

## Polyoxometalate-Derived Electrocatalysts Enabling Progress in Hydrogen Evolution Reactions

Shaohua Zhu<sup>a</sup>, Haijun Pang<sup>\*a</sup>, Zhe Sun<sup>a</sup>, Shifa Ullah Khan<sup>\*b</sup>, Ghulam Mustafa<sup>b</sup>, Huiyuan Ma<sup>\*a</sup>, Xinming Wang<sup>a</sup>, and Guixin Yang<sup>a</sup>

**Table S1** Comparison of HER performance of POM-based Electrocatalysts

Catalysts	Polyoxometalate	$\eta_{10}$ (mV)	Tafel slope (mV·dec <sup>-1</sup> )	Electrolyte	Refs
CoP/MoP@NC	PMo <sub>12</sub> O <sub>40</sub>	94	81	1M KOH	1
PMo <sub>12</sub> @PVP@Zn/Ni-ZIF	PMo <sub>12</sub> O <sub>40</sub>	151	112	1M KOH	2
Co/Ni-POM/NFs	PMo <sub>12</sub> O <sub>40</sub>	68	60.8	1M KOH	3
HPOM-MoP/C	PMo <sub>12</sub> O <sub>40</sub>	135	—	1M KOH	4
		163	—	0.5 M H <sub>2</sub> SO <sub>4</sub>	
		166	—	PBS	
MoP/MoNiP@NC	PMo <sub>12</sub>	94	88	1M KOH	5
		137	70	0.5 M H <sub>2</sub> SO <sub>4</sub>	
Co <sub>9</sub> S <sub>8</sub> @MoS <sub>2</sub>	PMo <sub>12</sub>	230	84	1M KOH	6
CoS <sub>2</sub> -MoS <sub>2</sub> -VS <sub>2</sub> -CC	PMoV <sub>4</sub> Mo <sup>VI</sup> <sub>8</sub> O <sub>40</sub> (V <sup>IV</sup> O) <sub>2</sub>	152	107	1M KOH	7
	and PMoV <sub>10</sub> Mo <sup>VI</sup> <sub>2</sub> O <sub>40</sub> (V <sup>IV</sup> O) <sub>2</sub>				
Co/WC@NC	PW <sub>12</sub> O <sub>40</sub>	158	95	1M KOH	8
		142	93	0.5 M H <sub>2</sub> SO <sub>4</sub>	
NiCo-POM/Ni	PW <sub>12</sub> O <sub>40</sub>	64	75	1M KOH	9
POM@ZnCoS/NF	PW <sub>12</sub> O <sub>40</sub>	170	67.7	1M KOH	10
NiCo <sub>2</sub> S <sub>4</sub> /PANI@POM/rGO	PW <sub>12</sub> O <sub>40</sub>	197	47.5	1M KOH	11
CNT-g-PSSCo/PW <sub>12</sub>	PW <sub>12</sub> O <sub>40</sub>	31	25	0.5 M H <sub>2</sub> SO <sub>4</sub>	12
Pd <sup>0</sup> @POM/GC	PW <sub>17</sub> V <sup>IV</sup> O <sub>62</sub>	~20	52-83	0.5 M H <sub>2</sub> SO <sub>4</sub>	13
Co <sub>5</sub> Mo <sub>10</sub> S <sub>x</sub>	Co <sub>2</sub> Mo <sub>10</sub> O <sub>38</sub>	35	56	1M KOH	14
CoS <sub>2</sub> @MoS <sub>2</sub>	GeMo <sub>12</sub> O <sub>40</sub>	87	87	1M KOH	15
		65	122	0.5 M H <sub>2</sub> SO <sub>4</sub>	
RuPOM/KB	SiW <sub>10</sub> O <sub>36</sub>	760	—	Seawater (pH 8.1)	16
NiFe LDH-POM/NF	SiW <sub>11</sub> O <sub>39</sub>	156	86	0.1M KOH	17
Pt-SiW <sub>11</sub> Co/SiW <sub>11</sub> Co-CNP/GC	SiW <sub>11</sub> O <sub>39</sub> Co	150±4	61±1	0.5 M H <sub>2</sub> SO <sub>4</sub>	18

[Co <sub>2</sub> (3,3'-bpy)(3,5'-bpy)(4,3'-bpy)](H <sub>2</sub> O) <sub>3</sub> [SiW <sub>12</sub> O <sub>40</sub> ]	SiW <sub>12</sub> O <sub>40</sub>	92	92.1	1M KOH	19
Pt-STA-CB	SiW <sub>12</sub> O <sub>40</sub>	33.8	27.9	0.5 M H <sub>2</sub> SO <sub>4</sub>	20
{Cu <sub>2</sub> (3-bptzp) <sub>3</sub> (H <sub>2</sub> O) <sub>4</sub> [SiW <sub>12</sub> O <sub>40</sub> ]}·H <sub>2</sub> O	SiW <sub>12</sub> O <sub>40</sub>	59.4	74.2	0.1M KOH	21
{Cu <sub>2</sub> (3-bptzpe) <sub>2</sub> (H <sub>2</sub> O) <sub>8</sub> [SiW <sub>12</sub> O <sub>40</sub> ]}·4H <sub>2</sub> O					
{Cu <sub>2</sub> (3-bptzh) <sub>3</sub> (H <sub>2</sub> O) <sub>6</sub> [SiW <sub>12</sub> O <sub>40</sub> ]}					
Ni-Mo <sub>2</sub> C/NPC	NiMo <sub>6</sub> O <sub>24</sub>	η <sub>500</sub> =295	64	1M KOH	22
		η <sub>500</sub> =268	59	0.5 M H <sub>2</sub> SO <sub>4</sub>	
CoP-WP/rGO	Co <sub>8</sub> W <sub>18</sub>	96	62	1M KOH	23
		130	54	0.5 M H <sub>2</sub> SO <sub>4</sub>	
		138	80	PBS	

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