Supporting information

Mesoporous CoO/Co-N-C Nanofibers as Efficient Cathode Catalysts for Li-O_2 Batteries.

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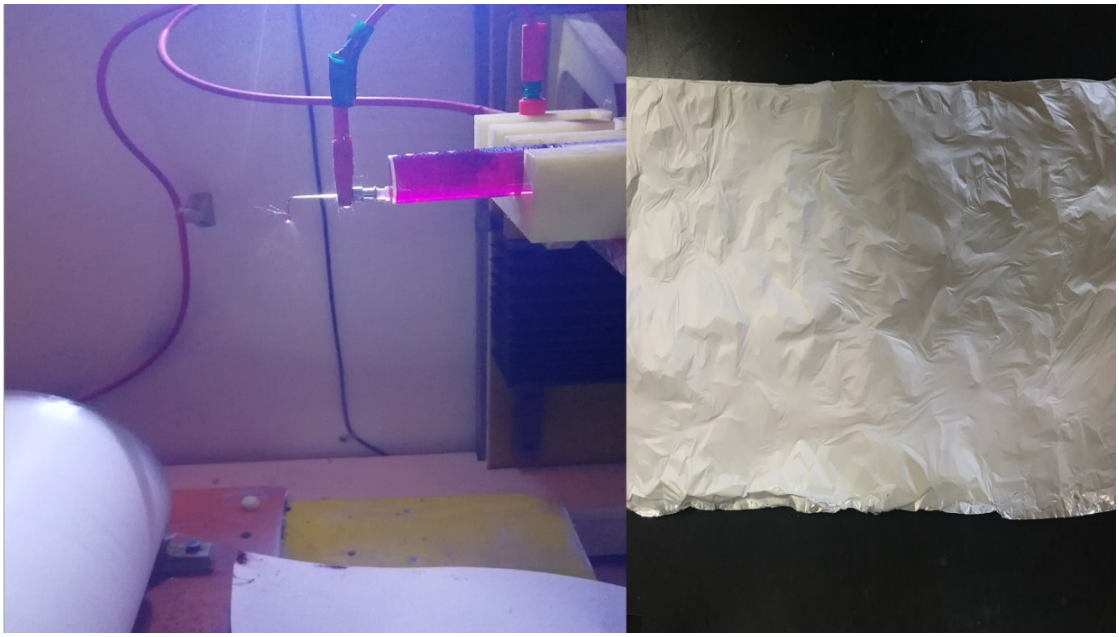

Fig. S1 Photo of the electrospinning process to fabricate the nanofibers with collected $Co(NO_3)_2$/PVP mat on Al foil.

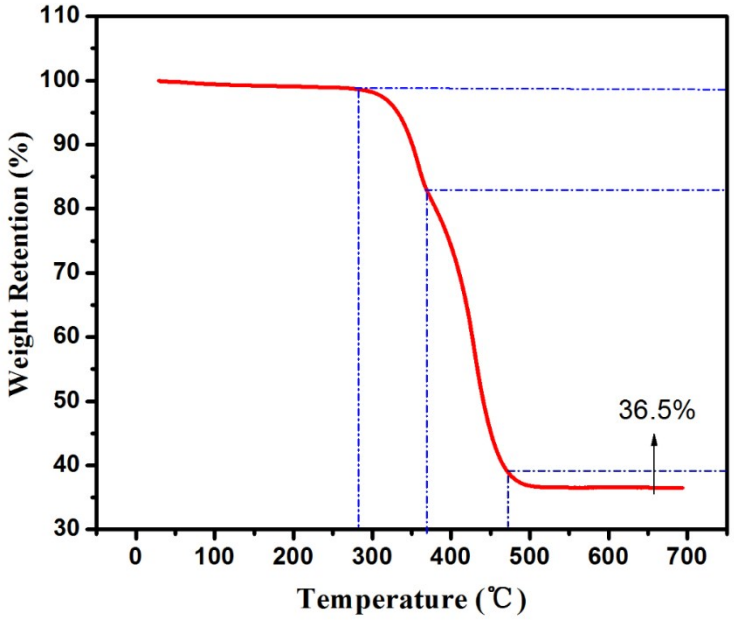

Fig. S2 TG survey of CoO/Co-N-C-2 under air.

Table S1. Schematic illustration of weight ratio calculated from TGA results of CoO/Co-N-C-2.

Adding weight	**Terminal weight ratio**	**Remain in the sample**
$Co(NO_3)_2 \cdot 6H_2O$ 0.15g	Co_3O_4 36.5%; Co 26.8%	Co 0.03036g 100%
PVP 0.4g	Else 73.2%	N+O+C (PVP) 0.08296g 20.75%

The CoO/Co-N-C fibers transform into Co_3O_4 after TGA measurements in air. Assuming that the Co elements remain in the sample through the process, the weight ratio of Co is calculated to be 26.8% from the final products weight ratio (36.5%).

Table S2. Weight ratio of CoO: Co for different $Co(NO_3)_2 \cdot 6H_2O$ contented samples

Sample	$Co(NO_3)_2 \cdot 6H_2O$/g	CoO: Co
CoO/Co-N-C-1	0.1	28: 72
CoO/Co-N-C-2	0.15	45: 55
CoO/Co-N-C-3	0.2	36: 64

We use the RIR method based on the XRD results to calculate the mass ratio of Co/CoO according to the previous reports[1] and the formula:

$$w_x = \frac{I_{Xi}}{K_A^X \sum_{i=A}^{N} \frac{I_i}{K_A^i}}$$

The "x" represent one of the "N" phases, "K" is calculated from the RIR values (6.16 for CoO, 10.15 for Co) if one of the phases is defined as internal standard, and "I" represent the intensity result from the XRD survey. By applying this calculation method, it is found that the mass ratios of CoO/Co can be adjusted with changing the adding amounts of $Co(NO_3)_2 \cdot 6H_2O$ in the systhesis.

1. P. Zhang, R. Wang, M. He, J. Lang, S. Xu and X. Yan, *Adv. Funct. Mater.,* 2016, 26, 1354-1364.

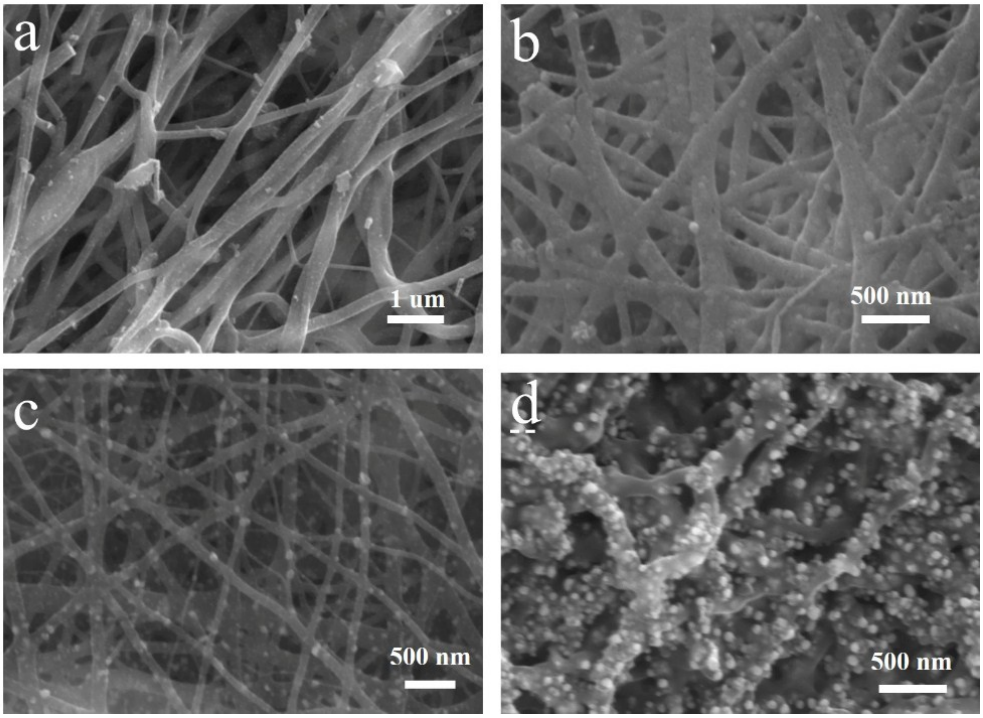

Fig. S3 SEM image of a) N-C; b) CoO/Co-N-C-1; c) CoO/Co-N-C-2; d) CoO/Co-N-C-3.

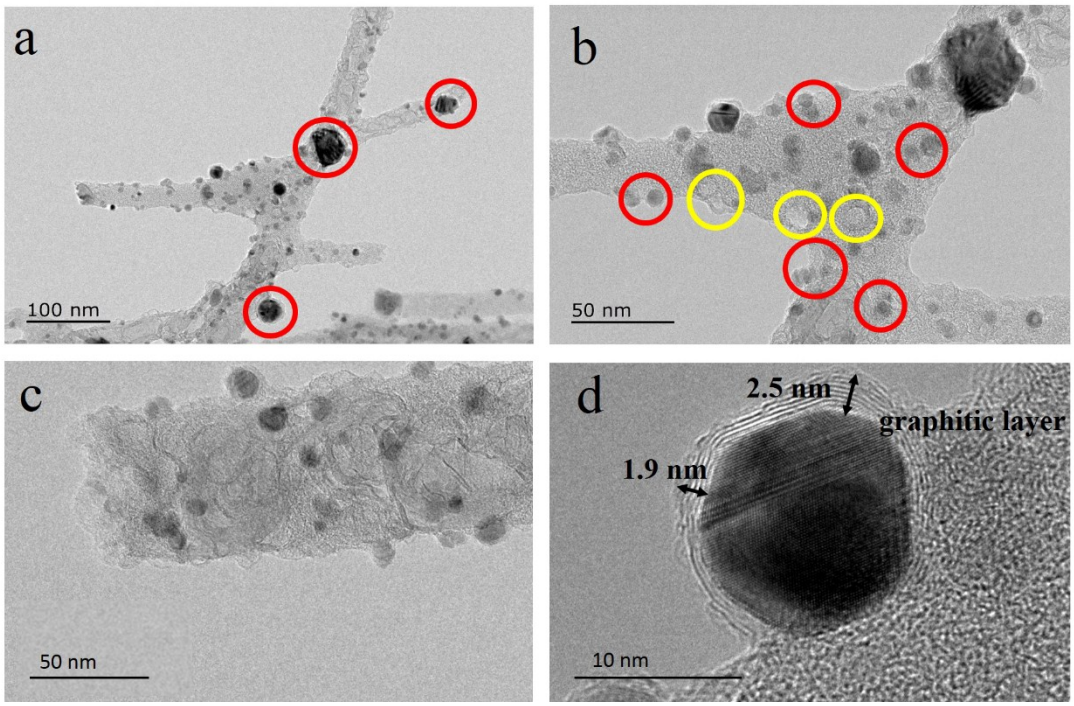

Fig. S4 TEM images of CoO/Co-N-C-2 nanofibers.

The pores are marked by yellow circles, and the CoO/Co particles are marked by red circles. While the small particle covered with graphitic layer is measured to be around 2 nm.

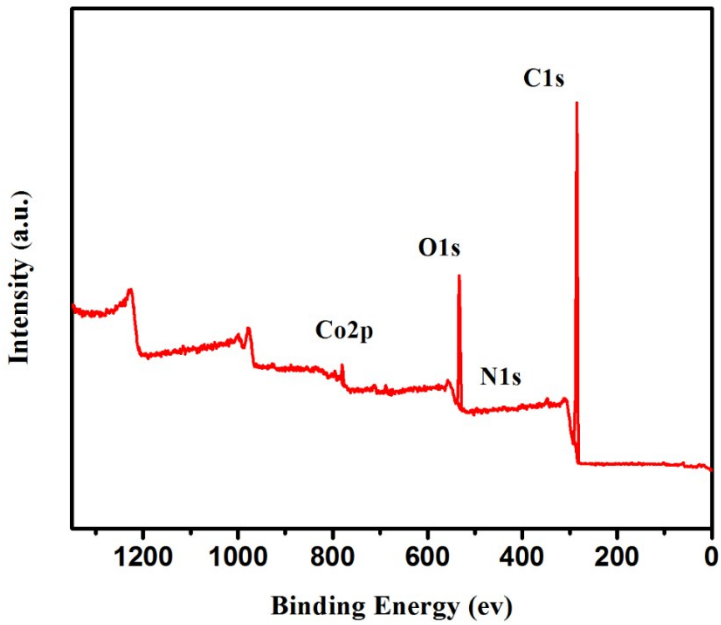

Fig. S5 XPS survey spectra of CoO/Co-N-C, and the content of C, N, O and Co elements are C 85.38 at%，N 0.82 at%, O 13.51at%, and Co 0.29 at%, respectively.

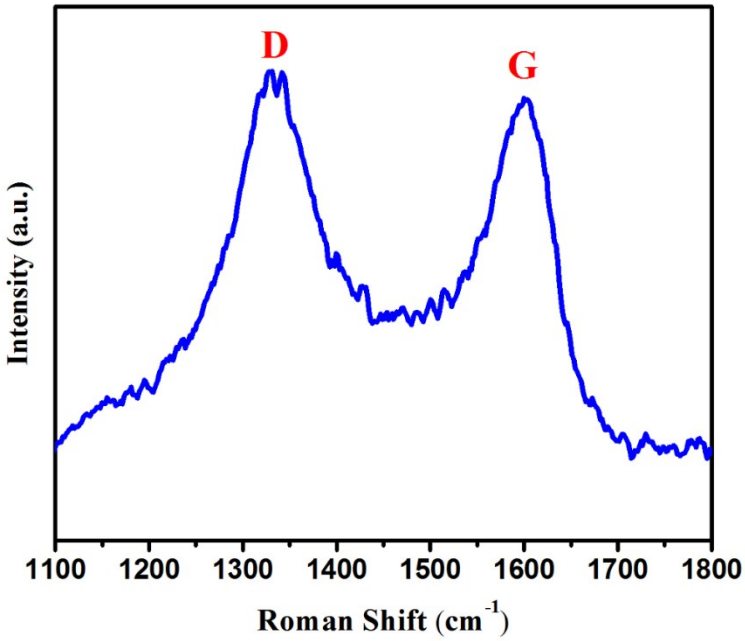

Fig. S6 Raman spectra of CoO/Co-N-C-2 with the corresponding intensity ratio of D and G bands (I_D/I_G=1.094).

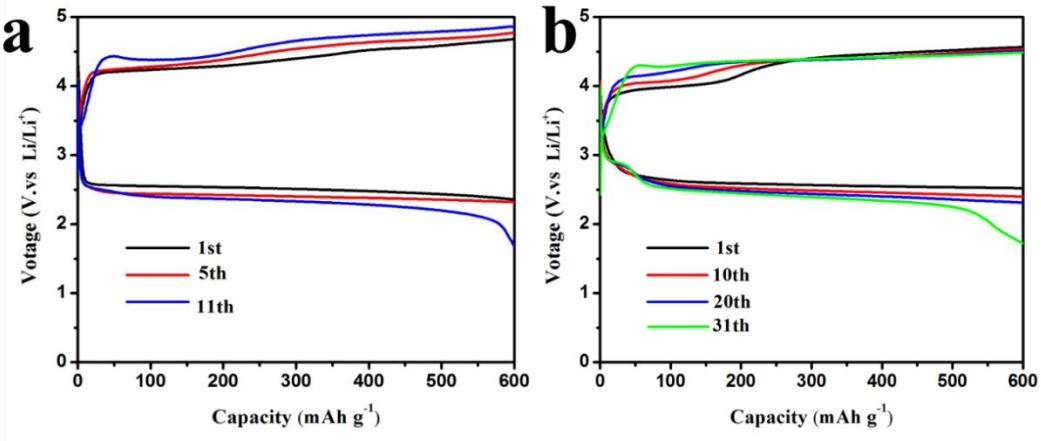

Fig. S7 The cycle performance of a) Super P carbon and b) N-C cathode at a current density of 100 mA g^{-1} with a specific capacity limit of 600mAh g^{-1}.

It is evident that N-C cathode shows a better cycle performance and a lower charge potential than those of Super P carbon electrode, mainly attributed to the N/O dual-doping nanofiber structure. However, when adding applicable amount of Co, the remarkable performance of the cathode catalyst can be achieved.

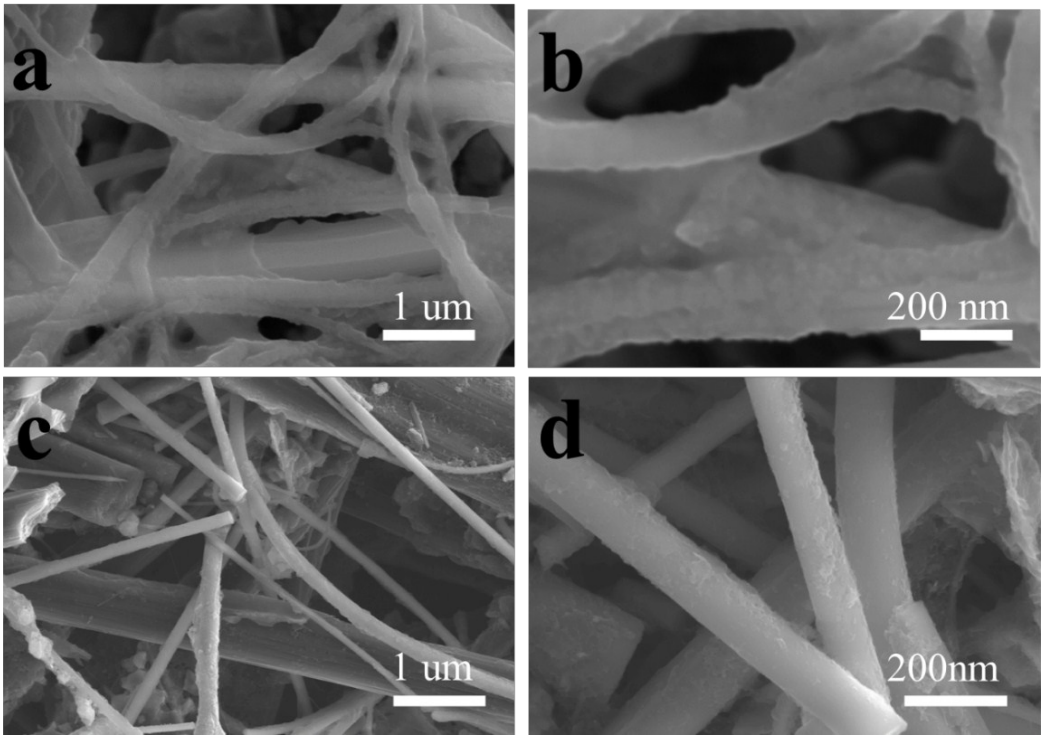

Fig. S8 SEM images of CoO/Co-N-C-2 cathodes at different stages a) and b) after 140th discharged; c) and d) after 140th charged.

The vast majority of discharge products can still be recycled leaving a smooth fiber surface. It is no doubt that the CoO/Co-N-C-2 electrode can still handle more discharge/charge cycles, and it possesses a great durability and cycle ability.

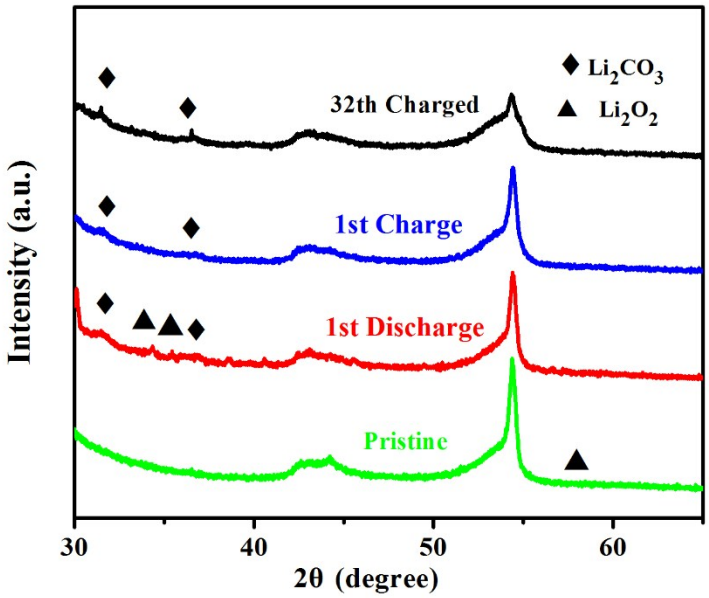

Fig. S9 XRD patterns of N-C cathode at different stages.

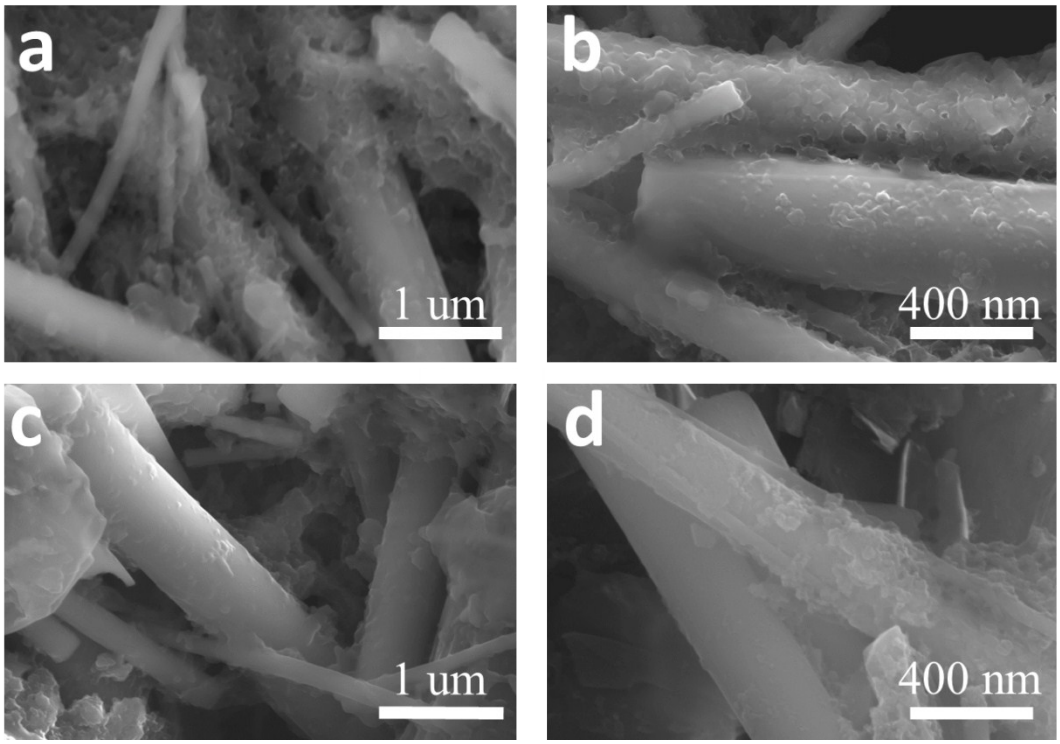

Fig. S10 SEM images of N-C cathode at different stages under a current of 100 mAh g^{-1}: a) and b) after 1st discharged; c) and d) after 1st charged.

After discharging, the products accumulated on the fibers surface. However, the surface cannot recover to the smooth appearance. Therefore, with the increasing of by-products, the active sites are encased, leading to a limited cycle performance.

Table S3. Electrochemical performance comparison of CoO/Co-N-C catalysts with those of representative carbon based CoO and/or Co decorated materials reported in the literature.

Ref. No.	**Materials**	**Electrolyte**	**Current Density** (mA g^{-1})	**Specific Capacity** (mAh g^{-1})	**Cycles/Fixed Capacity** (mAh g^{-1})
Our work	CoO/Co-N-C-2	1 M $LiCF_3SO_3$ in TEGDM	100	8798.6	140/600 94/1000
1	Co/CoO@PCNS	0.1 M $LiClO_4$ in DMSO	100	2660	55/800
2	Co/CoO@NGNS	1 M $LiCF_3SO_3$ in TEGDME	100	7800	70/500
3	Carbon-dotted defective CoO	1 M LiTFSI in TEGDME	100	7011	50/1000 (200 mAh g^{-1})
4	Co@PNCF	1 M LiTFSI in TEGDME	100	4583	40/500
5	Co@NGNS	1 M $LiCF_3SO_3$ in TEGDME	100	3630	30/1000
6	Oxygen vacancy bearing CoO	1 M LiTFSI in TEGDME	200	4623	25/1000
7	CNT@Ni@NiCo silicate core–shell	1 M $LiCF_3SO_3$ in TEGDME	200	10046	50/1000
8	CoO/CNF	1 M LiTFSI in TEGDME	80	3882.5	50/1000
9	Co-CNF	0.1 M $LiClO_4$ DMSO/TEGDME	100	-	70/500
10	Co@N-C	1 M LiTFSI in TEGDME	0.1 mA cm^{-2}	3862	40/500
11	CoO nanowire array	1 M LiTFSI in TEGDME	100	4888	50/500

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