ZrB_2-HfB_2 Solid Solutions as Electrode Materials for Hydrogen Reaction in Acidic and Basic Solutions

Steven J. Sitler[a†], Krishnan S. Raja[a], Indrajit Charit[a]

[†]Corresponding author: sitl1428@vandals.uidaho.edu; University of Idaho, 875 Perimeter Dr. MS3024 Moscow, Id 83844.

[a] Department of Chemical and Materials Engineering, University of Idaho, Moscow, Idaho 83844

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Abstract

Spark plasma sintered transition metal diborides such as HfB_2, ZrB_2 and their solid solutions were investigated as electrode materials for electrochemical hydrogen evolutions reactions (HER) in 1 M H_2SO_4 and 1 M NaOH electrolytes. HfB_2 and ZrB_2 formed complete solid solutions when mixed in 1:1, 1:4, and 4:1 ratios and they were stable in both electrolytes. The HER kinetics of the diborides were slower in the basic solution than in the acidic solutions. The Tafel slopes in 1 M H_2SO_4 were in the range of 0.15 - 0.18 V/decade except for pure HfB_2 which showed a Tafel slope of 0.38 V/decade. In 1 M NaOH the Tafel slopes were in the range of 0.12 - 0.27 V/decade. The composition of $Hf_xZr_{1-x}B_2$ solid solutions with x = 0.2 - 0.8, influenced the exchange current densities, overpotentials and Tafel slopes of the HER. The EIS data were fitted with a porous film equivalent circuit model in order to better understand the HER behavior. In addition, modeling calculations, using density functional theory approach, were carried out to estimate the density of states and band structure of the boride solid solutions.

Introduction

Earth abundant electrocatalysts for hydrogen evolutions reactions (HER) are being actively investigated as low cost alternatives for platinum group materials.[1] Transition metal based chalcogenides, carbides, nitrides, phosphides, and borides are the candidate materials for HER catalysts. Molybdenum boride (MoB) showed an overpotential of 220 mV in pH 14 and 210 mV in pH 0 solutions at current densities of 10 mA/cm^2 with Tafel slopes in the range of 55 - 59 mV/decade.[2] Amorphous cobalt boride in the form of Co-B[3] and Co_2B[4] was observed to be highly active for HER. Amorphous nickel boride was reported to be a stable HER catalyst in both acidic and alkaline electrolytes with high activity[5,6] The high electrocatalytic activity of the amorphous transition metal borides (TMB_x, with $x < 2$) was attributed to their electronic structure that transferred electrons from boron to *d*-orbitals of the transition metals.[7] The electron rich *d*-orbitals of metal atoms are considered to be highly active for HER.

Recently, Lim et al.[8] investigated electrochemical behavior of layered TiB_2 modified by sodium naphthalenide and butylithium in order to exfoliate the TiB_2. The unmodified TiB_2 required an overpotential of 1.1 V for HER activity of -10 mA/cm^2 and the exfoliated TiB_2 required 1.0 V for -10 mA/cm^2. Transition metal diborides are considered for ultra-high temperature applications due to their high melting point and stability in extreme conditions. High electrical conductivity and enhanced chemical resistance render the diborides a great candidate material for HER electrocatalysts with enhanced stability in a wide pH range of electrolyte. The HER catalytic behavior of solid solutions of two transition metal diborides mixtures has not been reported to the best of the authors' knowledge. In this investigation, HfB_2 and ZrB_2 are investigated as individual borides as well as solid solutions of $Hf_xZr_{1-x} B_2$ with x varying between 0.2 and 0.8. Samples were prepared through high energy ball milling followed by spark plasma sintering.

Experimental

Commercially available HfB_2 and ZrB_2 powders (Alfa-Aesar, -325 mesh) were mixed at different ratios to achieve stoichiometries of $Hf_xZr_{1-x}B_2$ with x in the range of 0.2 - 0.8. The mixed powders were ball milled for 3 hours in a zirconia vial with 6.5 mm diameter spherical zirconia grinding material using a powder-to-ball mass ratio of 1:10. The ball milled powder mixtures were sintered using a spark plasma sinter Machine (Fuji electronics, Japan, model: Dr. Sinter SPS-515 S) using a 20.6 mm graphite die with 5 KN force at 1700 °C for 600 seconds under 10^{-3} Torr vacuum.

The ~4 mm thick sintered pellets were sectioned to yield small coupons of about 0.4 cm^2 exposed area. After attaching copper wires to the back side of the coupons using highly conductive silver epoxy, the coupons were masked using an acrylic mold exposing only the top surface. The exposed surface was metallographically polished to at least 1 µm surface finish. Table 1 shows the naming schemes used hereafter.

Electrochemical experiments were carried out in 1 M H_2SO_4 and 1 M NaOH electrolytes. Initially, samples were activated by carrying out 10 cycles of cyclic voltammetry from open circuit potential to -1 V_{RHE} at a scan rate of 100 mV/s. A platinum flag (3.75 cm^2 was used as a counter electrode and Ag/AgCl immersed in saturated KCL was used as the reference electrode (199 mV vs. SHE), the potentials were converted to RHE scale using the relation $V_{RHE} = V_{Ag/AgCl} + 0.199 + (0.059 \bullet pH)$

After the initial activation, cathodic polarization to -1 V_{RHE} at a scan rate of 5 mV/s was initiated to record the I-V plot. Potentiostatic tests were carried out at two different potentials followed by electrochemical impedance spectroscopy (EIS) at two potentials; -0.2 and -0.5 V_{RHE} in pH 14 and -0.4 and -0.6 V_{RHE} in pH 0.

The samples were characterized using SEM and XRD. Density measurements were carried out on the sintered pellets using the Archimedes' principle following the ASTM standard B962-08. The details of the density functional calculations are given in the supporting information.

Results and Discussion

Figure 1(a) - (e) shows the FESEM results of the spark plasma sintered samples. Theoretical density and relative density of the samples are given in Table 1. The relative densities of the samples varied from 76.1 - 91.4% of their respective theoretical densities. AB and 4AB showed higher porosity levels at about 24% more than other samples. The surface morphology as observed from the FESEM images was not the real representation of the porosity level due to grain pull-outs during polishing. The grain sizes were in the range of 1.5 - 3.0 µm. Figure 1(f) shows the XRD patterns of the samples. The XRD results indicated that a complete solid solution formed at different ratios of HfB_2 to ZrB_2, as the peaks of $Hf_xZr_{1-x}B_2$ samples were placed between the corresponding peaks of pure HfB_2 and ZrB_2. These results are similar to the conclusions drawn by Otani et al.[9], who reported perfect and continuous solid solutionizing between HfB_2 and ZrB_2. The lattice parameters calculated from the XRD spectra are summarized in Table S1.

Figure 2(a) - (d) shows the electrochemical hydrogen evolution behavior of the HfB_2-ZrB_2 solid solutions in two different pH conditions. Figure 2(a) illustrates the *I-V* characteristics of the diborides in 1 M H_2SO_4. The Tafel slopes were in the range of 150 - 380 mV/decade illustrating a volcano type trend with the stoichiometry of the solid solutions as shown by Zeng and Li[1] in Fig. 2 of their paper. Sample A exhibited the highest Tafel slope of 380 mV/decade and, 4AB and AB, showed the lowest Tafel slopes of about 150 mV/decade. The Tafel slopes, exchange current densities, and the overpotentials for 10 mA/cm^2 are listed in Table S2.

It is noted that the Tafel slopes of the diborides are higher than the reported values for the mono-borides of nickel and cobalt.[3,4] However, Tafel slopes of 146 - 158 mV/decade were reported for TiB_2.[8] If the rate determining step of HER is a Volmer reaction ($H_3O^+ + e^- + M \rightarrow M\text{-}H + H_20$), a Tafel slope of 120 mV/decade is usually observed.[10] The steeper Tafel slopes indicated the possibility of high coverage of adsorbed hydrogen atoms and the formation of a hydride layer on the surface as the open circuit potential shifted to more negative potentials. Similar observations were noted on amorphous nickel boride electrodes.[5]

Figure 2(b) illustrates the *I-t* plots of the diborides in the 1 M H_2SO_4 at -0.4 V_{RHE} and -0.6 V_{RHE}. At -0.4 V_{RHE}, the current densities were about 0.5 mA/cm^2 for A, B, and A4B. AB and 4AB showed current densities of 5.6 and 4 mV/cm^2 at -0.4 V_{RHE}. The current densities showed an increasing trend with time. Switching to a higher potential of -0.6 V_{RHE} increased the current densities significantly as noted from both the I-V and I-t plots. B and AB showed similar current densities of around 18.5 mA/cm^2 at -0.6 V_{RHE} and A4B showed slightly lower current density of 15.5 mA/cm^2. The highest current density of 77.7 mA/cm^2 was observed with 4AB. It should be noted that both AB and 4AB had similar porosity levels. 4AB showed the shallowest Tafel slope and highest current density among all samples investigated in 1 M H_2SO_4.

Figure 2(c) shows the *I-V* plots in 1 M NaOH. Sample A showed the lowest Tafel slope of 100 mV/decade indicating that the Volmer step is the operating mechanism of HER in A. Other samples showed much higher Tafel slopes and relatively high exchange current densities. The higher exchange current densities of AB and 4AB could be attributed to their higher porosity levels. Figure 2(d) shows the *I-t* plots in 1 M NaOH at -0.2 V_{RHE} and -0.5 V_{RHE}. 4AB showed 2 and 12.8 mA/cm^2 at -0.2 and -0.5 V_{RHE} respectively. The current values increased initially with time under the potentiostatic condition and plateaued after about 1 h of polarization. No visible corrosion was noticed. Therefore, the observed high current densities were not attributed to the corrosion current. Crystalline boron is considered to be resistant to acid and concentrated alkaline solutions.[11] Since alkaline zirconates are not soluble and therefore form a protective film in alkaline solutions, preferential dissolutions of zirconium could be ruled out.[12] Similarly, hafnium is also stable in alkaline solutions. Interestingly, sample AB showed the highest current density of 97 mA/cm^2 at -0.5 V_{RHE}. Overall, the HER tests indicated the superiority of AB in both acidic and alkaline electrolytes.

In order to further understand the HER behavior, electrochemical impedance spectroscopy (EIS) and density functional theory (DFT) analyses were carried out. Figure 3(a) shows the bode plots of EIS in 1 M

H_2SO_4 obtained at -0.6 V_{RHE}. Samples A and B showed no significant variation of the impedance at low frequencies and thus exhibited more of a resistor-like behavior which could be associated with low porosity levels in these samples. The solid solution samples showed a decrease in impedance at low frequencies. This implies a mass transfer controlled redox reaction because of the relatively higher porosity levels in these samples. The EIS data were fitted with an equivalent circuit as shown in Figure S1 and the values of the electrical circuit components are summarized in Table S3. The EIS data fit well with the porous film equivalent circuit model commonly reported by other investigators.[10,13] R_f is associated with the charge transfer resistance, R_p is attributed to the mass transfer resistance due to porosity and the adsorption intermediates. Y_f and Y_p are constant phase elements due to distributed time constants because of surface roughness and associated with double layer capacitance and pseudo capacitance respectively.

Sample A showed the highest charge transfer and mass transfer resistance values, and samples AB, and 4AB showed the lowest values. The EIS behavior of the samples could be directly correlated to the HER performance. The values of the constant phase elements are given in the unit of admittance as $S \bullet s^n$. When n is unity, the behavior is purely capacitive, but when n is ½, it acts as a Warburg element. Because of high porosity levels, samples AB and 4AB exhibited pure capacitance behavior while others showed leaky capacitance.

Figure 3(b) shows the EIS results of the samples in 1 M NaOH at -0.5 V_{RHE}. Interestingly, the redox reaction was not significantly mass transfer controlled in the alkaline solution in contrast to that observed in acidic solution. Sample A showed the highest impedance spectrum while sample 4AB showed the lowest impedance spectrum. It is interesting to note that in spite of exhibiting higher impedance spectrum, sample AB possessed the best HER catalytic properties in 1 M NaOH. The EIS data were fitted into a porous film equivalent circuit model as described previously and the results are summarized in Table S4 and S5 for -0.2 V_{RHE} and -0.5 V_{RHE}, respectively.

Electron Density of States (DOS) calculations were carried out using DFT based on the CASTEP method using Materials Studio® software. The calculation details are given in supporting information. Table S6 and Figures S2(a) and (b) show the band structure and DOS of a unit cell of HfB_2. The lines at 0 eV indicate the Fermi level of the material. The overlapping of the valance and conduction bands indicates metallic conductivity of HfB_2. Finite level DOS were observed at the Fermi level. A valley region (a sharp drop in DOS near Fermi level) is observed in the DOS plot which is called a pseudogap.[14]

Ionic character and hybridization effects are attributed to pseudogaps. In hexagonal diborides, the pseudogap is due to TM-*d* and B-*2p* orbital hybridization and also the resonance of the *d*-orbital.[15] If the minimum of the pseudogap aligns with the Fermi level, then the stability of the compound is considered to be better in terms of melting point and chemical inertness. It should be noted that the pseudogap minimum of HfB_2 occurs at its Femi level, indicating a high melting point and high chemical inertness. On the other hand, the low DOS at the Fermi level could adversely affect the catalytic properties. Therefore, the limited HER electrocatalytic activity of HfB_2 could be associated with its electronic structure.

The band structure and DOS of ZrB_2 are illustrated in Figure S3(a) and (b) respectively. The results are similar to HfB_2 and match values reported in literature.[16] However, no reports are available on the electronic structure of the solid solutions of HfB_2-ZrB_2. The density of states of AB, 4AB, and A4B are illustrated in Figures S4(a) - (c).

The 1:1 HfB_2-ZrB_2 solid solution shifted the valley of the pseudogap to more negative energy levels. The DOS peak near -10 eV is attributed to the *s*-electrons of boron. The peak around -5 eV is associated with degenerate *d*-orbitals of Hf and Zr and the *2p*-orbitals of boron. The antibonding states at higher energy levels are attributed to the *d*-states of Hf and Zr.[16] Geometry optimization of the lattice of the HfB_2-ZrB_2 solid solutions indicated contraction of the cell volume for AB and A4B and very little expansion of 4AB as compared to B. The change in the cell volume modified the bond lengths of the TM-TM and TM-B bonds which altered the electronic structure. The electron density at the Fermi level of the solid solutions of HfB_2-ZrB_2 was higher than that of the unmixed borides. The extension of the DOS over the Fermi level suggests higher reactivity of the material.[17] The higher HER activity of the solid solution samples could be attributed to their anti-bonding electron structure and relatively higher electron density at the Fermi Level. HFB_2 showed high HER activity in alkaline solution, which could be attributed to the chemical stability under the alkaline experimental conditions. The modeling of DOS in A4B and AB samples showed higher electron densities at the Fermi level than the 4AB. The HER activity of A4B was lower than that of 4AB, which could be due to the relatively lower chemical stability of the Zr in both acidic and alkaline condition than that of Hf. It is believed that HfB_2 will be more stable than ZrB_2 because *5d*-orbitals of Hf are delocalized more than the *4d*-orbitals of Zr and undergo strong covalent bonding with boron.[18]

Conclusions

HfB_2 showed high electrocatalytic behavior in 1 M NaOH for hydrogen evolution reactions where the Tafel slope was 100 mV/decade and the overpotential 540 mV for HER at 10 mA/cm^2. In 1 M H_2SO_4, the performance of HfB_2 was poor.

ZrB_2 showed Tafel slopes of 270 mV/decade and 180 mV/decade in 1 M NaOH and 1 M H_2SO_4, respectively. The overpotentials were 650 and 690 mV at 10 mA/cm^2 in the electrolytes, respectively.

Among the HfB_2-ZrB_2 solid solutions samples, AB showed the best results. The Tafel slopes and overpotentials of AB at 10 mA/cm^2, were 120 and 150 mV/decade and 420 and 590 mV in 1 M NaOH and 1 M H_2SO_4 respectively. The HER catalytic activities can be directly related to the DOS at the Fermi level.

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