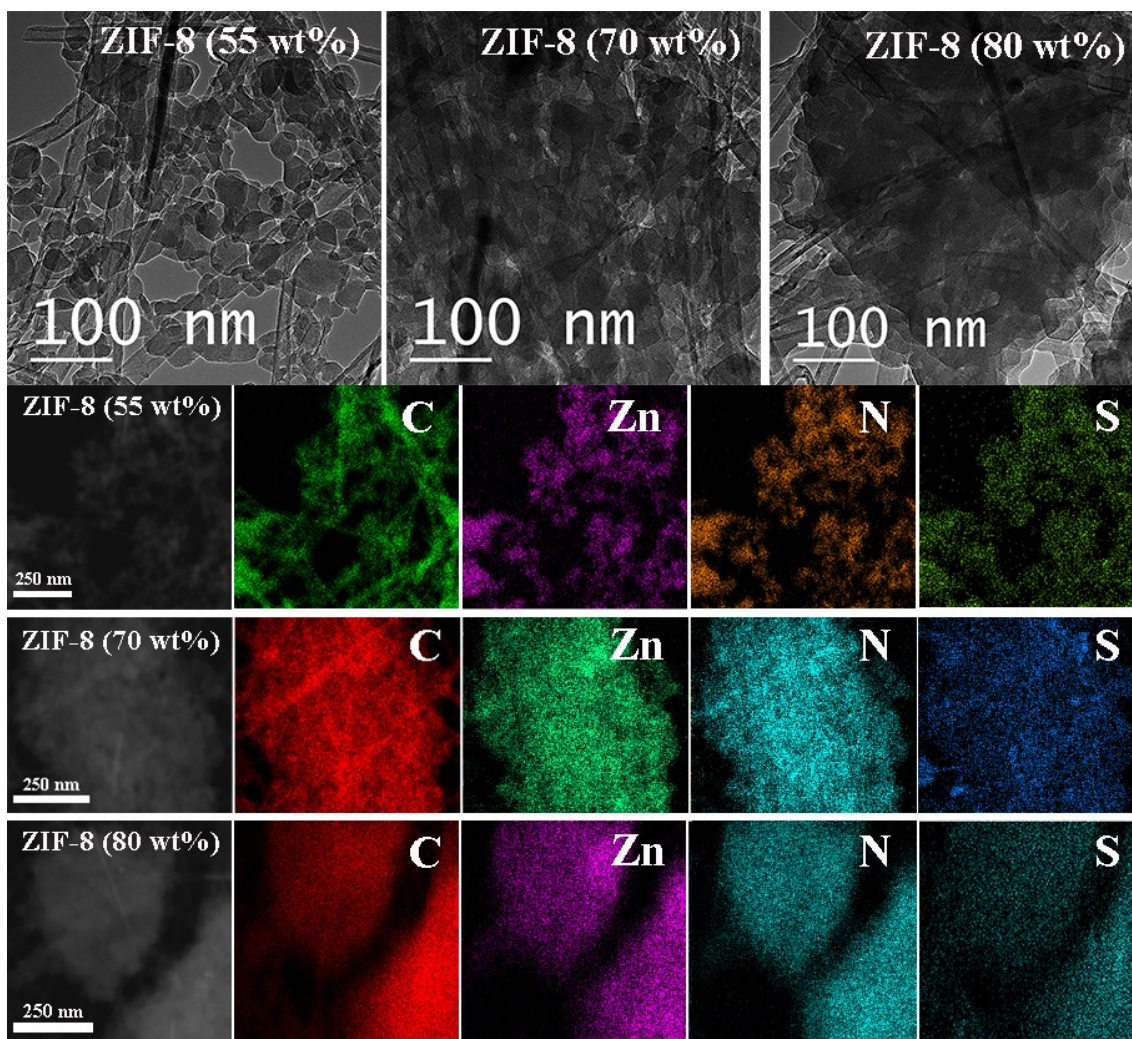


Figure S5. TEM images of D-CNTs@ZIF-8 (55, 70 and 80 wt%) after being loaded with sulfur, and the corresponding elemental mapping of C, Zn, N and S.

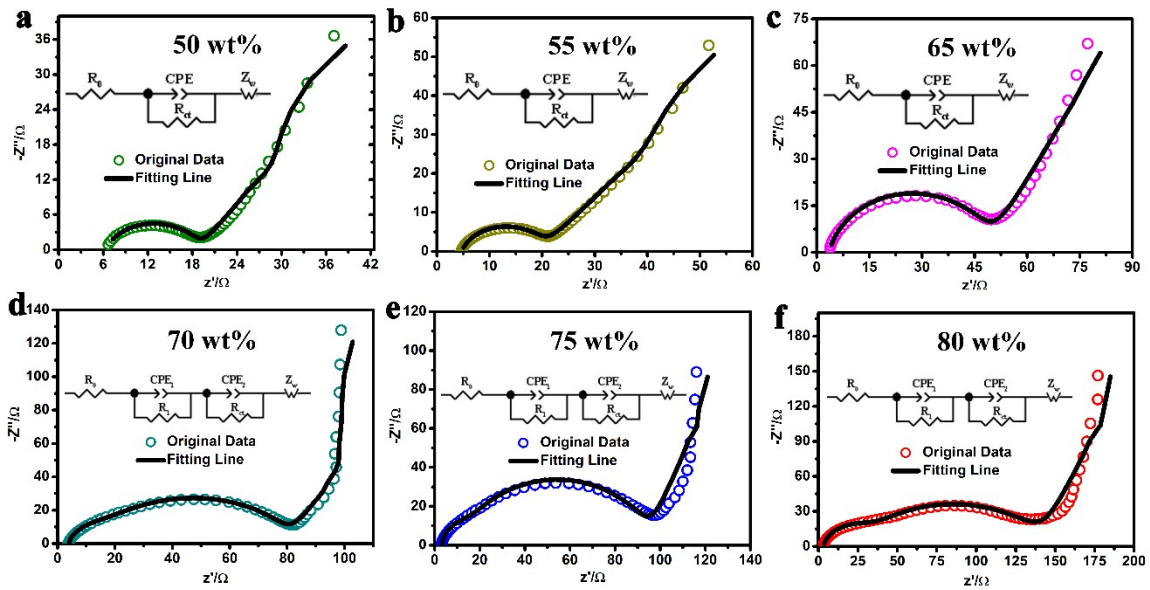


Figure S6. (a-f) Original EIS data (separate points) and fitted curves (solid lines) based on the equivalent circuits of the densified CNTs@ZIF-8 hybrids with MOF contents of 50-80 wt%.

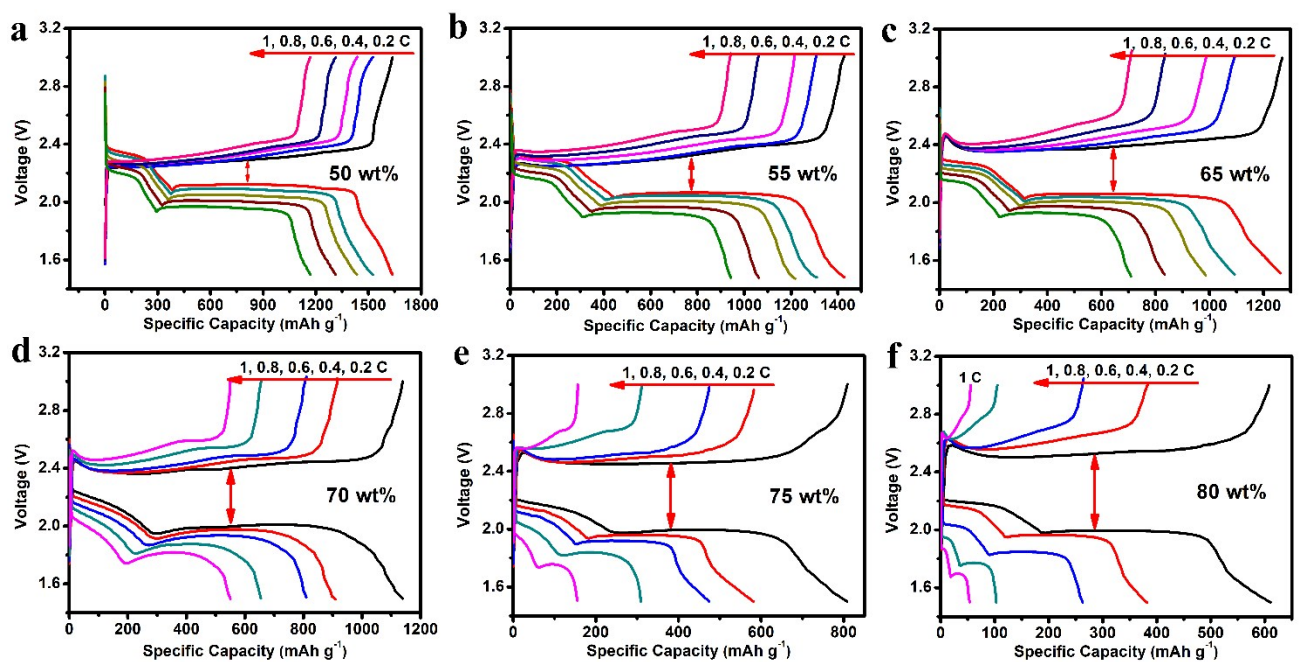


Figure S7. (a-f) Charge-discharge curves of all S/D-CNTs@ZIF-8 electrodes at different current densities of 0.2, 0.4, 0.6, 0.8 and 1 C.

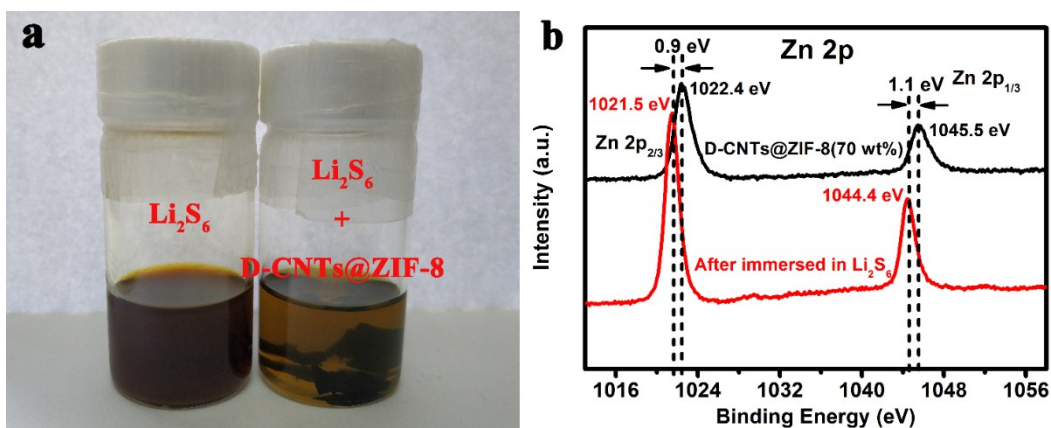


Figure S8. Chemical interaction test between D-CNTs@ZIF-8 (70 wt%) and polysulfides. (a) Adsorption test by immersing the D-CNTs@ZIF-8 (70 wt%) within the Li_2S_6 electrolyte. (b) Zn 2p XPS patterns of the D-CNTs@ZIF-8 (70 wt%) before and after being immersed in the Li_2S_6 electrolyte.

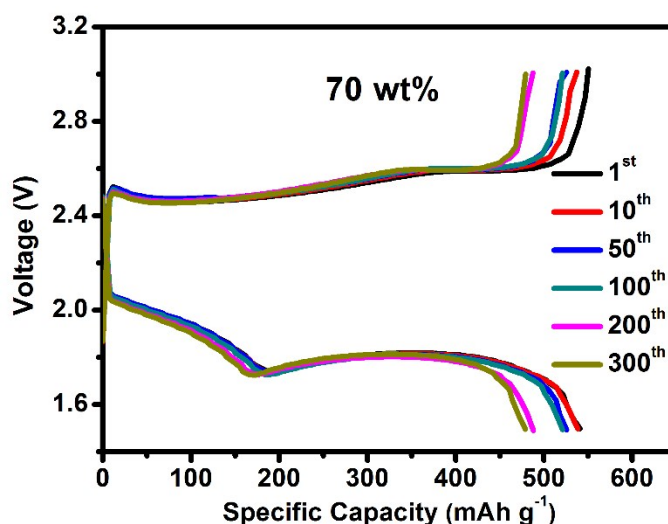


Figure S9. Charge-discharge curves of S/D-CNTs@ZIF-8 (70 wt%) at 1th, 10th, 50th, 100th, 200th and 300th cycles during long cycling test under the current density of 1 C.

Table S1. Fitting parameters of the EIS results based on the equivalent circuits.

	R_0	R_1	R_{ct}	CPE-T	CPE-P	Z_w -R	Z_w -T	Z_w -P
50 wt%	6		12.96	$2.1982e^{-5}$	0.74995	69.03	0.28691	0.63064
55 wt%	4		16.48	$3.46e^{-5}$	0.75854	123.2	0.35612	0.60339
65 wt%	3.44		44.95	$4.5775e^{-6}$	0.86178	397.8	0.27775	0.69631
70 wt%	3.447	1.888	77.52	1: $9.6527e^{-7}$ 2: $6.8154e^{-5}$	1: 1.346 2: 0.73197	353.4	2.69	0.7991
75 wt%	3.17	10	80.97	1: $4.6713e^{-6}$ 2: $4.1866e^{-5}$	1: 1.05 2: 0.8586	469.5	3.595	0.78242
80 wt%	3.032	24.8	113.5	1: $4.6713e^{-6}$ 2: $9.3483e^{-5}$	1: 0.96946 2: 0.7024	817.1	8.035	0.78093