Highly Active and Abundant MAB Phases $\text{Ni}_n\text{ZnB}_n$ ($n=1, 2$) toward Hydrogen Evolution

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WHIST MXENES (2D carbides and nitrides) have become highly popular in several research fields including the hydrogen evolution reaction (HER), unfortunately they are not competitive HER electrocatalysts in their bulk form (MAX phases). The related MAB (2D-like bulk borides) phases and the derived 2D MBenes, however, are less studied but show better HER properties. Herein, two highly HER-active and abundant MAB phases, $\text{Ni}_{n+1}\text{ZnB}_n$ ($n=1, 2$), are studied experimentally and computationally. The pressed pellet electrodes from bulk polycrystalline powders of these phases drive a current density of 10 mA cm$^{-2}$ at impressive overpotentials of $\eta_{10} = -0.171$ V ($n=1$) and $\eta_{10} = -0.145$ V ($n=2$) to efficiently produce hydrogen. Density functional theory (DFT) calculations prove that the most active site is the hollow site on the nickel basal plane, showing a free energy value comparable to that of the hollow site of Pt (111). This study paves the way for further development of bulk and nanoscale MAB phases for clean energy applications.

1. Introduction

Fossil fuels attenuation and their hazardous impact on the environment have made alternative renewable energy sources highly attractive. Among all the renewable energy sources, hydrogen has been one of the most promising candidates due to its high energy density and numerous production routes. Electrochemical water splitting through hydrogen evolution reaction (HER) is the most attractive method to produce hydrogen. However, high cost and scarcity of the most efficient electrocatalysts (platinum group metals) have made the process more challenging. Thus, the study of highly active and abundant electrocatalysts would provide a path for a more sustainable and clean energy supply.

2D materials such as graphene, borophene, phosphorene, h-BN, transition metal dichalcogenides (TMDs), etc. have recently received a great deal of attention due to their unique and enhanced properties if compared with their parent bulk forms. MoS$_2$, which is one of the most studied 2D materials for the HER is known to have only active edge sites, thus its basal plane is inactive making it a poor catalyst in bulk form. In fact, most TMDs have the same behavior. Therefore, discovering other 2D/layered materials which show HER active basal plane is of high current interest. Recently, a new family of 2D carbides and nitrides named MXenes have seen high interest for a wide variety of applications including HER. These MXenes are directly exfoliated from their parent-layered MAX phases ($\text{M}_{n+1}\text{AX}_n$ where $\text{M}$: early transition metal, $\text{A}$: main group element, $\text{X}$: C/N) by selectively etching out the “A” atoms. Similar to most TMDs, MAX electrocatalysts are not competitive toward HER. In fact, they exhibit overpotentials ($\eta_{10} \approx -10$ mA cm$^{-2}$) ranging from 0.74 to $-0.88$ V to drive a current density of $-10$ mA cm$^{-2}$. A MAX-related family of layered ternary borides, called MAB phases is currently receiving increased interest. Compared with MAX phases, MAB phases hold a large variety of structures. Typical MAB phases contain aluminum as the “A” element and exhibit orthorhombic symmetry. However, they also include phases such as hexagonal Ti$_3$InB$_2$, tetragonal Y$_5$Si$_3$B$_6$, tetragonal Ru$_2$ZnB$_5$, hexagonal Cr$_5$Si$_3$B$_6$ and monoclinic Ni$_{n+1}$ZnB$_n$. Even though these MAB phases are chemically and structurally different from the MAX phases, they have similar properties such as high electrical conductivity, stiffness, and resistance to thermal shock. In contrast to MAX phases whose chemical exfoliations to produce MXenes have been extensively studied, the exfoliation of MAB phases is still in its infancy, and only partially etched samples have been reported. Interestingly, nonetched and partially etched MoAB samples are active electrocatalysts for HER with $\eta_{10}$ values of $-0.40$ and $-0.31$ V, respectively. The activity was ascribed to the exposed active basal plane sites due to partial Al-etching. Similarly, bulk Fe$_2$AlB$_2$ was found to be an excellent OER electrocatalyst. Consequently, the studied
Further theoretical studies have shown that the synthesis of MABs is still elusive. They have been predicted as promising alternative candidates to substitute Pt as HER catalysts. Further theoretical studies have suggested MABs as potential catalysts for nitrogen reduction reaction (NRR) and HER upon embedding single atoms such as V and Zn. For example, the calculated Gibbs free energy ($\Delta G_{10}$) values for Zn-$\text{W}_2\text{B}_2\text{O}_7$ and V-$\text{W}_2\text{B}_2\text{O}_7$ are close to the upper point of the volcano plot ($\Delta G_{10} = -0.146$ and 0.013 eV, respectively). However, even the bulk MAB phases are still experimentally unexplored and warrant more attention given the aforementioned results and the fact that abundant bulk borides, especially those with layer-like AlB$_2$-type structures have been demonstrated to have excellent HER activities.

Herein, we investigate Ni$_{n+1}$ZnB$_n$ MAB borides as HER catalysts for the first time. We demonstrate that pellet electrodes of Ni$_{n+1}$ZnB$_n$ ($n = 1, 2$) exhibit abundant basal plane active sites that drive a 10 mA cm$^{-2}$ current density at the lowest overpotential of all MAB, MAX phases, and their derivatives MXenes so far reported. In addition, we have carried out free energy density functional theory (DFT) calculations which have indeed identified many active sites on the Ni basal planes of these MAB phases.

2. Results and Discussion

The Ni–Zn–B system is very attractive and many ternary phases have been discovered. Among these phases, Ni$_2$ZnB and Ni$_1$ZnB$_2$ have an atomically laminated structure similar to MAX/MAB phases (Figure 1, inset). On the one hand, these monolayer structures differ from the typical MAX hexagonal symmetry and the common MAB orthorhombic symmetry. On the other hand, they hold a general chemical composition (Ni$_{n+1}$ZnB$_n$) similar to MAX phases (M$_{n+1}$AX$_n$). Samples of Ni$_{n+1}$ZnB$_n$ ($n = 1, 2$) were synthesized as described previously (also explained in the Supporting Information). As shown in Figure 1a,c, the Rietveld-refined powder X-ray diffraction (PXRD) patterns of both bulk phases show single-phase products. However, severe intensity mismatches were observed mainly for the (00l) reflections, but they were corrected using preferred orientation refinement along the c-axis, indicating a possible layer-like morphology of the samples. Indeed, scanning electron microscopy (SEM) images of the bulk products confirmed the expected stacking of thin sheets (Figure 1, inset). Furthermore, the presence of all elements and their homogeneous distribution were confirmed through energy dispersive X-ray spectroscopy (EDS) and mapping, respectively (Figure S1, Supporting Information).

X-ray photoelectron spectroscopy (XPS) was used to investigate the surface species on the synthesized Ni$_2$ZnB$_2$ and Ni$_1$ZnB$_3$ powders. Figure 2 shows that the Ni 2p, Zn 2p, and B 1s spectra of the two phases are expectedly similar, and the peak fitting values are given in the Supporting Information (Table S2). The Ni 2p spectrum is deconvoluted into Ni 2p$_{1/2}$ and Ni 2p$_{3/2}$, which are composed of two different peaks corresponding to Ni$^{2+}$ and Ni$^0$ species. In both phases, the metallic Ni$^0$ peaks show by far the highest intensities if compared with the Ni$^{2+}$ peaks, indicating that the nickel oxide layer (from atmospheric exposure) present on the surface of these MAB phases is so thin that the bulk boride underneath dominates the XPS spectrum. A similar observation can be made for the Zn species, but the opposite situation is found for the B species. The Zn 2p spectrum is deconvoluted into Zn 2p$_{1/2}$ and Zn 2p$_{3/2}$, which are each composed of Zn$^{2+}$ peaks from the thin zinc oxide layer and the Zn$^0$ peaks of the boride underneath. The B 1s spectra of both Ni$_2$ZnB$_2$ and Ni$_1$ZnB$_3$ are each composed of two peaks corresponding to B$^{3-}$ and B$^0$, the oxide peak being more intense than the boride one. These XPS results indicate that all the aforementioned species are present on the surfaces of these materials, thus suggesting them as potentially active species for HER.

To investigate the electrocatalytic HER activity of Ni$_{n+1}$ZnB$_n$, the crushed particles (Figure 3a,c) were drop casted on a carbon cloth electrode using Nafton as a binder and examined in a 1 M KOH solution (check the Supporting Information for more details). The linear sweep voltammetry (LSV) curves show good performances for Ni$_2$ZnB$_2$ and Ni$_1$ZnB$_3$, as they require overpotentials ($\eta_{10}$) of $-0.25$ and $-0.31$ V, respectively, to reach a current density of 10 mA cm$^{-2}$ (Figure 4a). These values far

![Figure 1](https://example.com/figure1.png)

**Figure 1.** PXRD patterns of a) as synthesized bulk Ni$_2$ZnB$_2$, b) pressed Ni$_2$ZnB$_2$ pellet, c) bulk Ni$_1$ZnB$_3$, and d) pressed Ni$_1$ZnB$_3$ pellet. Insets are the SEM images (a and c insets) and the crystal structures (b and d insets) of the two phases.
exceed those of other experimentally evaluated MAB/MAX phases for HER, to the best of our knowledge. MAX phases generally do not show good catalytic activity. Among all the MAX phases, Mo$_2$Ga$_2$C was reported as one of the most promising HER electrocatalysts with an overpotential $\eta_{10} = 0.74$ V,\cite{11} and the two most studied MAX phases, Ti$_2$AlC and Ti$_3$AlC$_2$, have even higher overpotential values (Figure 4d).\cite{14} Interestingly, the few studied MAB phases are better electrocatalysts if compared with the MAX phases. MoAlB for example has the best HER activity so far with an overpotential of $-0.40$ V at 10 mA cm$^{-2}$ for nonetched crystals.\cite{25} The lower overpotential of Ni$_2$ZnB$_2$ if compared to Ni$_2$ZnB may be due to the different metal to boron ratios. Previously, our group discovered a boron dependency of molybdenum and vanadium borides electrocatalysts for

![X-ray photoelectron spectroscopy spectra](image)

**Figure 2.** X-ray photoelectron spectroscopy spectra of Ni 2p, Zn 2p, and B 1s for a–c) bulk Ni$_2$ZnB$_2$ and d–f) bulk Ni$_2$ZnB (dash line = measured data, solid line = fitted data).

![SEM micrographs](image)

**Figure 3.** SEM micrographs of crushed bulk powders of a) Ni$_2$ZnB$_2$ and c) Ni$_2$ZnB and b,d) the corresponding pressed pellet electrodes.
We found that the lower the M:B ratio (higher boron content) the better the overall HER activity. Interestingly, the two new electrocatalysts are significantly better than the two reported bulk metal-rich borides to date (Mo$_2$B, $\eta_{10} = -0.41$ V$^{[30a]}$ and MoAlB, $\eta_{10} = -0.40$ V) despite having similar or even higher M:B ratio. One reason may be the presence of late transition metals (Ni and Zn), another may be related to the difference in the M:B ratio which affects the type of boron bonds in these MAB structures. In fact, Ni$_3$ZnB$_2$ shows not only a low M:B content (M:B = 2:1) but it also has the most B–B bonds (B$_4$ zigzag units) if compared with Ni$_2$ZnB (M:B = 3:1 and B$_2$ dumbbells). These arguments indeed support the 18% lower overpotential observed for Ni$_3$ZnB$_2$.

As shown in Figure 1 and 3 and as reported previously$^{[22]}$, the investigated bulk polycrystalline Ni$_2$ZnB and Ni$_2$ZnB$_2$ phases already hold a preferred orientation along the c direction (dominating basal planes), meaning that the basal planes may be preferably exposed during HER, hinting at a dominant role for the basal planes in the overall activity of these borides. To study the effect of the basal plane on the HER activity, new electrodes were prepared by pressing the powdered MAB phases to pellets (using a hydraulic press at room temperature, see Supporting Information for more details). This method exposes more basal planes of the MAB particles parallel to the force direction, forming a pellet with even more pronounced preferred orientation along the [001] direction, as confirmed by PXRD (Figure 1) and through SEM images of the electrodes (Figure 3b,d). In fact, the PXRD patterns of the pressed pellets showed a single-crystal-like behavior with mainly intensified (00l) peaks. Other peaks were observed in the PXRD but with much smaller intensities if compared with the (00l) peaks. For instance, the (11l) peak for Ni$_3$ZnB$_2$ should have been the highest intensity peak based on the theoretical pattern. However, after pressing, only a small trace of this peak still prevailed while the (00l) peaks increased. To measure the HER activity of these pellet electrodes, the edges were covered with epoxy. Astonishingly, the overpotentials of these pellet electrodes were lowered by 42–44% if compared with the drop casted electrodes, reaching overpotentials of $\eta_{10} = -0.14$ V and $-0.17$ V for Ni$_2$ZnB and Ni$_3$ZnB$_2$, respectively. These values are the lowest reported experimentally for any form of layered ternary metal-rich borides, to the best of our knowledge. This finding was further confirmed by measurements of the electrochemically active surface area through the double layer capacitance values ($C_{dl} = 22.3$ mF cm$^{-2}$ for $n = 1$ and 35.4 mF cm$^{-2}$ for $n = 2$) which were noticeably higher if compared with those of the drop casted electrodes (Figure S2 and S3, Supporting Information). This drastic increase in the pellet’s active area sites points to the dominating role of the basal plane in the HER activity of these materials. The pellet also provides tightly packed MAB particles, thus facilitating the interlayer electron transfer in the electrode$^{[33]}$, thereby increasing the activity. This was confirmed by Figure 4. a) Polarization curves of various Ni$_{n+1}$ZnB$_n$ MAB electrodes in 1 M KOH at a scan rate of 5 mV s$^{-1}$ with ohmic potential correction. b) Tafel plots derived from the polarization curves. c) Electrochemical impedance spectra (Nyquist plots): The points represent the experimental data, and the solid curves indicate the fitting lines. d) Overpotential of reported bulk MAB and MAX phases compared with different Ni$_{n+1}$ZnB$_n$ electrodes (* obtained from the study by Rosli et al.$^{[14]}$).
three sites were found to be the most active for each surface (Figure 5b,c): the hollow site (Hol) between three Ni atoms, the top site on a Ni atom (Top), and the site bridging two Ni atoms (Brdg). The calculated ΔGH\text{f1} values for Ni2ZnB were: −0.12 eV (Hol), 0.19 eV (Brdg), and 0.44 eV (Top); whereas −0.14 eV (Hol), 0.21 eV (Brdg), and 0.31 eV (Top) were obtained for Ni3ZnB2. Consequently, the Hol site in both materials is the most HER active with ΔGH\text{f1} values similar to that calculated for Hol Pt (111). While the Top sites were the least active, they were still low enough to be considered as active sites. The ΔGH\text{f1} values of Hol and Brdg sites are almost the same (0.02 eV difference) for the two phases, whereas those of the Top sites are significantly different (0.13 eV lower for Ni3ZnB2). This may explain the significantly better HER activity found experimentally for Ni3ZnB2. These DFT results validate the experimental findings of high HER activity of both Ni2ZnB and Ni3ZnB2 MAB phases, the latter being more active.

3. Conclusion

The HER properties of different electrodes (drop casted and pressed pellet) of Ni_{n+1}ZnB_{n} (n = 1, 2) MAB phases were investigated for the first time. The electrodes, analyzed through PXRD and SEM, show high preferred orientation along the c-axis (exposed basal planes), the pressed pellet showing the highest. The pressed electrode had the best HER performance showing low overpotentials to drive a 10 mA cm \(^{-2}\) current density. The DFT free energy calculations showed that the nickel basal plane is more active than the zinc plane and that the hollow site is the most active site for both materials with free energy values close to that of the hollow site of Pt (111), thus supporting the experimental results. This study introduces Ni_{n+1}ZnB_{n} as active basal plane electrocatalysts for hydrogen evolution and paves the way for applications of these other MAB phases in clean energy reactions.

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