Supporting information

Intermetallic Compounds with High Hydrogen Evolution Reaction Performance: A Case study of MCo_2 (M = Ti, Zr, Hf and Sc) Series.

Peng Zhang^a, Huai-Guo Xue^a and Nian-Tzu Suen^{a,*}

^a College of Chemistry & Chemical Engineering, Yangzhou University, Yangzhou 225002, P.R. China

*Corresponding author: Nian-Tzu Suen (006641@yzu.edu.cn)

Experimental Section

Materials and samples preparation. Most of the chemicals were purchased from Aladdin and used without further purification. These include titanium powder (99.5%), hafnium grains (99.9%), zirconium powder (99.5%), scandium grains (99.9%), cobalt tablets (99.5%) and KOH (ACS grade). The Pt/C used in this work was acquired from Suzhou Yilong Energy Technology Co., Ltd. and the loading amount of Pt is 20 %. The synthesis procedure is quite simple and straightforward. Titanium powder and cobalt tablets were first weighted based on the stoichiometric ratio (1:2) of the nominal chemical formula. We then pressed these raw materials into a pellet and placed in a homemade stainless steel chamber. After refresh the atmosphere in the chamber with argon gas three times, we applied electric arc on the pellet in order to melt it. To ensure the homogeneity of the synthesized material, the pellet was flip over and arc-melting several times. After this process, the pellet complete melt and became a sliver shinny bead. We carefully polished the surface and file the bead into powder. Although the acquired material appears to be stable in the air and in highly concentrated alkaline electrolyte (1.0 M KOH). To avoid possible surface oxidation that could interfere later characterization and electrochemical measurement, the powder was transfer and stored in an argon-filled glovebox before any investigation. The same method was used to synthesize ZrCo₂, HfCo₂ and ScCo₂.

Characterization. The powder X-ray diffraction (XRD) patterns of as-synthesized materials were measured by using Bruker D8 ADVANCE diffractometer. The range of 2 ϑ was fixed from 30° to 60° with 5°/ min scan rate. Scanning electron microscopy (SEM, Zeiss, model: Supra 55) equipped with energy dispersive X-ray spectrometer (EDS) were used to examine the morphology and chemical composition of as-synthesized materials. In order to understand the electronic state of Co element in the compounds, X-ray photoelectron spectroscopy (XPS, Thermo Scientific, model: ESCALAB 250Xi) of as-synthesized materials were also acquired to analyze the valence states of Co atoms in materials. The reported photon energy of these spectra were all calibrated based on the carbon internal standard.

Electrochemical measurement. All electrochemical measurements were performed by using CHI-660E (CHI-potentiostat) with a standard three-electrode configuration cell (Hg/HgO reference electrode). The as-synthesized materials were pressed into pellets (~ 100 mg) as working electrode without any additives. Carbon rod was used as counter electrode instead of using Pt plate to prevent from the well-known "Pt contamination" and mask the intrinsic performance of tested materials. Typical electrochemical experiments were carried out in an electrolyte of 1.0 M KOH solution (pH = 14, ~ 40 ml) and all potentials were adjusted with respect to reversible hydrogen electrode (RHE) including 90% of ohmic potential drop losses.

$E_{RHE} = E_{ref}(Hg/HgO) + 0.05916*pH-i*R_u*0.9$

To have a fair comparison of electrocatalytic activity for all the tested materials in this work, their electrochemically active surface area (ECSA: specific capacitance 40 μ F/ cm²) and roughness factor (Rf) were evaluated from cyclic voltammograms analysis.

Calculation detail. With the intention to understand the reason beyond the elevated HER performance of MCo_2 (M = Ti, Zr, Hf and Sc) series, atomic simulation environment (ASE) software package with GPAW calculator was used to compute the adsorption energy of H* on Co₃ triangular site for TiCo₂. Exchange-correlation energy of the system was calculated based on the revised Perdew-Burke-Ernzerhof (RPBE) functional.¹⁻⁴

The initial lattice parameters of TiCo₂ was acquired and refined from the PXRD with using JADE software. These parameters were latter optimized with stress tensor and quasi-Newton method. The optimized lattice constants are very close to experimental ones and the difference is less than 1 %. The lattice constants after structural optimization were used to construct TiCo₂ (100) slab. This slab contains 4 atomic layers and 15 Å vacuum spacing was set between each slab. The adsorbate (H*) was placed on the triangular void and, to mimic the surface condition, the first two atomic layers were allowed to relaxed during geometry optimization. The final structure was determined when the maximum force of any atoms was lower than 0.05 eV Å⁻¹. To convert electronic energy to free energy ($\Delta G = \Delta E + \Delta ZPE - T\Delta S$), we included zero-point energies (ZPE) as well as entropy contribution of adsorbates (H*). The vibrational frequencies of adsorbates (H*) were calculated with harmonic oscillator approximation (3 *N* degrees of freedom) and the temperature was set at 298.15 K. For comparison, Pt (111) and Co (111) slabs were also examined to compute the adsorption energy of adsorbate (H*) on triangular site. The construction of

these models and calculation schemes were generally the same as for $TiCo_2$ described above except the initial lattice constants were directly from ASE default setting.

In addition to the adsorption energy, we also realized that the bonding interaction within MCo_2 (M = Ti, Zr, Hf and Sc) could be a crucial point to account for the decreasing adsorption energy of H* and accordingly increasing the HER performance. The total density and partial density of states (TDOS and PDOS) along with crystal orbital Hamiltonian populations (COHP) of selected atomic interactions for TiCo₂ were computed with Stuttgart TB-LMTO 4.7 program.⁵⁻⁶ Exchange and correlation terms were treated with local density approximation (LDA).⁷ The symmetry of the potential was considered spherical inside each Wigner–Seitz (WS) sphere,⁸ and the radii of WS spheres were determined by default as follows: Ti = 1.6 Å and Co = 1.31 Å. The basis sets contain 4s, 4p and 3d for Ti; 4s, 4p, and 3d orbitals for Co. Tetrahedron method was applied to integrate k-space with 72 irreducible k-points in the Brillouin zone.



Figure S1. SEM images and EDS of (a) TiCo₂, (b) ZrCo₂, (c) HfCo₂ and (d) ScCo₂.



TiCo₂



ZrCo₂



500 nm

 $HfCo_2$ ScCo_2Figure S2. TEM images of MCo_2 (M = Ti, Zr, Hf and Sc).



Figure S3. XRD patterns of MCo_2 (M = Ti, Zr, Hf and Sc). The asterisk denotes the peaks from Si standard.



Figure S4. Cyclic voltammograms of MCo_2 (M = Ti, Zr, Hf and Sc), Co and Pt/C in 1.0 M KOH.



Figure S5. Capacitive current density as a function of scan rate (20–80 mV/ s). The derived roughness factor (Rf) of each compound from the linear regression slope (specific capacitance 40 μ F/ cm²) is also included.



Figure S6. Electrochemical impedance spectroscopy analysis of MCo_2 (M = Ti, Zr, Hf and Sc) and Co during HER (η : 192 mV) in 1.0 M KOH. Inset is the magnified plot of origin spectroscopy. The estimated charge-transfer resistance (R_{ct}) for each sample was listed in the parentheses next to the sample label.



Figure S7. The corresponding models for calculated free-energy of ΔG_{H^*} on TiCo₂, Co and Pt.

	Element	Atomic ratio (%)		
TiCo ₂	Ti	35.68		
	Со	64.32		
	Co/Ti	1.8		
ZrCo ₂	Zr	32.71		
	Со	67.29		
	Co/Zr	2.1		
HfCo ₂	Hf	30.19		
	Со	69.81		
	Hf/Co	2.3		
ScCo ₂	Sc	34.38		
	Со	65.62		
	Co/Sc	1.9		

Table S1. The Atomic Ratio of MCo_2 (M = Ti, Zr, Hf and Sc).

Table S2. Overpotential (mV) and Tafel slope (mV•decade⁻¹) of MCo_2 (M = Ti, Zr, Hf and Sc) during Hydrogen Evolution Reaction (HER) in 1.0 M KOH.

Sample	η_{10} (mV)	Tafel (mV∙decade ⁻¹)	RF
TiCo ₂	70	33	454
ZrCo ₂	136	89	516
HfCo ₂	87	47	446
ScCo ₂	87	36	415
Со	252	149	369
Pt/C	76	44	761

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