Supporting Information for *Acta Phys. -Chim. Sin.* doi: 10.3866/PKU.WHXB201806191

盐封后碳化钼电催化剂的制备及其氢析出性能

林舟，申琳璠，瞿希铭，张俊明，姜艳霞*，孙世刚
厦门大学化学与化工学院化学系，固体表面物理化学国家重点实验室，福建 厦门 361005

Molybdenum Carbide Prepared by a Salt Sealing Approach as an Electrocatalyst for Enhanced Hydrogen Evolution Reaction

LIN Zhou, SHEN Linfan, QU Ximing, ZHANG Junming, JIANG Yanxia *, SUN Shigang
State Key Laboratory of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, Fujian Province, P. R. China.

*Corresponding author. Email: yxjiang@xmu.edu.cn.

Table S1 Summary of the previously reported molybdenum carbides in acidic media.

Catalyst	Loading/(mg·cm^{-2})	Current density/(mA·cm^{-2})	Overpotential/mV	Electrolyte	Tafel slope/(mV·dec^{-1})	Ref.
Mo_2C	0.21	10	~130	0.5 mol·L^{-1} H_2SO_4	~53	*Energ Environ Sci.* **2014,** *7*, 387–392
Mo_2C/CNT	2	10	~152	0.1 mol·L^{-1} $HClO_4$	55.2	*Energ Environ Sci.* **2013,** *6*, 943–951
MoCx	0.8	10	~142	0.5 mol·L^{-1} H_2SO_4	53	*Nat. Commun.* **2015,** *6*, 6512
Mo_2C/GCSs	0.36	10	~200	0.5 mol·L^{-1} H_2SO_4	62.6	*Acs Catalysis,* **2014,** *4*, 2658–2661
Mo_2C	1.4	20	225	1 mol·L^{-1} H_2SO_4	56	*Angew. Chem. Int. Ed.* **2012,** *51*, 12703–12706
β-Mo_2C	0.28	2.5	230	0.1 mol·L^{-1} $HClO_4$	120	*Angew. Chem. Int. Ed.* **2014,** *53*, 6407–6410
Mo_2C/SS	0.204	10	~175	0.1 mol·L^{-1} $HClO_4$	88	This work

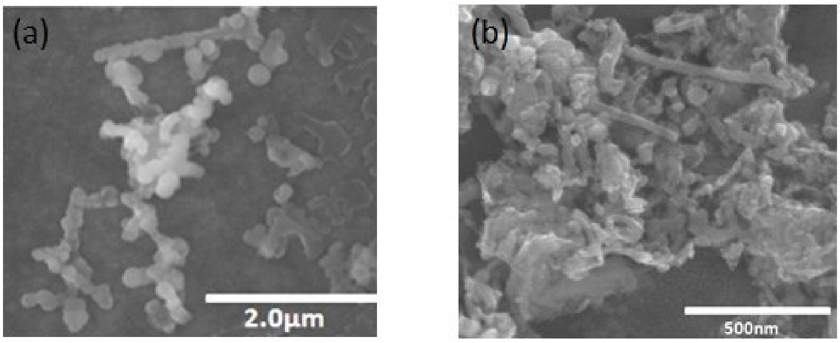

Fig. S1 SEM images of the precursor (a) and Mo_2C/SS (b).

In our work molybdenum carbides are the main active centers for the HER, and the HER activity of molybdenum oxides can be neglected compared with molybdenum carbides, which can be proved by the following experimental data shown in Fig. S2 and Ref. 1. In Ref. 1, the synthesized MoB and Mo_2C particles were also contaminated with molybdenum oxides such as MoO_3 and MoO_2 on the surface before activation. After activation by galvanostatic electrolysis, the amounts of MoO_3 and MoO_2 greatly diminished. And the Fig. S11 in Ref.1 shows the polarization curves of MoO_2, MoO_3, Mo, and carbon paste electrodes, those curves show that MoO_2, MoO_3, and Mo metal are not efficient catalysts for HER compared with the synthesized MoB and Mo_2C particles.

The molybdenum oxides were prepared as follows: the precursor DAP-2H$^+$/MoO_4^{2-} was covered and buried by the recrystallized NaCl *via* the process of salt sealing. And then the precursor was annealed at 900 °C for 3 h in the atmosphere of oxygen, followed by centrifugation process to remove the NaCl crystal, and then the molybdenum oxides would be obtained after drying. The preparation method of molybdenum oxides was similar to that of Mo_2C/SS, the only difference is the atmosphere replaced as oxygen during the process of carbonization.

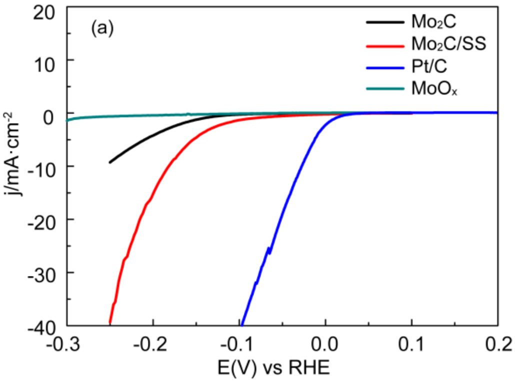

Fig. S2 HER polarization curves of Mo_2C/SS, Mo_2C, commercial Pt/C and MoO_x.

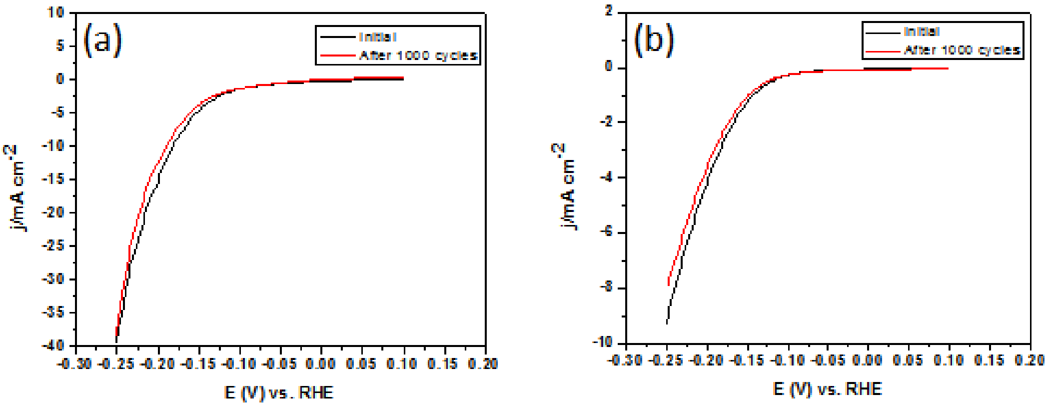

Fig. S3 The stability test of Mo_2C/SS(a) and Mo_2C (b) in 0.1 mol·L^{-1} $HClO_4$.

The stability is another important indicator of the catalytic performance of a HER catalyst. The stability test of Mo_2C/SS and Mo_2C were carried out by continuous scanning for 1000 cycles in the potential range of −0.2 V~+0.2 V (*vs* RHE) at a scan rate of 50 mV·s^{-1}. As shown in Fig. S3 (a) and (b), only slight deteriorations of cathodic current density were observed after 1000 CVs in 0.1 mol·L^{-1} $HClO_4$ solution, indicating their good durability of both catalysts (Mo_2C/SS and Mo_2C) for HER.

References

(1) Heron V., Xile H. *Angewandte Chemie* **2012,** *124* (51), 12875.