Supporting information:

Fig. S1 Cyclic performance of the CNT@Ni electrodes in different concentrations of $Fe(C_5H_5)_2$. (a) 0.03M (b) 0.50M $Fe(C_5H_5)_2$.The capacity was limited to 1000 mAh g^{-1} at the current density of 500 mA g^{-1}.

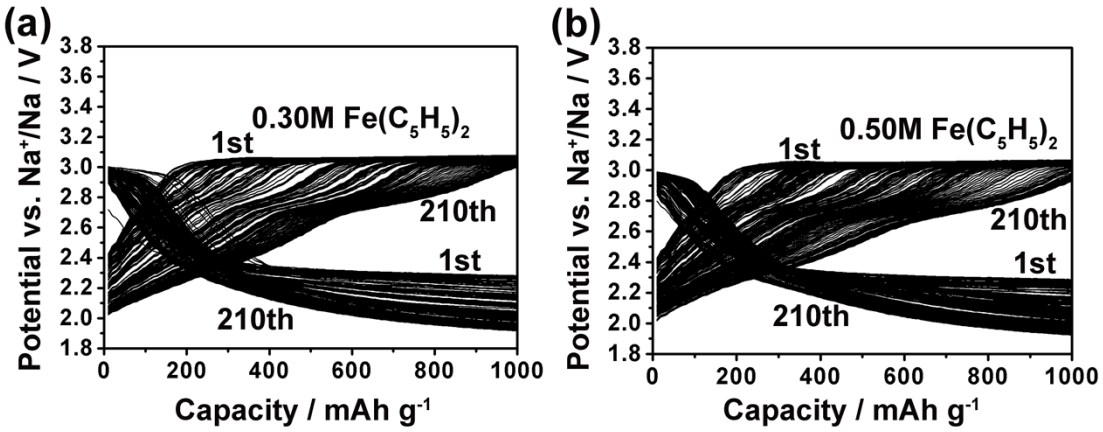

Fig. S2 The selected discharge & charge profiles of the cell in $Fe(C_5H_5)_2$-containing electrolyte at the 1st , 50th, 150th , 200th , 230th, 250th cycles . The black line is 1st cycle; the red line is 50th cycle; the green line is 100th cycle; the blue line is 150th cycle; the rose red line is 200th cycle; the yellow line is 230th cycle; the purple line is 250th cycle(the capacity was limited to 1000 mAh g^{-1}) at the current density of 500 mA g^{-1}.

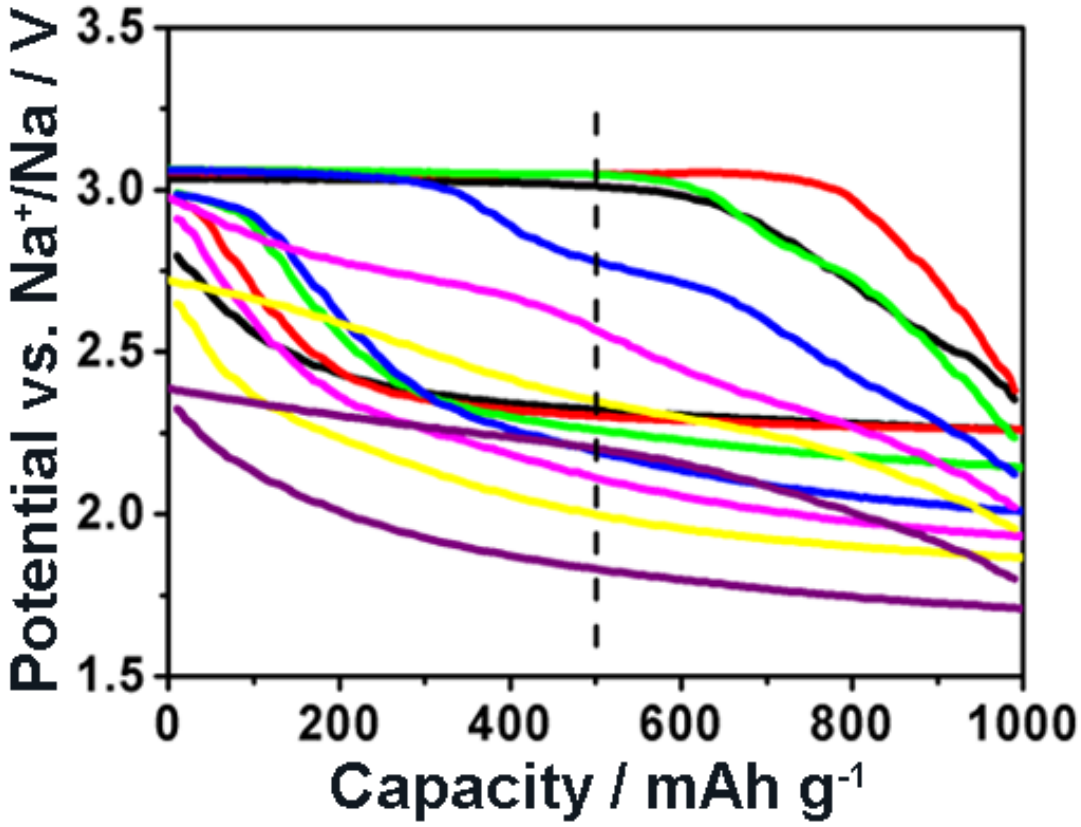

Fig. S3 The UV absorption spectra of the electrolyte. By the reaction between $FeCl_3$ and $Fe(C_5H_5)_2$ in a faintly acid environment, we have obtained the solution containing 10mg/ml $Fe(C_5H_5)_2^+$(the black line). It can be seen that the absorbance of $Fe(C_5H_5)_2^+$ at 619 nm decreases with the incremental amount of Na_2O_2(5mg, the red line; 10mg, the green line; 15mg, the blue line) into the electrolytes containing $Fe(C_5H_5)_2^+$.

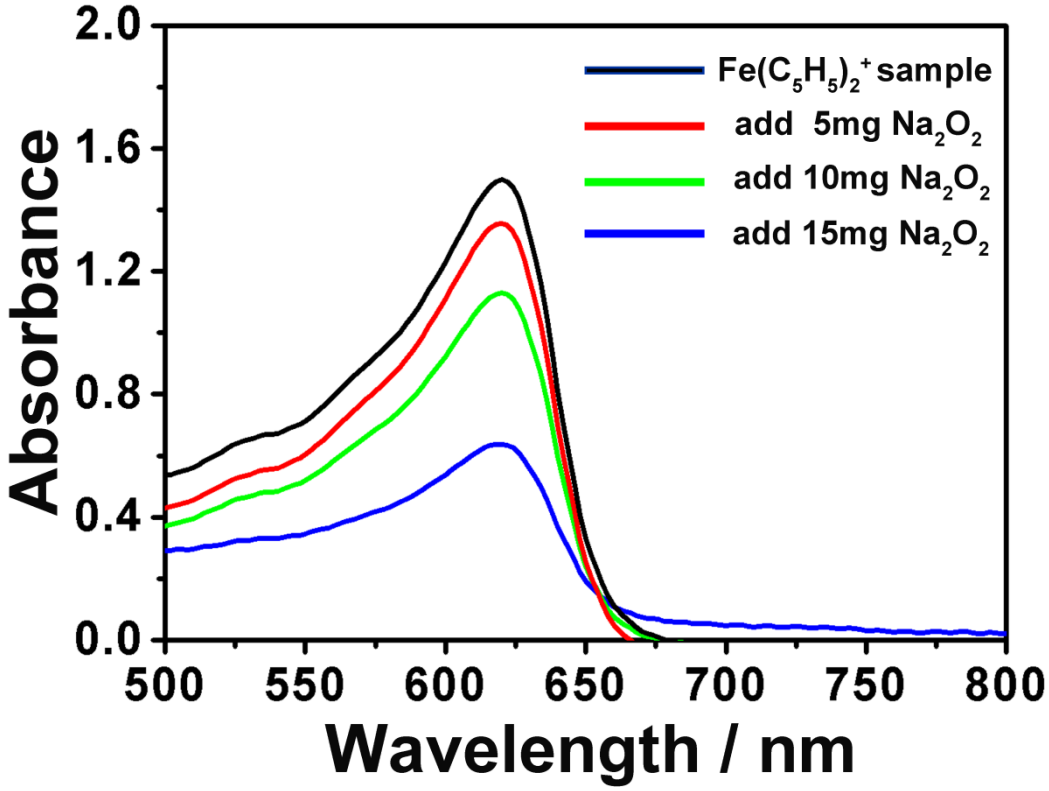

Table S1 the ORR and OER catalytic activity of Na-air batteries reported recently

Battery system	Discharge product	Air cathode	Voltage of ORR (vs.Na^+/Na/V)	Voltage of OER (vs.Na^+/Na/V)	Reference
Na-air	Na_2O_2	DLC	2.38-2.00	3.90	1
Na-air	Na_2O_2	GNS	2.10	4.20	2
Na-air	Na_2O_2	CNT paper	2.20	2.40	3
Na-air	Na_2O_2	$NiCo_2O_4$	2.15	3.00	4
Na-air	Na_2O_2	$CaMnO_3$/C	2.20	2.80	5
Na-air	NaO_2	GDL	2.10	2.20	6-8
Na-air	NaO_2	Ketjenblack	2.10	2.20	6
Na-air	NaO_2	VACNTs	2.05	2.29	9
Na-air	Na_2O_2 NaO_2	NCNT	1.80	2.50	10
Na-air	Na_2CO_3	Pt@GNS	2.30	3.40	11
Na-air	Na_2CO_3	OMC-2.7	2.01	3.26	12
Na-air	Na_2CO_3	Super P	1.86	3.71	12
Na-air	Na_2O_2	CNT@Ni	**2.10**	**2.20-2.80**	This work

Note DLC: diamond-like carbon thin films
GNS: graphene nanosheets
CNT: carbon nanotubes
GDL: carbon-fibre gas diffusion layer
VACNT: vertically aligned carbon nanotubes
NCNT: nitrogen-doped carbon nanotubes
OMC-2.7: ordered mesoporous carbon (pore size: 2.7nm)

Reference

1 Q. Sun, Y. Yang, Z. W. Fu, *Electrochem Commun.,* 2012, **16**, 22-25.
2 W. Liu, Q. Sun, Y. Yang, J. Y. Xie and Z. W. Fu, *Chem. Commun.,* 2013, **49**, 1951-1953.
3 Z. Jian, Y. Chen, F. J. Li, T. Zhang, C. Liu and H. S. Zhou, *J. Power Sources.,* 2014, **251**, 466-469.
4 W. M. Liu, W. W. Yin, F. Ding, L. Sang and Z. W. Fu, *Electrochem Commun.,* 2014, **45**, 87-90.
5 Y. X. Hu, X. P. Han, Q. Zhao, J. Du, F. Y. Cheng and J. Chen, *J. Mater. Chem. A.,* 2015, **3**, 3320-3324.
6 C. L. Bender, P. Hartmann, M. Vracar, P. Adelhelm and J. Janek, *Adv. Energy Mater.,* 2014, **4**, 1301863.
7 P. Hartmann, C. L. Bender, M. Vraˇcar, A. K. Durr, A. Garsuch, J. Janek and P. Adelhelm, *Nat. Mater.,* 2013, **12**, 228-232.
8 P. Hartmann, C. L. Bender, J. Sann, A. K. Durr, M. Jansen, J. Janek and P.

Adelhelm, *Phys. Chem. Chem.Phys.,* 2013, **15**, 11661-11672.
9 N. Zhao, C. L. Li and X. X. Guo, *Phys. Chem. Chem. Phys.,* 2014, **16**, 15646-15652.
10 Q. Sun, H. Yadegari, M. N. Banis, J. Liu, B. W. Xiao, B. Q. Wang, S. Lawes, X. Li, R. Y. Li, X. L. Sun, *Nano Energy.,* 2015,**12**,698-708.
11 S. P. Zhang, Z. Y. Wen, K. Rui, C. Shen, Y. Lu and J. H. Yang, *J. Mater. Chem. A.,* 2015, **3**, 2568-2571.
12 W. J. Kwak, Z. H. Chen, C. S. Yoon, J. K. Lee, K. Amine, Y. K. Sun, *Nano Energy.,* 2015,**12**, 123-130.