Supplementary Information (SI) for New Journal of Chemistry.

Electronic reconfiguration-multistage mass transfer synergies accelerate Zn-MoC high efficiency wide pH hydrogen evolution

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Supporting Information

1.Experimental Section

Materials

The carbon cloth was bought from Kunshan Jiayisheng Electronics Co., LTD. The sodium hydroxide (NaOH), Sulfuric acid (H_2SO_4) and Ethanol anhydrous (C_2H_6O) were purchased from Shandong Keyuan Biochemical Co., LTD. The $(NH_4)_6Mo_7O_{24}$, $C_3H_3N_3O_3$ and $C_3H_6N_6$ were obtained from Shanghai Aladdin Biochemical Technology Co., LTD. The $ZnCl_2$, $FeCl_3$, $CoCl_2$, $NiCl_2$ and $CuCl_2$ were purchased from Shanghai Maclin Biochemical Technology Co., LTD. The hydrochloric acid (HCl) was purchased from Tianjin Chemical Reagent Supply and Marketing Company. The experimental water selected was Wahaha purified water. The seawater was taken from the Bohai Sea and subsequently filtered for experiments.

Material characterization

The crystalline phases were studied by X-ray diffraction (XRD) with a Rigaku D/MAX-2500 powder diffraction. The crystal structure compositions of electrodes were analyzed by XRD with Cu Kα radiation at a scanning rate of $5° \ min^{-1}$ and 2θ range from 10° to 80°. The Raman spectrometer XploRA (HORIBA) was used to determine surface composition of electrode in these experiments. The morphological characteristics of the catalyst material were determined by field-emission scanning electron microscopy (SEM, FEI Apreo). High resolution transmission electron microscopy (TEM, Talos F200X G2) with an energy dispersive spectrometer (EDS) analyzer was used to test the lattice spacing and elemental composition of materials. X-ray photoelectron spectroscopy (XPS) characterization was conducted on a Thermo Scientific ESCA Lab 250Xi with the excitation source of Al Kα achromatic X-ray radiation.

Electrochemical measurements

All electrochemical measurements were performed using a classical three-electrode system at an electrochemical workstation (CHI660E). The synthesized electrode was directly used as working electrodes. Hg/Hg_2SO_4/Saturated K_2SO_4 electrode and Hg/HgO electrode were used as reference electrodes. A carbon rod electrode was used as a counter electrode. Linear sweep voltammetry (LSV) was collected in 0.5 M H_2SO_4 and 1 M KOH with the scan rate of 5 mV s^{-1}. Before performing the measurements, all the working electrodes were saturated by cyclic voltammetry (CV) scans at the scan rate of 100 mV s^{-1}. All the potentials were calibrated according to reversible hydrogen electrode (RHE) by using the Nernst equation E(RHE) = E (test potential) + 0.05916 * pH + E (reference electrode), where E(RHE) was the potential referred to RHE. Electrochemical impedance spectroscopy (EIS) was measured in the faradaic region to compare the charge transfer resistance among different catalysts (R_{ct}). To evaluate the electrochemical active surface area (ECSA) of the present electrode, the geometric double-layer capacitance (C_{dl}) value was firstly obtained by cyclic voltammetry (CV) owing to the relation below: ECSA = C_{dl}/Cs. The cyclic voltammetry (CV) curves are tested at different scan rates (20-200 mV s^{-1}). The CV potentials range for alkaline condition is 0.292 ~ 0.352 V (vs. RHE). The electrocatalytic active surface area (ECSA) calculated through the double layer capacitance (C_{dl}) value.

Theoretical calculations

We performed first-principles calculations using the Vienna ab initio Simulation Package (VASP). All the results were obtained using the projector-augmented plane-wave (PAW) method within the Perdew, Burke, and Ernzerh of (PBE) parameterization scheme for the generalized gradient approximation (GGA). Monk horst-Pack (MP) mesh of 3 × 3 × 1 was employed for geometry optimization. Full structural optimization was performed in which all lattice parameters and internal atomic positions were relaxed until the Hellmann-Feynman forces acting on each atom were less than 0.01 eV/Å and until the energy difference between two consecutive iterations was less than 0.0001 eV. Brillouin zone integrations were performed with a Gaussian broadening of 0.05 eV during all relaxations. For both structural and static electronic structure calculations, a plane-wave energy cut off of 400 eV was used for the GGA approach. The free energy was calculated using the equation: $\Delta G = \Delta E + \Delta ZPE - T\Delta S$ where G, E, ZPE and TS are the free energy, total energy from DFT calculations, zero-point energy and entropic contributions (T was set to be 300K), respectively.

Preparation of MoC

Firstly, 8 mmol of $C_3H_6N_6$ and 8 mmol of $C_3H_3N_3O_3$ were dispersed in 35 mL of distilled water under vigorous magnetic stirring for 30 min. secondly, 10 ml of an aqueous solution containing 0.4 mmol of $(NH_4)_6Mo_7O_{24}$-$4H_2O$ was added dropwise slowly to the mixed solution, and the mixture was stirred continuously at room temperature for 12 h. The mixture was transferred to an oven for drying at 60 °C overnight. Finally, the dried sample was ground into powder and calcined under N_2 atmosphere at a heating rate of 4 °C/min at 750 °C for 3 h. After cooling to room temperature, the reaction products were washed several times with deionised water and anhydrous ethanol, and then dried in a vacuum drying chamber at 60 °C for 12 h. The obtained sample was denoted as MoC.

Preparation of M-MoC (M = Fe, Co, Ni, Cu, Zn)

First, 8 mmol of $C_3H_6N_6$ and 8 mmol of $C_3H_3N_3O_3$ were dispersed in 35 mL of distilled water under vigorous magnetic stirring for 30 min. second, 10 ml of an aqueous solution containing 0.4 mmol of $(NH_4)_6Mo_7O_{24}$-$4H_2O$ and 3 ml of an aqueous solution of $ZnCl_2$ (containing 0.15 mmol of $ZnCl_2$) were added dropwise to the mixed solution and stirred continuously at room temperature for 12 h. The solution was transferred to an oven and dried at 60°C overnight. room temperature with continuous stirring for 12 h. It was transferred to an oven to dry at 60 °C overnight. Finally, the dried sample was ground into powder and calcined under N2 atmosphere at a heating rate of 4 °C/min at 750 °C for 3 h. After cooling to room temperature, the reaction products were washed several times with deionised water and anhydrous ethanol, and then dried in a vacuum drying chamber at 60 °C for 12 h. The resulting sample was denoted as Zn-MoC. To obtain M-MoC (M = Fe, Co, Ni, Cu), the above $ZnCl_2$ was replaced by $FeCl_3$, $CoCl_2$, $NiCl_2$ or $CuCl_2$, respectively, and other experimental conditions were kept constant.

Preparation of other catalysts

First, 8 mmol of $C_3H_6N_6$ and 8 mmol of $C_3H_3N_3O_3$ were dispersed in 35 mL of distilled water under vigorous magnetic stirring for 30 min. second, 10 ml of an aqueous solution containing 0.4 mmol of $(NH_4)_6Mo_7O_{24}$-$4H_2O$ and 5 ml of an aqueous solution containing 0.2 mmol of $ZnCl_2$ were added dropwise to the mixed solution and stirred continuously at room temperature for 12 h. The solution was transferred to an oven and dried at 60°C overnight. for 12 h. The sample was transferred to an oven and dried at 60 °C overnight. Finally, the dried sample was ground into powder and calcined under N_2 atmosphere at a heating rate of 4 °C/min at 750 °C for 3 h. After cooling to room temperature, the reaction products were washed several times with deionised water and anhydrous ethanol, and then dried in a vacuum drying chamber at 60 °C for 12 h. The sample obtained was denoted as Zn-MoC-0.2. To obtain Zn-MoC-0.1 or Zn MoC-0.25, the above 5 ml of aqueous solution containing 0.2 mmol of ZnCl2 was replaced by 5 ml of aqueous solution containing 0.1 mmol of $ZnCl_2$ or 5 ml of aqueous solution containing 0.25 mmol of $ZnCl_2$, and the other experimental conditions were kept unchanged.

Preparation of the Working Electrode

First, the carbon cloth (W0S1009) was pretreated by ultrasonication in acetone, methanol, and deionized water for 15 minutes each. Afterward, it was dried in an oven at 60 °C for 12 hours. Subsequently, the carbon cloth was immersed in a mixed acid solution of concentrated sulfuric acid and concentrated nitric acid (v:v = 1:1) for 1 hour. The treated carbon cloth was then cooled, thoroughly rinsed with large amounts of deionized water until no acid residue remained, and dried again at 60 °C for 12 hours. The dried carbon cloth was then cut into pieces measuring 1.3 × 0.8 cm^2.

Next, to prepare the working electrode, 5 mg of the sample and 1 mg of carbon black were dispersed in 980 μL of a water/anhydrous ethanol mixture (volume ratio 1:1) and 20 μL of 5 wt% Nafion solution. The mixture was sonicated for 30 minutes to obtain a uniform ink. Finally, 100 μL of the catalyst ink was drop-cast onto a clean piece of carbon cloth to form the working electrode, with a loading area of 0.8 × 0.8 cm^2.

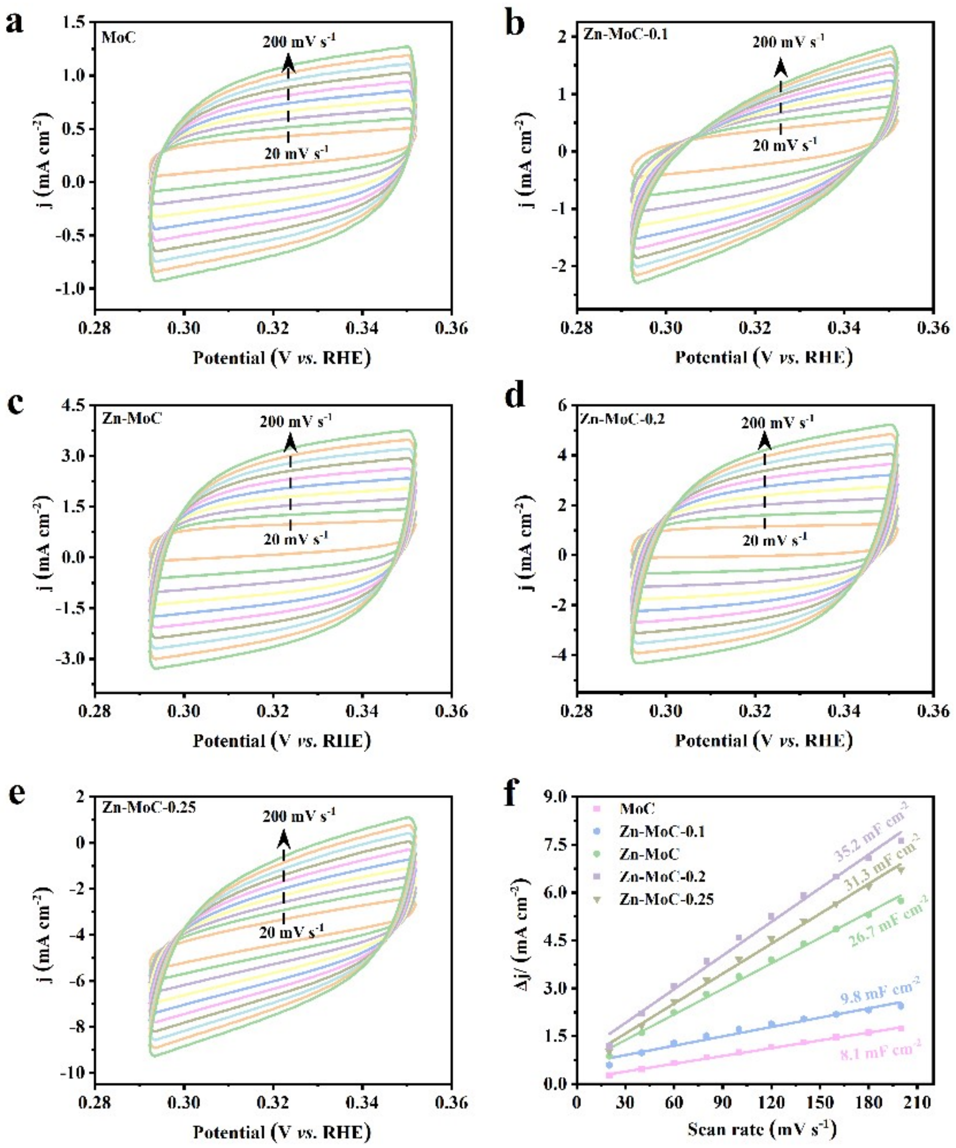

Fig.S1 Cyclic voltammetry curves at E=0.292 to 0.352 V vs RHE in 0.5 M H_2SO_4 electrolyte (a) MoC; (b) Zn-MoC-0.1; (c) Zn-MoC; (d) Zn-MoC-0.2; (e) Zn-MoC-0.25; (f) electrochemical double-layer capacitance (C_{dl}).

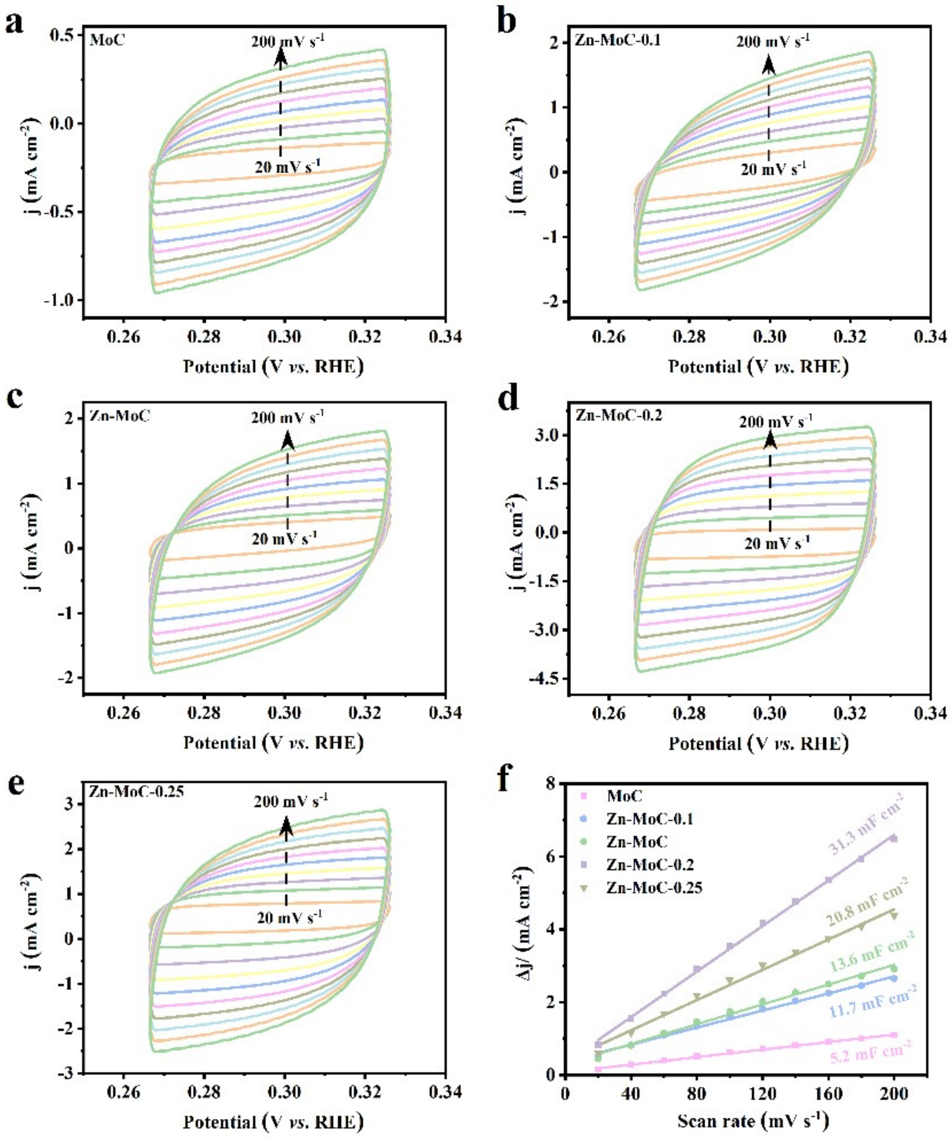

Fig.S2 Cyclic voltammetry curves at E=0.294 to 0.352 V vs RHE in 1.0 M KOH electrolyte (a) MoC; (b) Zn-MoC-0.1; (c) Zn-MoC; (d) Zn-MoC-0.2; (e) Zn-MoC-0.25; (f) electrochemical double-layer capacitance (C_{dl}).

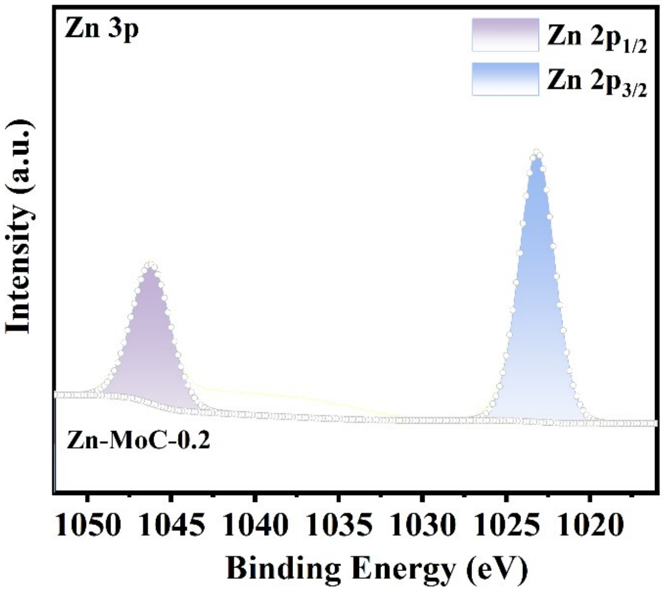

Fig. S3 XPS spectra of Zn 3p XPS.

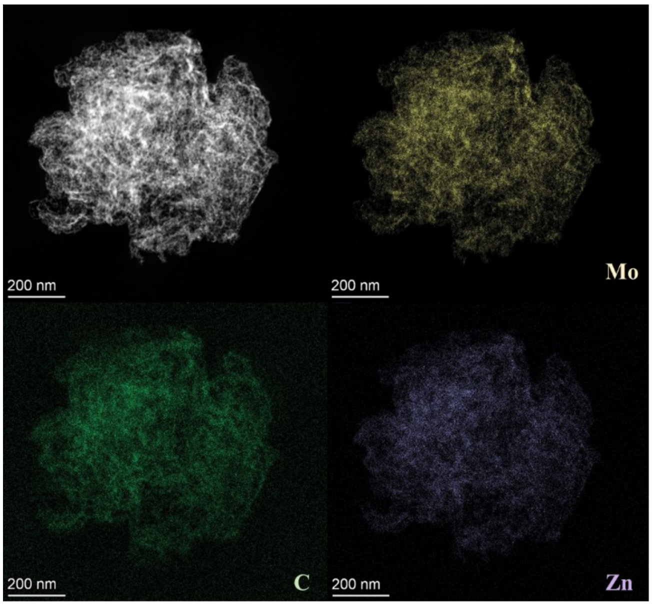

Fig. S4 TEM image of Zn-MoC-0.2 after durability test and the corresponding EDS elemental mapping.

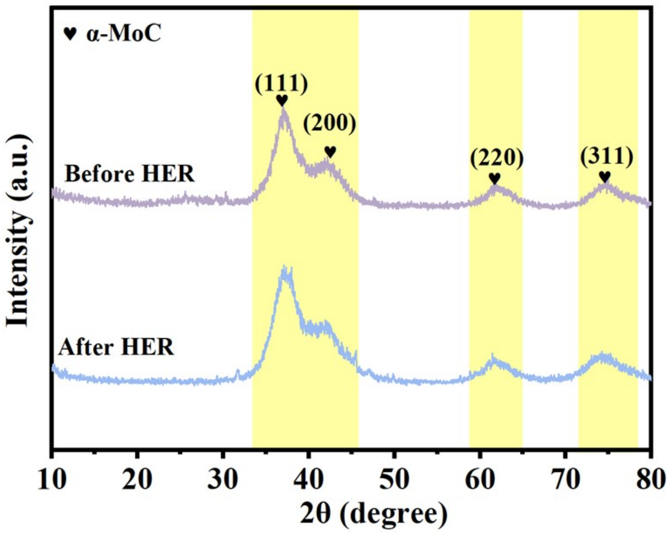

Fig. S5 XRD patterns of Zn-MoC-0.2 catalysts after durability.

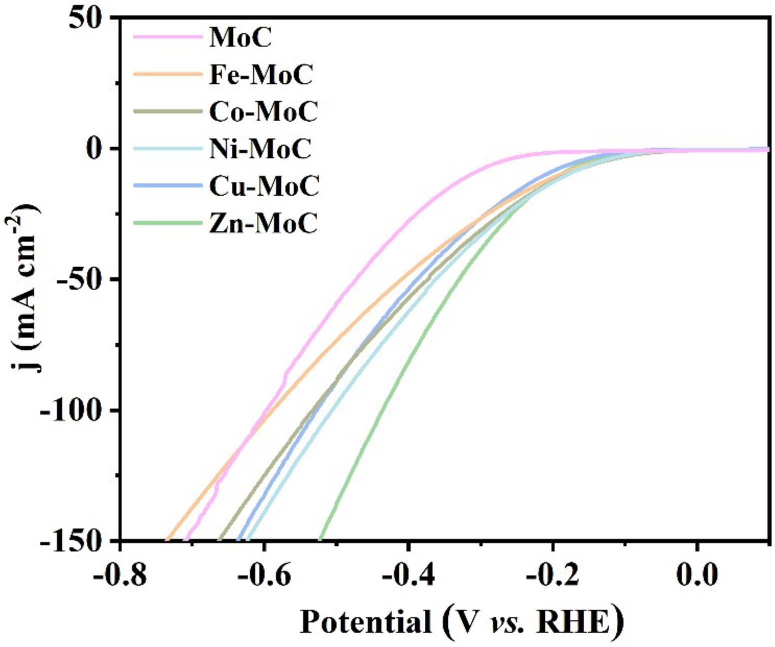

Fig. S6 LSV polarization curve of MoC, Fe-MoC, Co-MoC, Ni-MoC, Cu-MoC and Zn-MoC samples in 0.5 M H_2SO_4 aqueous solution.

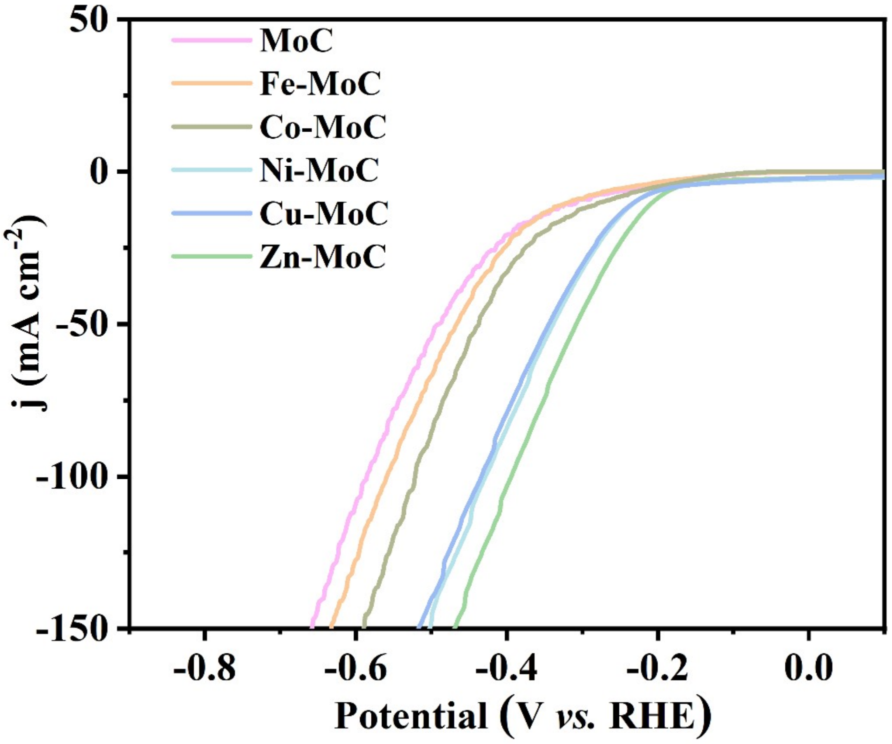

Fig. S7 LSV polarization curve of MoC, Fe-MoC, Co-MoC, Ni-MoC, Cu-MoC and Zn-MoC samples in 1.0 M KOH aqueous solution.

Table S1. The contents of Zn in prepared MoC electrodes by ICP-OES tests.

Samples	The Zn contents in MoC coating (mg/L)	The Mo contents in MoC coating (mg/L)
MoC	0	18.32
Zn-MoC-0.1	0.09	18.24
Zn-MoC	0.13	18.53
Zn-MoC-0.2	0.18	18.23
Zn-MoC-0.25	0.22	18.33