Electronic Supplementary Information

for

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Experimental

Preparation

$H_3PMo_{12}O_{40}\cdot 30H_2O$ was prepared according to the literature method[1], and was identified by its IR spectrum and thermogravimetric curve. All reagents were purchased from Sinopharm Chemical Reagent Co. (SCRC) and were used without further purification.

Nickel-cobalt layered double hydroxide nanosheets were grown on porous nickel foam by a facile electrodeposition method.[2-4] Typical, a piece of nickel foam (1.5 mm, 380 g/m^2) with a surface area of 1 × 1 cm^{-2} was immersed in a 0.1 M transition metal nitrates (c(Ni^{2+}):c(Co^{2+}) = 3:2, Aladdin Co.) aqueous solution. Electrodeposition was performed at a constant current mode (cathodic current, 10 mA) for 5 min by using a CHI 840D electrochemical workstation (Chenhua Co., Shanghai). Platinum mesh (1 × 1 cm^2) and saturated Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The obtained sample was denoted as sample Ni/Co-Ni foam, and was dried at room temperature. Prior to the experiments, Nickel foam was carefully cleaned with 1 M HCl aqueous solution (SCRC) in an ultrasound bath for 10 min in order to remove the surface NiO layer, and then deionized water and absolute ethanol were used for 5 min each to ensure the surface of the Ni foam was well cleaned. The cleaned nickel foam was dried in vacuum (60 ^oC, 30 min).

The loading of Pt nanoparticles on sample Ni/Co-Ni foam was performed by soaking the Ni/Co-Ni foam electrode in 5 mL of Na_2PtCl_6 aqueous solution (2 mg mL^{-1}, Adamas Co.) at room temperature for 4 h, in which a redox reaction occurred between transition metal ions in the nickel-cobalt layered double hydroxide and $PtCl_6^{2-}$ species.[5, 6] As a result, a black porous electrode (sample Pt-Ni/Co-Ni foam) was obtained, and was dried at room temperature.

A Pt/C-Ni foam electrode (sample Pt/C-Ni foam) was prepared by loading commercially 20 *wt*% Pt/C (Hesen Co., Shanghai) on Ni foam with a loading Pt amount of 0.4 mg cm^{-2}, in which a polymer binder (Nafion, Alfa Aesar Co.) was introduced for a purpose of fixation.

Assembly of Zn-phosphomolybdic acid battery

Zn-phosphomolybdic acid battery was mainly made up of carbon cloth cathode, Zn anode, bipolar membrane and electrolytes. In this system, a hydrophilic carbon cloth (2 × 2 cm^2, Hesen Co., Shanghai) was used as a cathode with 60 mL of 0.5 M phosphomolybdic acid as a catholyte in one compartment of a two-compartment H-cell, a Zn plate (2 × 2 cm^2, SCRC) was applied as an anode with 60 mL of 1.5 M NaOH (SCRC) as an anolyte, and the cathode and anode were separated by bipolar membrane (Tingrun Co., Beijing). Prior to the experiment, the system was bubbled with argon (20 mL min^{-1}) for 30 min, stirred vigorously and kept under an argon atmosphere throughout the experiment.

Characterizations

All electrochemical measurements were performed using a CHI 660E electrochemical workstation (Chenhua Co., Shanghai). For LSV tests, platinum mesh (1 × 1 cm^2) and saturated Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The Ag/AgCl electrode was caliberated with respect to RHE, $E\ (RHE) = E\ (Ag/AgCl) + E^{\theta}\ (Ag/AgCl) + 0.059pH$. Further, before LSV tests, the *i*R drop was automatically corrected on the electrochemical workstation. The *i*R compensation test was conducted at a compensation level of 95%, and the *i*R compensation modes was set to automatic. IR spectrum on a pellet of the sample mixed with KBr (SCRC) was recorded by a Nicolet Nexus 670 FT-IR spectrometer at a resolution of 4 cm^{-1}. ^{31}P NMR spectra were taken on a Bruker AVANCE III spectrometer in D_2O (Aladdin

Co.). Mass spectrum was obtained by an ultra-high-resolution time-of-flight LC/MS mass spectrometer (Impact II, Bruker Co.). Samples for mass spectrometry analysis were prepared by dissolving the samples in ethanol (SCRC). XRD patterns were collected on a Miniflex 600 X-ray diffractometer (Rigaku Co.) with a Cu Kα radiation. SEM images were obtained on a ZEISS SIGMA 300 field emission scanning electron microscope. TEM image was measured on a FEI Tencai 20 transmission electron microscope. Sample for TEM was prepared by ultrasounding in ethanol. Pt content was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on an Ultima 2 inductively coupled plasma OES spectrometer (Jobin Yvon Co.). Evolving H_2 or O_2 gas was measured by directly inject 200 μL of the gas from the headspace of the electrolytic cell into a Shimazu GC2014C gas chromatograph (TCD, molecular sieve 5A column, Ar carrier).

References

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Figure S1. Photographs of (a) the aqueous Zn-phosphomolybdic acid battery and (b) a clock driven by the aqueous Zn-phosphomolybdic acid battery.

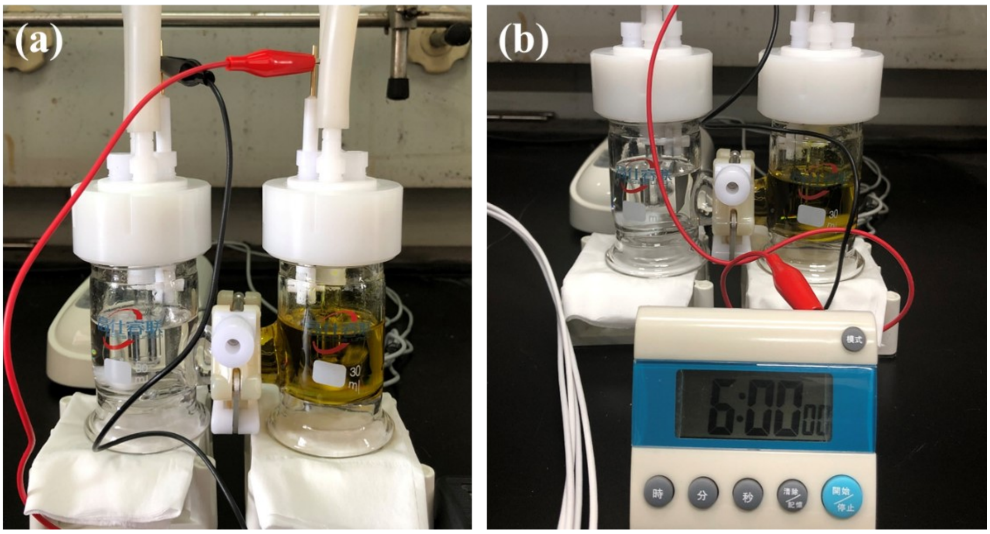

Figure S2. (a) Open circuit voltage plots and (b) polarization and power density curves for the aqueous Zn-phosphomolybdic acid battery.

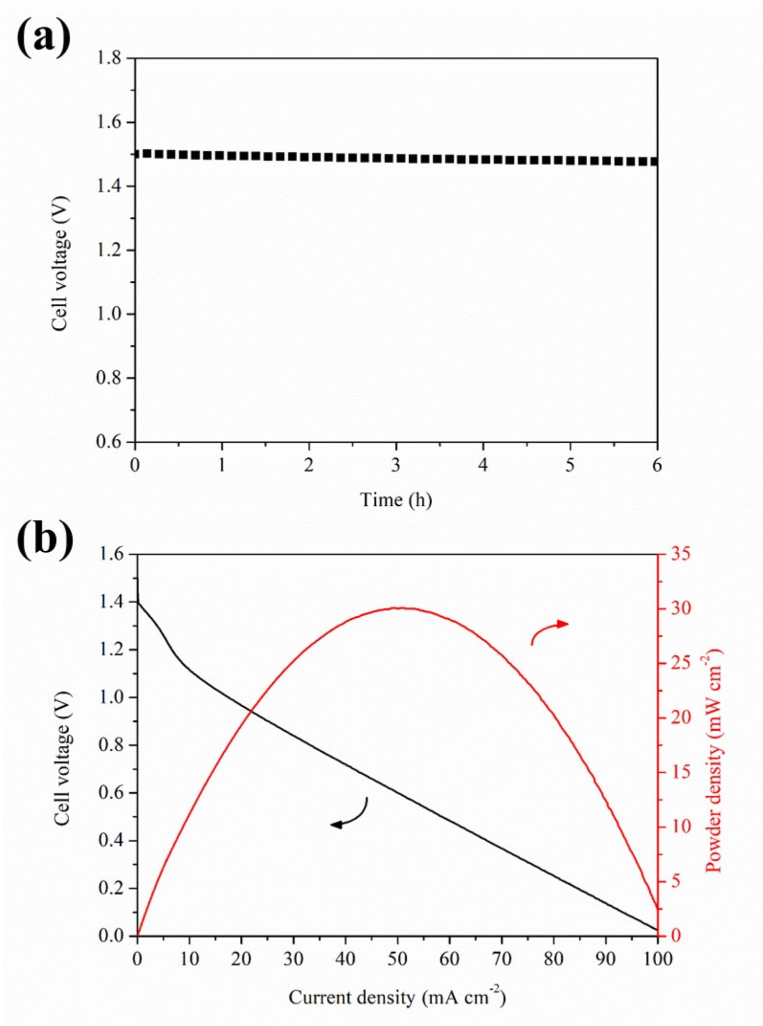

Figure S3. (a) Polarization curves and (b) open circuit voltage plots for the aqueous Zn-phosphomolybdic acid battery at various times. Phosphomolybdic acid was pre-reduced for 2 h at 20 mA cm^{-2}.

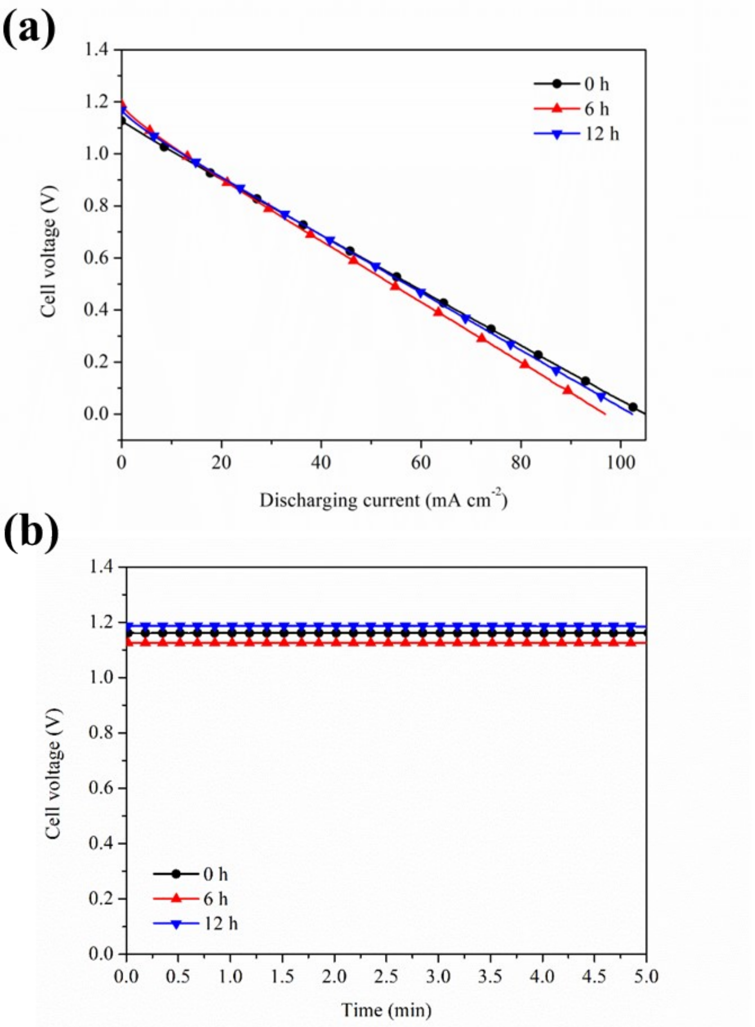

Figure S4. IR spectra of $H_3PMo_{12}O_{40}$ (a) before and (b, c) after the tests.

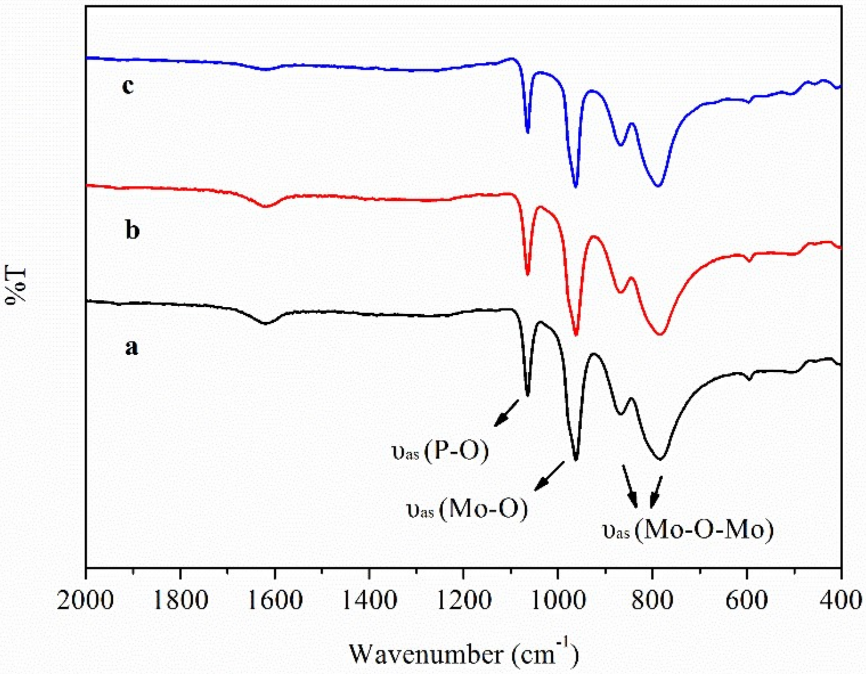

Figure S5. ^{31}P NMR of $H_3PMo_{12}O_{40}$ (a) before and (b, c) after the tests.

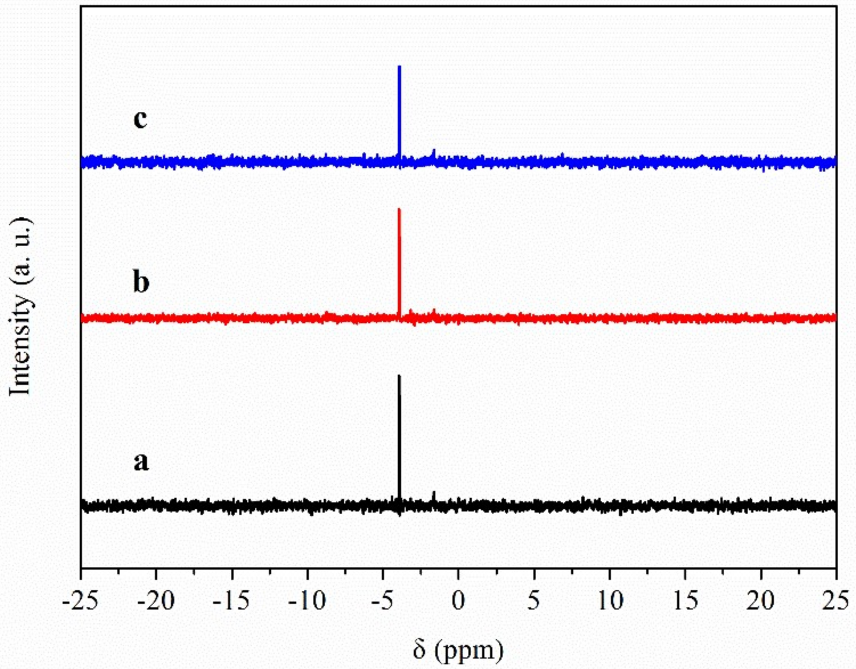

Figure S6. Mass spectra of $H_3PMo_{12}O_{40}$ (a) before and (b, c) after the tests.

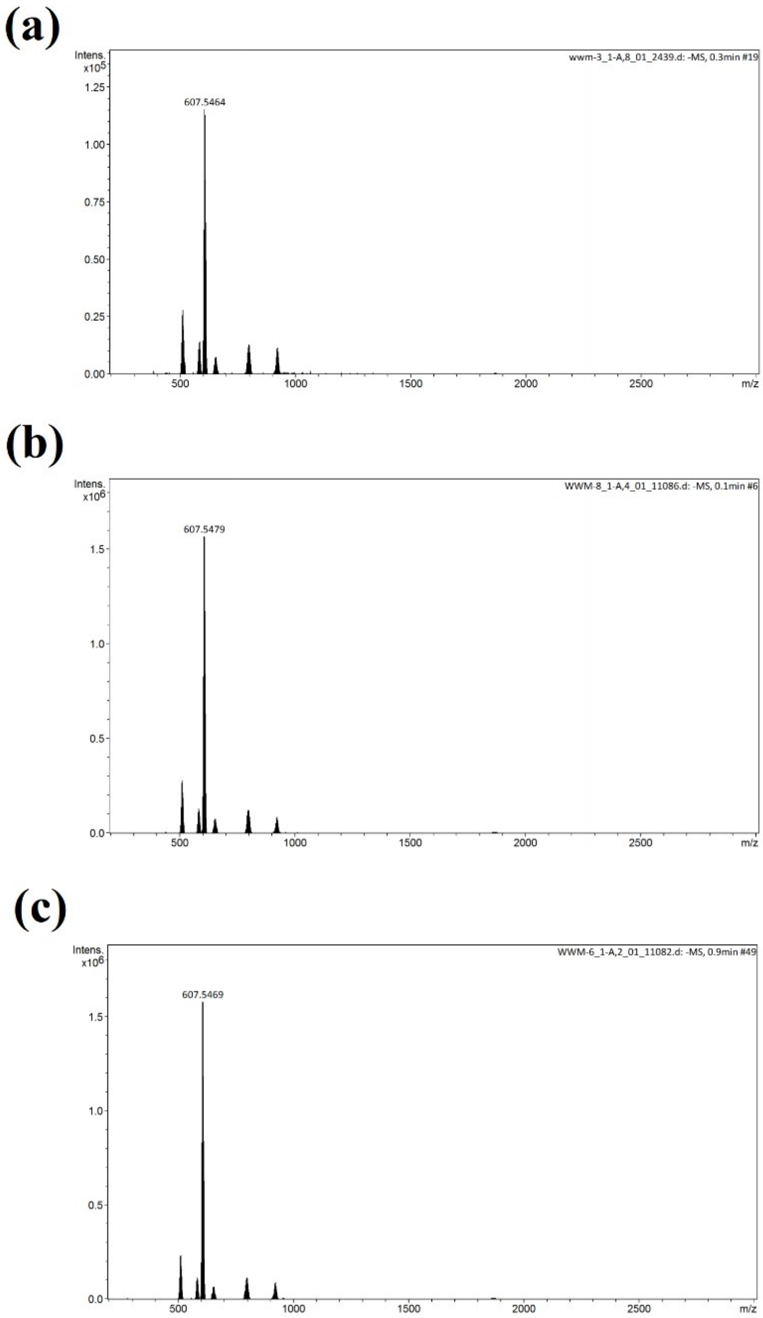

Figure S7. SEM images of sample Pt-Ni/Co-Ni foam after the durability test.

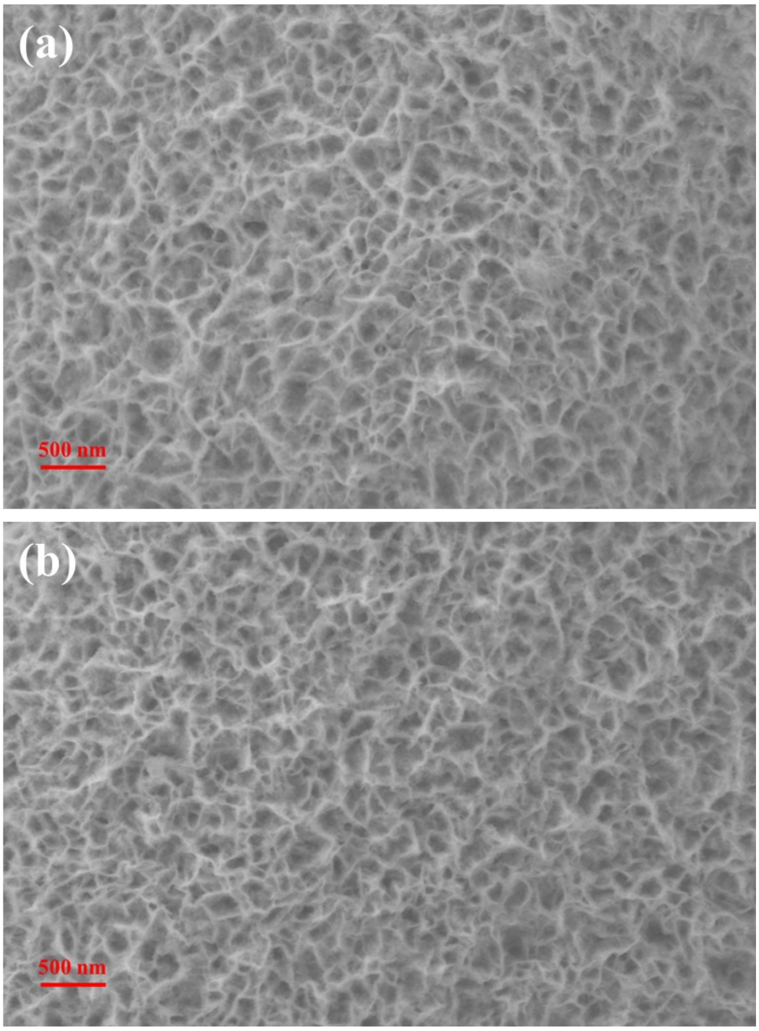

Figure S8. Schematic illustration of phosphomolybdic acid-mediated alkaline water electrolysis with decoupled OER and HER.