

*Supporting information*

## An ultrahigh energy density Mg-air battery with organic acid-solid anolyte biphasic electrolytes

Min Liu,<sup>1, a, b</sup> Qiang Zhang,<sup>1, b</sup> Xueliang Wang,<sup>b</sup> Jianxin Gao,<sup>b</sup> Qianfeng Liu,<sup>b</sup>

Erdong Wang<sup>\*,b</sup> and Zhenbo Wang<sup>\*,a</sup>

a MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, State Key Lab of Urban Water Resource and Environment, School of Chemistry and Chemical Engineering, Harbin Institute of Technology. Harbin 150001, China. E-mail: wangzhb@hit.edu.cn

b Division of Fuel Cell & Battery, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Dalian 116023, China. E-mail: edwang@dicp.ac.cn.

1 presents co-first author.

**Fig. S1:** The XRD pattern of the Mn<sub>3</sub>O<sub>4</sub>/C catalyst.

**Fig. S2:** The SEM image of the Mn<sub>3</sub>O<sub>4</sub>/C catalyst.

**Fig. S3:** LSV curves of ORR for Mn<sub>3</sub>O<sub>4</sub>/C and commercial Pt/C catalysts in O<sub>2</sub> (solid) saturated 0.1 M HClO<sub>4</sub> (a) and 0.1 M KOH (b) electrolyte. (c) LSV plots of Mn<sub>3</sub>O<sub>4</sub>/C catalyst with different rotating rate in O<sub>2</sub> (solid) saturated 0.1 M KOH electrolyte. (d) Respective K-L profiles for Mn<sub>3</sub>O<sub>4</sub>/C catalyst.

**Fig. S4:** The ion conductivity of the prepared SA/NaCl solid electrolyte.

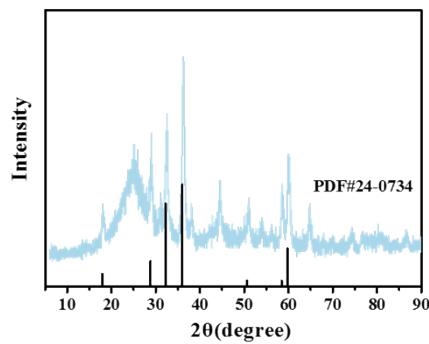
**Fig. S5:** The first and second discharge performance without changing SA/NaCl solid electrolyte.

**Fig. S6:** (a) The open circuit potential (OCP) curves and (b) discharge performance at 0.1 mA cm<sup>-2</sup> of the designed Mg-air battery using solid anolyte with different solid solution salts and 10 wt.% NaCl aqueous solution.

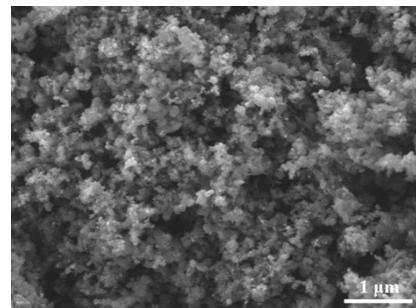
**Fig. S7:** (a) The pristine AZ61 Mg alloy anodes; (b) covered by SA/NaCl solid electrolyte with equal area and after leaving them for 20 days. (c) The comparison of self-corrosion rates with the one in 10 wt.% NaCl aqueous solution.

**Fig. S8:** The SEM image of pristine AZ61 Mg alloy anode.

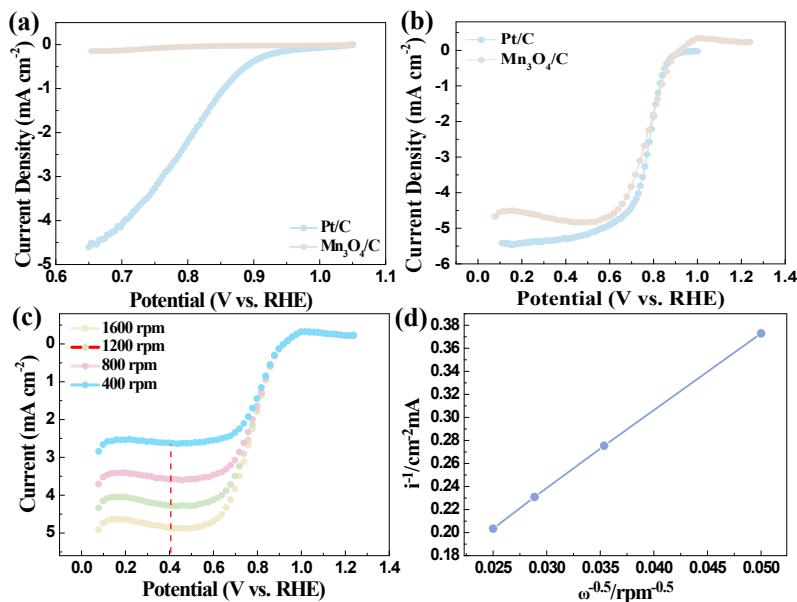
**Fig. S9:** The structural diagram of the designed novel Mg-air battery.



**Fig. S1**

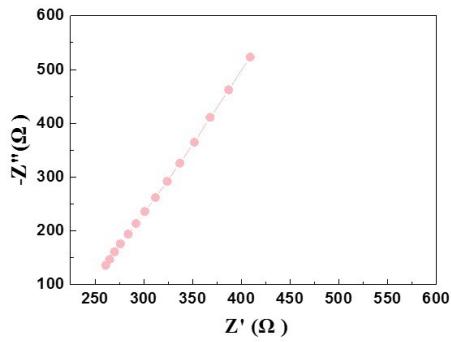


**Fig. S2**

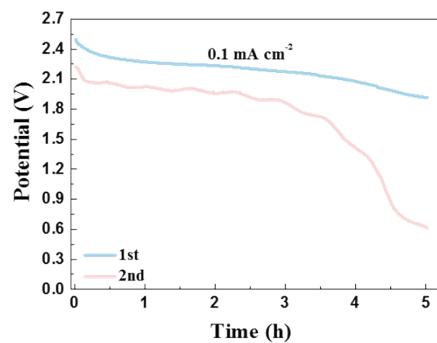


**Fig. S3**

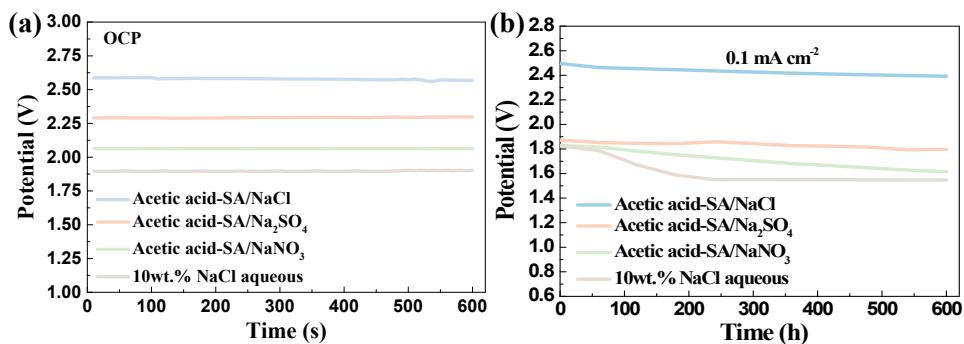
The  $\text{Mn}_3\text{O}_4/\text{C}$  catalyst has ORR ( $E_{1/2} = 0.76 \text{ V}$ ) with inferior activity in  $\text{O}_2$  (solid) saturated 0.1 M  $\text{HClO}_4$ . In  $\text{O}_2$  (solid) saturated 0.1 M KOH electrolyte, the  $\text{Mn}_3\text{O}_4/\text{C}$  catalyst exhibits ORR ( $E_{1/2} = 0.77 \text{ V}$ ) with higher activity and stability, and the electron transfer number is about 3.33.



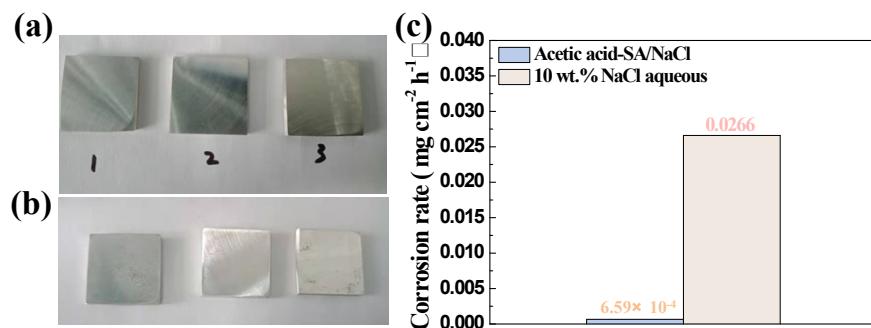
**Fig. S4**



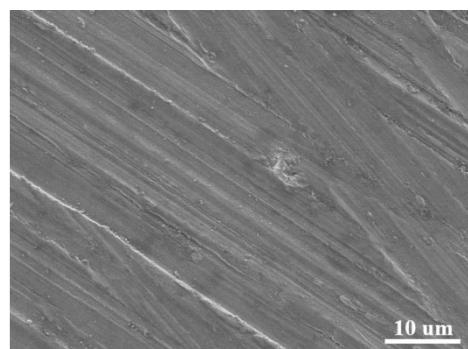
**Fig. S5**



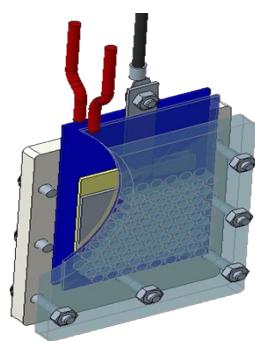
**Fig. S6**



**Fig. S7**



**Fig. S8**



**Fig. S9**