

ChemComm

Chemical Communications

rsc.li/chemcomm



ISSN 1359-7345

COMMUNICATION

Georgiy Akopov *et al.*
Probing layered $Y(TM)B_4$ ($TM = Cr, Mo$ and W) borides as
efficient hydrogen evolution reaction electrocatalysts


 Cite this: *Chem. Commun.*, 2026, 62, 1497

 Received 18th November 2025,
Accepted 2nd December 2025

DOI: 10.1039/d5cc06558e

rsc.li/chemcomm

Probing layered Y(TM)B₄ (TM = Cr, Mo and W) borides as efficient hydrogen evolution reaction electrocatalysts

 MD Ali Hossain,^{ib} Lesly Delgado,^{ib} Rutva Joshi,^a Sylvie Rangan^{ib} and Georgiy Akopov^{ib}*^a

In this study, three layered ternary metal borides were analyzed: YCrB₄, YMoB₄, and YWB₄. YWB₄ demonstrated the highest catalytic activity, surpassing the Pt/C catalyst by 185 mV overpotential at an industrially relevant current density of 1000 mA cm⁻². Furthermore, stability testing revealed that YWB₄ retained 95% of its initial activity after 25 hours of continuous operation (5000 cycles) at 1000 mA cm⁻², underscoring its potential as a robust and sustainable HER catalyst for hydrogen production.

Due to growing public concern over limited fossil fuel reserves, environmental issues, and climate change, there has been a significant rise in interest towards sustainable and renewable energy sources.¹ Hydrogen has stood out as a highly promising solution to the global energy crisis in recent years due to its high energy density, zero-carbon emission, and eco-friendly nature, and consequently, it is viewed as a viable alternative to fossil fuels.^{2–5} The industrial generation of hydrogen from fossil fuels, which releases CO₂ alongside H₂, is inconsistent with the principles of sustainable development in today's society and economy.⁶ Water splitting powered by renewable resources is regarded as one of the most promising technologies.^{7,8} Electrochemical and photoelectrochemical processes are the two leading methods for water splitting.⁹ Practically, electrocatalysis is preferred over photocatalysis due to its superior efficiency.¹⁰ Recently, water electrolysis has attracted significant interest as a method for hydrogen production. This process involves using electrical energy to split water into hydrogen (*via* the hydrogen evolution reaction, HER) and oxygen (*via* the oxygen evolution reaction, OER), making it a promising approach for generating hydrogen using renewable energy sources.^{11–13} Electrocatalysts are crucial for efficiently producing hydrogen and minimizing the overpotential in water electrolysis. Platinum group metals are

recognized as the most efficient electrocatalysts for the HER, offering low overpotentials.¹⁴ Due to their high cost and limited availability, their applications remain restricted.¹⁵ Consequently, developing highly efficient, low-cost HER electrocatalysts to replace Pt-based materials is crucial for large-scale hydrogen production.

Bulk metal borides have recently attracted attention for their remarkable properties, such as superhardness,¹⁶ thermoelectric behavior,¹⁷ magnetic characteristics^{18,19} and potential solid-state fuels.²⁰ In recent years, compounds derived from earth-abundant transition metals have gained significant research attention because of their affordability and widespread availability.^{21,22} Some transition-metal-derived materials found to be more active and stable for the HER are transition metal alloys (TMAs),¹³ dichalcogenides (TMDs),²³ nitrides (TMNs)²⁴ and carbides (TMCs).²⁵ In recent times, transition metal borides like Mo-B (in both bulk and nanoscale forms),^{26–30} MoAlB (bulk),³¹ Co-B (amorphous),^{32,33} Ni-B (amorphous and nanoscale),³⁴ Co-Ni-B (amorphous),³⁵ and FeB₂ (nanoscale)⁹ have emerged as promising HER electrocatalysts. This is attributed to their abundance, cost-effectiveness, and excellent HER performance and stability in acidic and alkaline environments. Metal borides, compared to metal carbides, sulphides, and phosphides, exhibit better HER activity (Table S3). Although these materials are superior at low current densities, they underperform at high current densities (Table S3).

In recent years, molybdenum-based materials like molybdenum disulfide,³⁶ molybdenum carbide,³⁷ and molybdenum phosphides³⁸ have been widely studied as cost-effective alternative electrocatalysts for the hydrogen evolution reaction (HER). Although molybdenum and tungsten share similar chemical and physical properties, tungsten-based materials have been significantly less explored than molybdenum. For instance, tungsten disulfide,³⁹ carbides,⁴⁰ and phosphides⁴¹ demonstrate comparable or even superior HER activity relative to their molybdenum analogues. Nevertheless, tungsten-based borides have not yet been explored. Chromium belongs to the

^a Department of Chemistry, Rutgers University, Newark, Newark, NJ 07102, USA.
E-mail: georgiy.akopov@rutgers.edu

^b Department of Physics and Astronomy and Laboratory for Surface Modification, Rutgers University – New Brunswick, Piscataway, NJ 08854, USA





Fig. 3 (a) Electrochemical impedance spectroscopy (EIS) Nyquist plots of YCrB₄, YMoB₄, and YWB₄. (b) Cyclic voltammetry curve of YWB₄. (Inset showing the difference in the current density of $\Delta J (J_a - J_c)$ at 0.1 V vs. RHE plotted against the scan rate is fitted to a linear regression to estimate C_{dl} .)

challenging to identify the RDS from Tafel analysis alone. Nonetheless, YWB₄ displays the smallest Tafel slope, indicating a more rapid and efficient HER process compared to the other boride samples. Fig. 2d and Fig. 2e represent the working electrode assembly after polishing on sandpaper and the electrode surface of YWB₄, respectively.

As shown in Fig. 3a, the solution resistance (R_s) that was used for IR-drop compensation was nearly identical for all samples, attributed to the consistent electrode preparation method. The Nyquist plots for each sample were fitted using an equivalent circuit model incorporating a constant phase element (CPE). The excellent HER performance of YWB₄ can be linked to its high electrochemically active surface area (ECSA). The ECSA of YWB₄ is shown in Fig. 3b and estimated by determining its double-layer capacitance (C_{dl}) using cyclic voltammetry (CV) at scan rates ranging from 80 to 200 mV s^{-1} in the non-faradaic region (0.05–0.15 V vs. RHE).⁴² YWB₄ exhibited a C_{dl} value of 19.38 mF cm^{-2} , which exceeds several previously reported values,^{28,42,48} further highlighting its superior catalytic activity.

X-ray photoelectron spectroscopy (XPS) data were collected to investigate the surface composition of YCrB₄, YMoB₄, and YWB₄ before and after electrocatalysis (Fig. S4–S12). The starting surfaces indicate typical metal boride features, with a thin oxide/hydroxide formation upon exposure to air. Metallic features are clearly derived from the asymmetry of the boride core levels. After electrocatalysis, a thicker oxide/hydroxide layer of similar composition as the initial surface is measured. The SEM–EDS characterization (Fig. S13–S15) and XPS data (Table S1) confirm the uniform distribution of Y, transition metals (Cr, Mo, W), and B in YCrB₄, YMoB₄, and YWB₄. The obtained atomic ratios closely match the desired stoichiometric ratios, confirming homogeneous mixing and successful formation of the desired borides.

Catalyst stability and durability are essential factors for real-world applications, particularly in acidic media. To evaluate these characteristics, comprehensive tests were conducted on the Y(TM)B₄ electrodes. Long-term stability was assessed *via* cyclic voltammetry over 2500 (≈ 12.5 hours) to 5000 cycles (≈ 25 hours) for YCrB₄, YMoB₄, and YWB₄ at a high current density of 1000 mA cm^{-2} . As illustrated in Fig. 4a, the post-test polarization curve showed only a slight deviation for all the



Fig. 4 (a) Polarization curve of YCrB₄, YMoB₄, and YWB₄ before and after 2500, 2500, and 5000 cycles, respectively. (b) Chronoamperometry curve of YWB₄ for 24 h.

electrodes, with the YWB₄ electrode retaining a high percentage (95%) of its initial catalytic activity. Durability was further examined for YWB₄ through a continuous electrolysis experiment (chronoamperometry) at a constant current density of approximately 80 mA cm^{-2} for 24 hours. As shown in Fig. 4b, the current density remained nearly unchanged, indicating excellent durability. These findings demonstrate that YWB₄ exhibits outstanding stability and durability under extended, industrial scale operating conditions, making it a strong candidate for sustainable hydrogen production in harsh environments.

In conclusion, the ternary metal borides YCrB₄, YMoB₄, and YWB₄ were successfully synthesized *via* arc melting, characterized, and evaluated for their hydrogen evolution reaction (HER) performance in a highly acidic environment for the first time. Among them, YWB₄ demonstrated the highest HER activity, outperforming both its counterparts and even surpassing the performance of the commercial Pt/C catalyst at elevated current densities. Additionally, YWB₄ exhibited remarkable long-term stability and durability, with negligible loss in HER activity after 5000 cycles and 25 hours of continuous operation in an acidic electrolyte. These findings highlight the significant potential of boride-based materials as promising HER electrocatalysts for future sustainable hydrogen production.

This manuscript is dedicated in loving memory of a dear friend Rebecca Lin Li. This research was supported by a Rutgers University, Newark startup grant (A. H., L. D., R. J., G. A.). The X-ray diffractometer was purchased with support from the National Science Foundation Grant No. [2018753]. L. D. was supported by the Rutgers University – Newark Dean's 2024 Summer Undergraduate Research Fellowship (SURF). Supplement funding for this project was provided by the Rutgers University – Newark Chancellor's Research Office (A. H.). This research was supported by a Rutgers University Research Council Award (L. D. and G. A.). This work was supported by the donors of ACS Petroleum Research Fund under ACS PRF Doctoral New Investigator Grant 68959-DNI10 (A. H. and G. A.). The authors acknowledge the Laboratory for Surface Modifications facilities for XPS analysis.

Conflicts of interest

There are no conflicts to declare.



Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: details of synthesis and characterization of the metal borides. See DOI: <https://doi.org/10.1039/d5cc06558e>.

References

- 1 N. Armaroli and V. Balzani, *Angew. Chem., Int. Ed.*, 2007, **46**(1–2), 52–66.
- 2 C. Liu, F. Li, L.-P. Ma and H.-M. Cheng, *Adv. Mater.*, 2010, **22**(8), E28–E62.
- 3 K. Mazloomi and C. Gomes, *Renewable Sustainable Energy Rev.*, 2012, **16**(5), 3024–3033.
- 4 M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori and N. S. Lewis, *Chem. Rev.*, 2010, **110**(11), 6446–6473.
- 5 J. A. Turner, *Science*, 2004, **305**(5686), 972–974.
- 6 S. Anantharaj, S. R. Ede, K. Sakthikumar, K. Karthick, S. Mishra and S. Kundu, *ACS Catal.*, 2016, **6**(12), 8069–8097.
- 7 Z. W. Seh, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Nørskov and T. F. Jaramillo, *Science*, 2017, **355**(6321), eaad4998.
- 8 A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, 2008, **38**(1), 253–278.
- 9 I. Roger, M. A. Shipman and M. D. Symes, *Nat. Rev. Chem.*, 2017, **1**(1), 1–13.
- 10 Q. Lu, Y. Yu, Q. Ma, B. Chen and H. Zhang, *Adv. Mater.*, 2016, **28**(10), 1917–1933.
- 11 C. G. Morales-Guio, L.-A. Stern and X. Hu, *Chem. Soc. Rev.*, 2014, **43**(18), 6555–6569.
- 12 D. Merki and X. Hu, *Energy Environ. Sci.*, 2011, **4**(10), 3878–3888.
- 13 M. Zeng and Y. Li, *J. Mater. Chem. A*, 2015, **3**(29), 14942–14962.
- 14 C. C. L. McCrory, S. Jung, I. M. Ferrer, S. M. Chatman, J. C. Peters and T. F. Jaramillo, *J. Am. Chem. Soc.*, 2015, **137**(13), 4347–4357.
- 15 X. Zou and Y. Zhang, *Chem. Soc. Rev.*, 2015, **44**(15), 5148–5180.
- 16 G. Akopov, H. Yin, I. Roh, L. E. Pangilinan and R. B. Kaner, *Chem. Mater.*, 2018, **30**(18), 6494–6502.
- 17 G. Akopov, W. H. Mak, D. Koumoulis, H. Yin, B. Owens-Baird, M. T. Yeung, M. H. Muni, S. Lee, I. Roh, Z. C. Sobell, P. L. Diaconescu, R. Mohammadi, K. Kovnir and R. B. Kaner, *J. Am. Chem. Soc.*, 2019, **141**(22), 9047–9062.
- 18 B. P. T. Fokwa, *Encyclopedia of Inorganic and Bioinorganic Chemistry*, John Wiley & Sons, Ltd, 2014; pp 1–14.
- 19 G. Akopov, M. T. Yeung and R. B. Kaner, *Adv. Mater.*, 2017, **29**(21), 1604506.
- 20 J. T. Doane, G. M. John, A. Kolakji, A. A. Rosenberg, Y. Zhang, A. A. Chen and M. T. Yeung, *J. Am. Chem. Soc.*, 2025, **147**(19), 16578–16584.
- 21 M. C. Weidman, D. V. Esposito, Y.-C. Hsu and J. G. Chen, *J. Power Sources*, 2012, **202**, 11–17.
- 22 E. Lee and B. P. T. Fokwa, *Acc. Chem. Res.*, 2022, **55**(1), 56–64.
- 23 G. Zhu, J. Liu, Q. Zheng, R. Zhang, D. Li, D. Banerjee and D. G. Cahill, *Nat. Commun.*, 2016, **7**(1), 13211.
- 24 W.-F. Chen, J. T. Muckerman and E. Fujita, *Chem. Commun.*, 2013, **49**(79), 8896–8909.
- 25 Y. Zhong, X. Xia, F. Shi, J. Zhan, J. Tu and H. J. Fan, *Adv. Sci.*, 2016, **3**(5), 1500286.
- 26 X. Wang, G. Tai, Z. Wu, T. Hu and R. Wang, *J. Mater. Chem. A*, 2017, **5**(45), 23471–23475.
- 27 H. Vrubel and X. Hu, *Angew. Chem., Int. Ed.*, 2012, **51**(51), 12703–12706.
- 28 H. Park, A. Encinas, J. P. Scheifers, Y. Zhang and B. P. T. Fokwa, *Angew. Chem. Int. Ed.*, 2017, **56**(20), 5575–5578.
- 29 P. R. Jothi, Y. Zhang, J. P. Scheifers, H. Park and B. P. T. Fokwa, *Sustainable Energy Fuels*, 2017, **1**(9), 1928–1934.
- 30 H. Park, Y. Zhang, J. P. Scheifers, P. R. Jothi, A. Encinas and B. P. T. Fokwa, *J. Am. Chem. Soc.*, 2017, **139**(37), 12915–12918.
- 31 L. T. Alameda, C. F. Holder, J. L. Fenton and R. E. Schaak, *Chem. Mater.*, 2017, **29**(21), 8953–8957.
- 32 Z. Chen, Q. Kang, G. Cao, N. Xu, H. Dai and P. Wang, *Int. J. Hydrogen Energy*, 2018, **43**(12), 6076–6087.
- 33 S. Gupta, N. Patel, A. Miotello and D. C. Kothari, *J. Power Sources*, 2015, **279**, 620–625.
- 34 M. Zeng, H. Wang, C. Zhao, J. Wei, K. Qi, W. Wang and X. Bai, *ChemCatChem*, 2016, **8**(4), 708–712.
- 35 N. Xu, G. Cao, Z. Chen, Q. Kang, H. Dai and P. Wang, *J. Mater. Chem. A*, 2017, **5**(24), 12379–12384.
- 36 J. Kibsgaard, Z. Chen, B. N. Reinecke and T. F. Jaramillo, *Nat. Mater.*, 2012, **11**(11), 963–969.
- 37 W.-F. Chen, C.-H. Wang, K. Sasaki, N. Marinkovic, W. Xu, J. T. Muckerman, Y. Zhu and R. R. Adzic, *Energy Environ. Sci.*, 2013, **6**(3), 943–951.
- 38 P. Xiao, M. A. Sk, L. Thia, X. Ge, R. J. Lim, J.-Y. Wang, K. H. Lim and X. Wang, *Energy Environ. Sci.*, 2014, **7**(8), 2624–2629.
- 39 D. Voiry, H. Yamaguchi, J. Li, R. Silva, D. C. B. Alves, T. Fujita, M. Chen, T. Asefa, V. B. Shenoy, G. Eda and M. Chhowalla, *Nat. Mater.*, 2013, **12**(9), 850–855.
- 40 S. Wirth, F. Harnisch, M. Weinmann and U. Schröder, *Appl. Catal., B*, 2012, **126**, 225–230.
- 41 J. M. McEnaney, J. C. Crompton, J. F. Callejas, E. J. Popczun, C. G. Read, N. S. Lewis and R. E. Schaak, *Chem. Commun.*, 2014, **50**(75), 11026–11028.
- 42 H. Park, E. Lee, M. Lei, H. Joo, S. Coh and B. P. T. Fokwa, *Adv. Mater.*, 2020, **32**(28), 2000855.
- 43 P. Rogl, *Mater. Res. Bull.*, 1978, **13**(5), 519–523.
- 44 J. C. Slater, *J. Chem. Phys.*, 1964, **41**(10), 3199–3204.
- 45 M. Tokuda, K. Yubuta, T. Shishido and K. Sugiyama, *Acta Crystallogr., Sect. E: Crystallogr. Commun.*, 2023, **79**(11), 1072–1075.
- 46 C. Benndorf, M. De Oliveira, C. Doerenkamp, F. Haarmann, T. Fickenscher, J. Kösters, H. Eckert and R. Pöttgen, *Dalton Trans.*, 2019, **48**(3), 1118–1128.
- 47 K. Zeng and D. Zhang, *Prog. Energy Combust. Sci.*, 2010, **36**(3), 307–326.
- 48 S. B. Kim, J. A. Yapo, A. Yasuhara, K. Yubuta and B. P. T. Fokwa, *Small*, 2025, **21**, 2412693.

