Deep-Breathing Fe-Doped Superstructure Modified by Polyethyleneimine as Oxygen Reduction Electrocatalysts for Zn-Air Batteries

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Characterization:

The phase compositions of the samples were performed by Raman spectroscopy (inVia-Reflex,Renishaw, UK) and XRD (Bruker D8 Advance diffractometer) using Cu Kα radiation (λ = 1.5406 Å), which was scanned from 10° to 80° at 0.02° s^{-1}. Field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Japan), transmission electron microscopy (TEM, JEM-2100, JEOL, Japan) were also performed. X-ray photoelectron spectroscopy (XPS) was conducted using a Mg *K*α achromatic X-ray source. The binding energies were calibrated using the C 1s peak of adventitious carbon at 284.8 eV as a reference.

Electrochemical Measurements:

All the electrochemical measurements were conducted with electrochemical workstation (CHI 760E, Chenhua). Platinum wire serves as counter electrode. Glassy carbon rotating disk electrode (RDE) loaded with catalysts acts as working electrode. Ag/AgCl electrode is reference electrode. The catalyst ink was obtained by dispersing

0.005 g sample and 0.05 mL Nafion solution (5 wt%) in 1 mL mixed solution of purified water and isopropyl alcohol (3:1). Then, 0.008 mL catalyst ink was dropped onto the surface of the RDE for natural drying. Linear sweep voltammetry (LSV) curves from -0.8 to 0.2 V (vs. Ag/AgCl) under different rotating speed (400~2500 rpm) were conducted to investigate ORR activity. LSV curves from 0 to 1.0 V were used to research OER activity of samples in O_2-saturated 0.1 M KOH solution. Both scanning speed is 5 mV s^{-1}. Cyclic voltammetry (CV) was scanned from −0.9 to 0.1 V with 20 mV s^{-1} sweep speed in oxygen/nitrogen saturated 0.1 M KOH solution. The electron transfer number (n) can be obtained according to K-L curve:

$$\frac{1}{j}=\frac{1}{j_k}+\frac{1}{B\times\omega^{1/2}}$$

$$B=0.2\times n\times F\times C_{O_2}\times D_{O_2}^{\frac{2}{3}}\times v^{-\frac{1}{6}}$$

Here, n represents electron transfer number, F represents Faraday constant (96,485 C mol^{-1}), C_{O2} represents saturated concentration of O_2 in 0.1M KOH aqueous solution (1.2×10^{-6} mol cm^{-3}), D_{O2} represents diffusion coefficient of O_2 (1.9×10^{-5} cm^2 s^{-1}) in 0.1 M KOH aqueous solution, ν represents kinematic viscosity of the solution (0.01 cm^2 s^{-1}), ω represents angular velocity of the disk, and J_k represents kinetic current density. Rotating ring-disk electrode (RRDE) measures were conducted using the same catalyst inks. The RRDE curve was scanned with 5 mV s^{-1}. The electron transfer numbers (n) and peroxide yield (HO_2^- %) are calculated with the subsequent equations:

$$n=4\times\frac{I_d}{I_d+I_r/N}$$

$$HO_2^-\%=200\frac{I_r/N}{I_d+I_r/N}$$

Here, I_d represents disk current, Ir represents ring current, and N represents collection efficiency of the Pt ring (0.37). The stability of the catalyst was examined through CV scanning of 10,000 cycles (300 mV s^{-1}).

Fabrication and test of liquid rechargeable ZABs

First, 0.01 g catalyst was suspended in 0.74 mL purified water, 0.2 mL isopropanol, and 60 μL 5 wt% Nafion solution to produce catalyst ink. Then, the air-cathode was fabricated via dropping 100 μL catalyst ink onto 1 cm^{-2} hydrophobic carbon cloth. Thus, the catalyst loading is ~0.001 g cm^{-2}. Combined with the Zn-foil anode and 6M KOH/0.2M Zn (Ac)$_2$ electrolyte, the liquid ZABs can be obtained. Battery tests were carried out an electrochemical workstation at room temperature.

The specific capacity was calculated according to the equation:

$$\frac{\text{current} \times \text{service hours}}{\text{weight of consumed zinc}}$$

The energy density was calculated according to the equation:

$$\frac{\text{current} \times \text{service hours} \times \text{average discharge voltage}}{\text{weight of consumed zinc}}$$

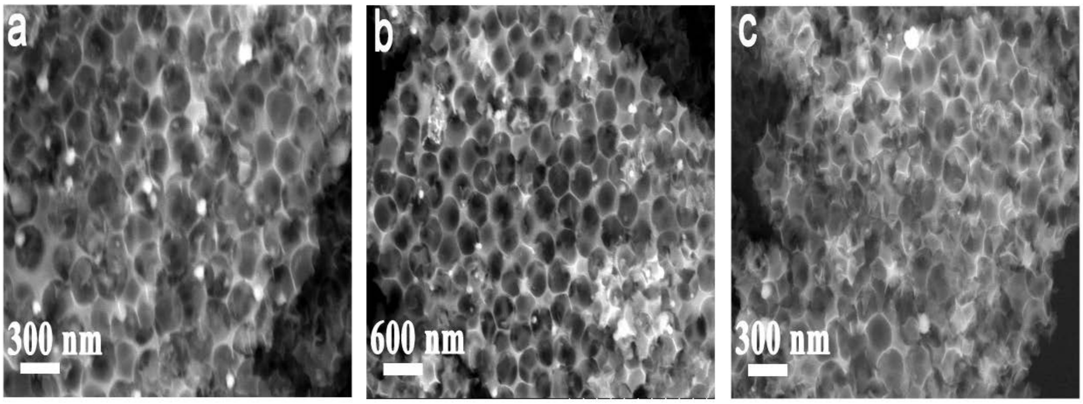

Figure S1. SEM images of the samples. a) cal-FeZIF-NSC-0, b) cal-FeZIF-NSC-0.5, c) cal-FeZIF-NSC-1.

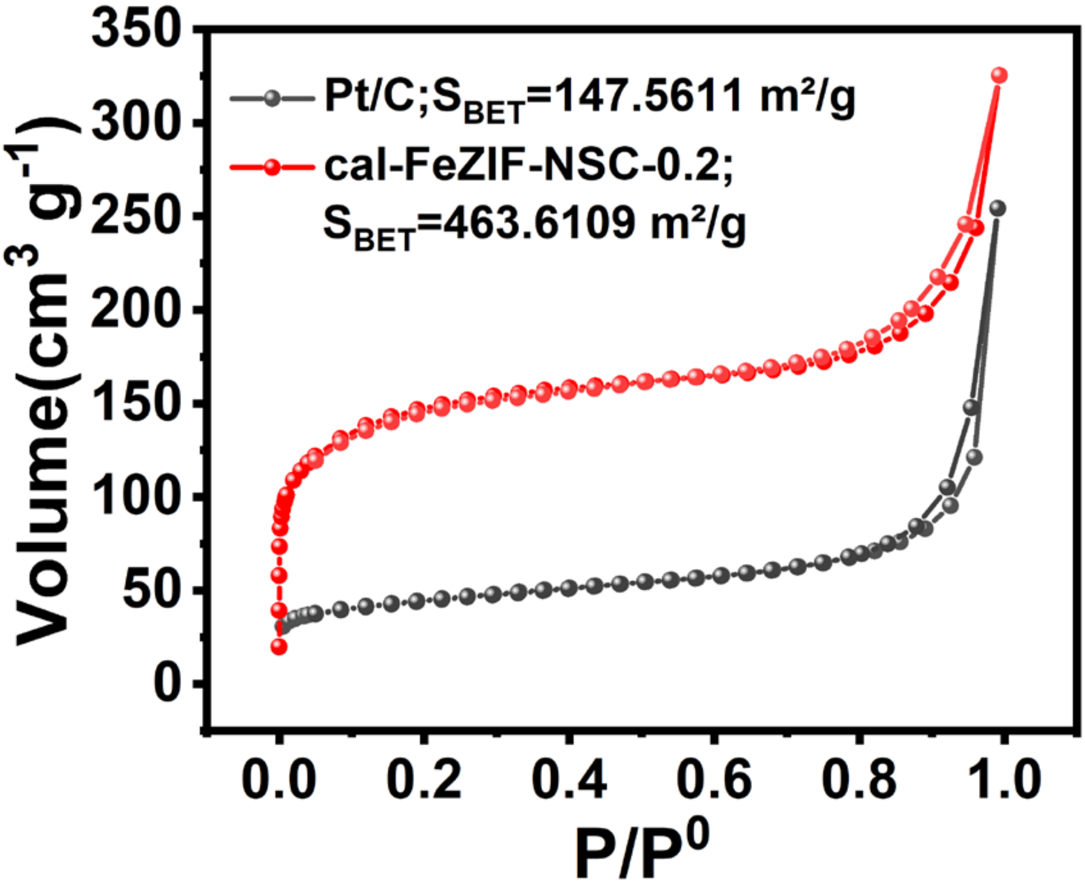

Figure S2. N_2 sorption isotherms of Pt/C and cal-FeZIF-NSC-0.2 samples.

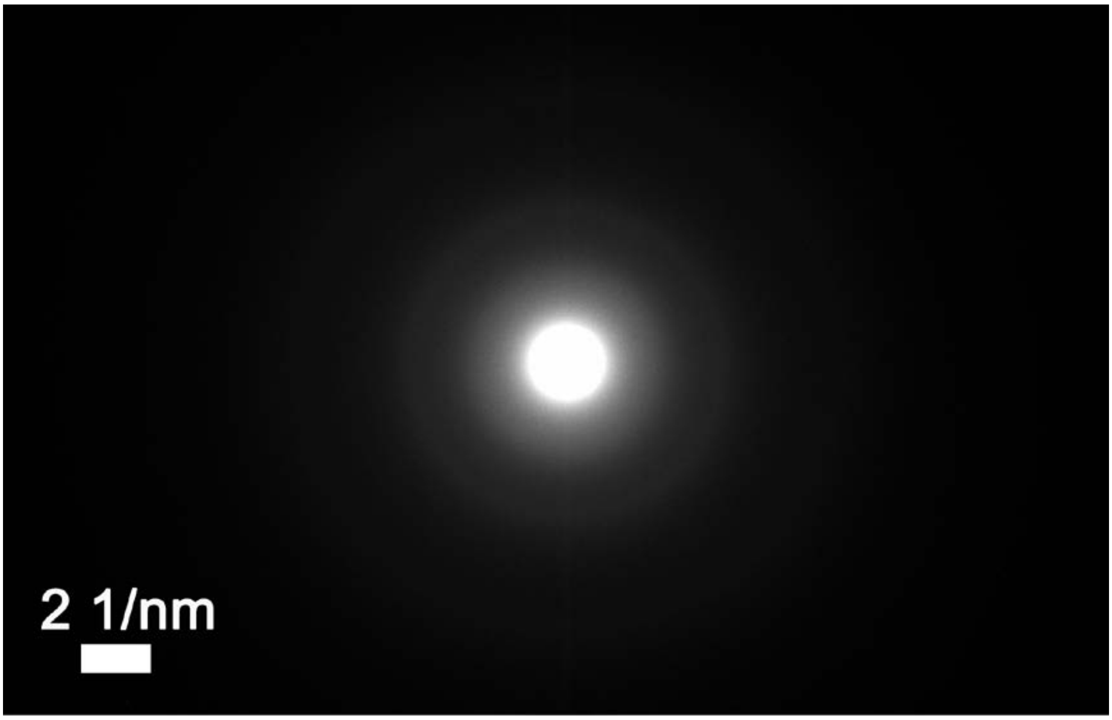

Figure S3. electron diffraction pattern image of the cal-FeZIF-NSC-0.2 composite.

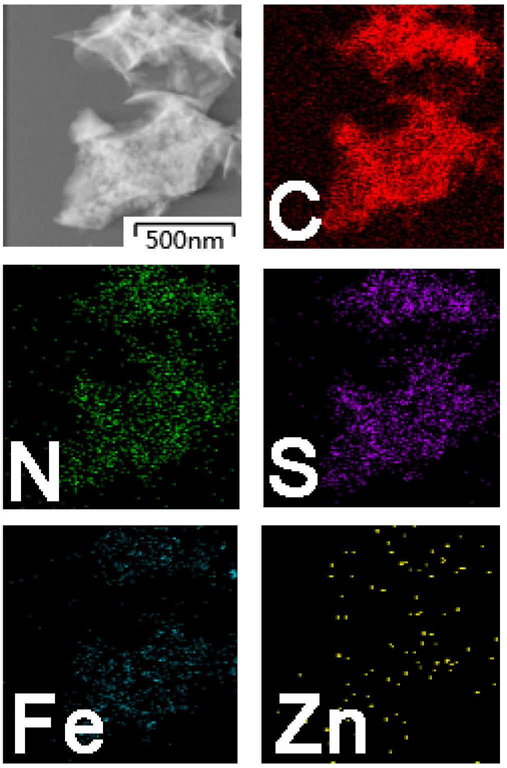

Figure S4. C, N, S, Fe and Zn elemental mapping the synthesized cal-FeZIF-NSC-0.2

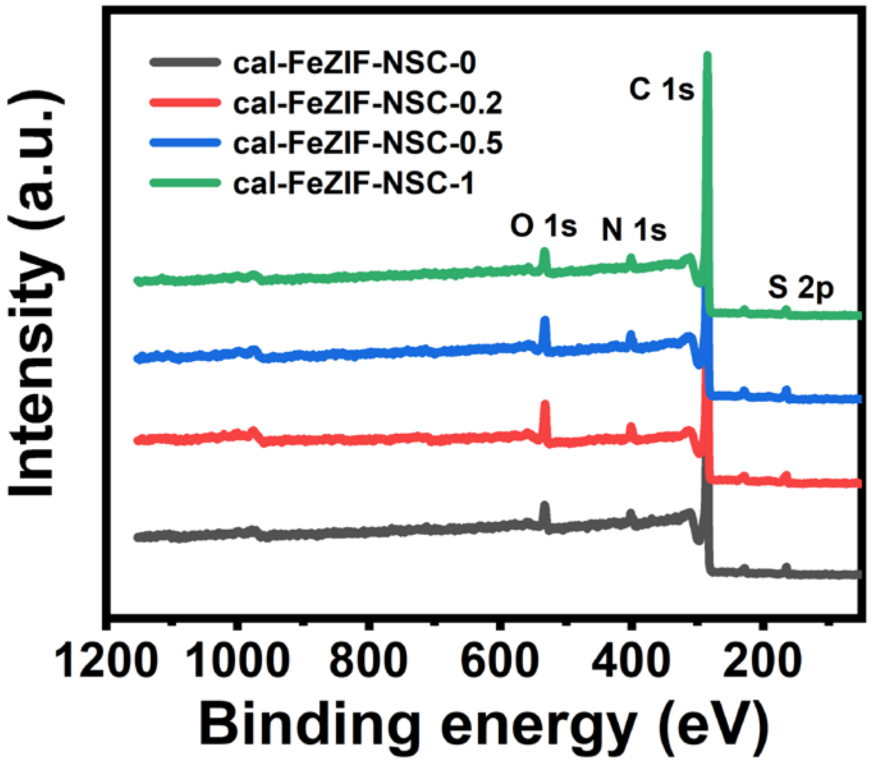

Figure S5. XPS survey spectrum of cal-FeZIF-NSC-0, cal-FeZIF-NSC-0.2, cal-FeZIF-NSC-0.5 and cal-FeZIF-NSC-1.

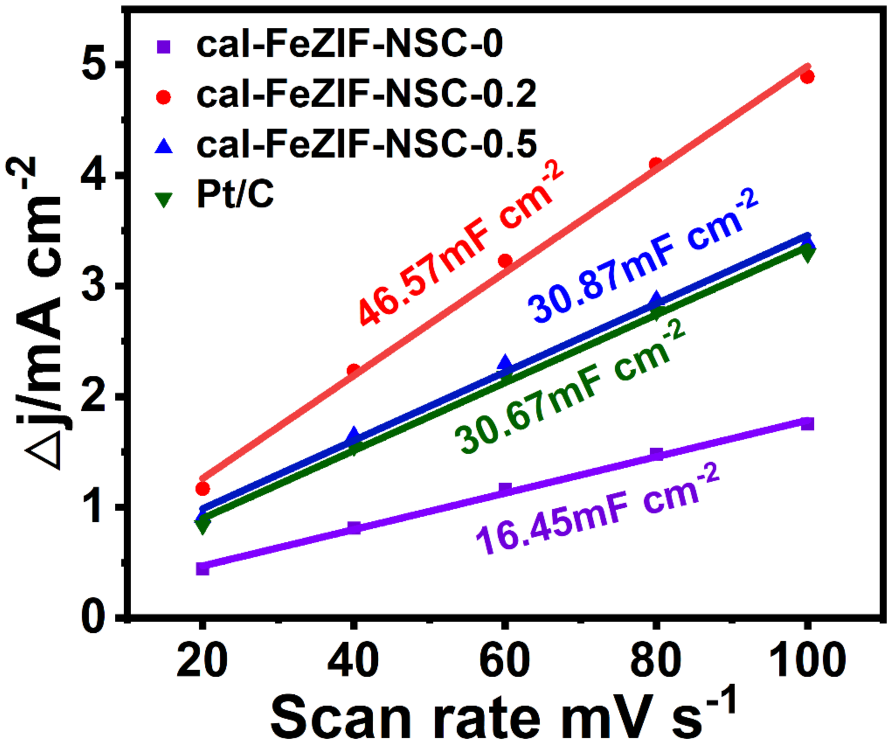

Figure S6.Linear fit of capacitive current to CV scan rate for synthesized cal-FeZIF-NSC-0, cal-FeZIF-NSC-0.2, cal-FeZIF-NSC-0.5 and Pt/C catalysts.

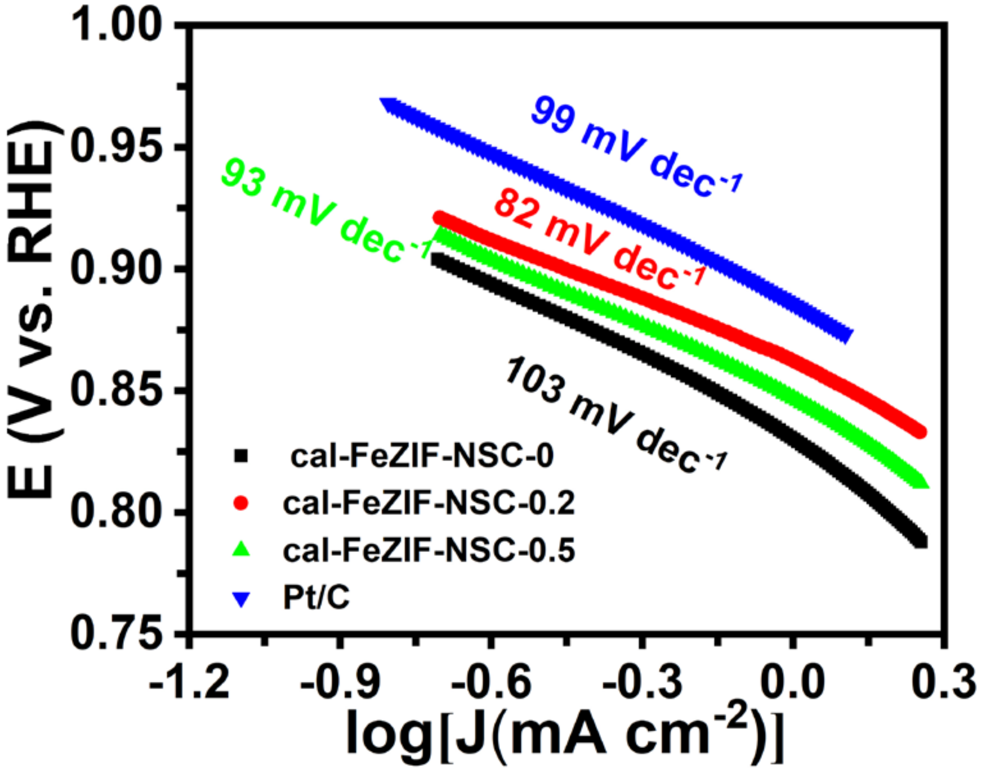

Figure S7. Tafel plot of cal-FeZIF-NSC-0, cal-FeZIF-NSC-0.2, cal-FeZIF-NSC-0.5 and Pt/C.

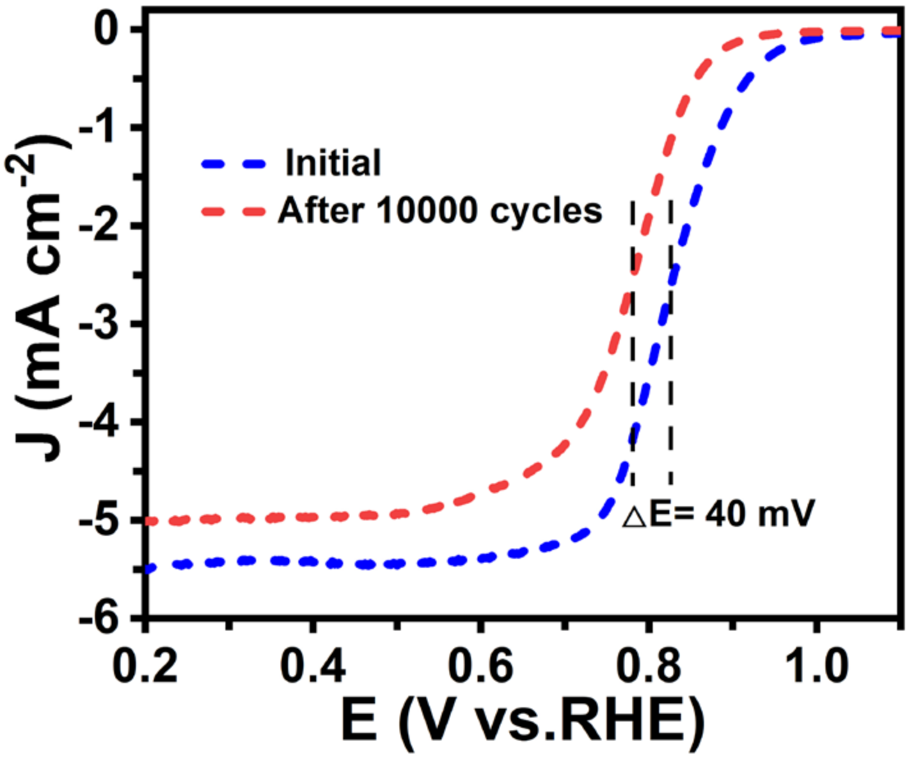

Figure S8. LSV curves before and after 10000 cycles of the commercial Pt/C catalyst.

Figure S9. OCP of the ZAB based on Pt/C-RuO_2.

Table 1 Comparisons of electrocatalytic performance (vs RHE) for cal-FeZIF-NSC with other reported bi-functional ORR/OER catalysts in 0.1 M KOH electrolyte.

Catalyst	$E_{1/2}$[V]	E_{onset}[V]	Ref
S and N co-doped carbon	0.78	0.96	[1]
N-G	0.78	0.95	[2]
Ni/NiO	0.76	0.87	[3]
(Ni,Co)S2	0.71	0.82	[4]
CoNi/BCF	0.80	0.91	[5]
NiCo2S4@g-C3N4-CNT	0.76	0.87	[6]
Co/CoFe@NC	0.84	0.97	[7]
Co-N4/NC	0.81	0.93	[8]
Pt/C	0.82	0.99	This work
cal-FeZIF-NSC	0.80	0.97	This work

Table 2 Comparisons of electrocatalytic performance for Zn-air batteries with cal-FeZIF-NSC cathodes with other reported ones.

Catalyst	Peak power destiny [mW cm^{-2}]	specifc capacity [mAh g_{Zn}^{-1}]	Stability	Ref
S and N co-doped carbon	94.8	--	60 min/cycle for 500 cycles(500 h)	[1]
CoNi/BCF	155.1	710.9	20 min/cycle for 180 cycles(60h)	[5]
Co/CoFe@NC	146.6	775.2	40 min/cycle for 550 cycles(360h)	[7]
Co-N4/NC	101.62	762.8	10 min/cycle for 100 cycles(17h)	[8]
N-GRW	65	873	10 min/cycle for 150 cycles(30 h)	[9]
Zn/Co-ZIFs/PAN	83.5	640.3	10 min/cycle for 108 cycles(18h)	[10]
NPHG	30	--	60 min/cycle for 176 cycles(176h)	[11]
NPMC foam	55	--	60 min/cycle for 600 cycles(100h)	[12]
NiO/CoN PINWs	70	690	10 min/cycle for 50 cycles(8h)	[13]
Pt/C-RuO_2	70	673	20 min/cycle for 165 cycles(55h)	This work
cal-FeZIF-NSC	85	744	20 min/cycle for 165 cycles(55h)	This work

References

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