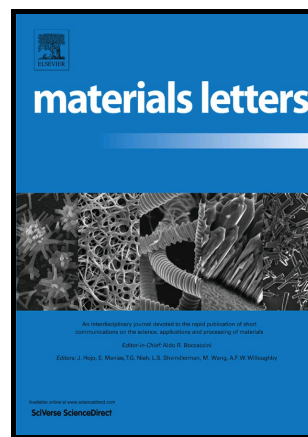


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# ZrB<sub>2</sub>-HfB<sub>2</sub> Solid Solutions as Electrode Materials for Hydrogen Reaction in Acidic and Basic Solutions

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## Abstract

Spark plasma sintered transition metal diborides such as HfB<sub>2</sub>, ZrB<sub>2</sub> and their solid solutions were investigated as electrode materials for electrochemical hydrogen evolutions reactions (HER) in 1 M H<sub>2</sub>SO<sub>4</sub> and 1 M NaOH electrolytes. HfB<sub>2</sub> and ZrB<sub>2</sub> 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<sub>2</sub>SO<sub>4</sub> were in the range of 0.15 - 0.18 V/decade except for pure HfB<sub>2</sub> 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<sub>x</sub>Zr<sub>1-x</sub>B<sub>2</sub> 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.

Keywords: Electroceramics; Energy storage and conversion; Solar energy materials; Borides; Ceramic composites.

## Introduction

Earth abundant electrocatalysts for hydrogen evolutions reactions (HER) are being actively investigated as low cost alternatives for platinum group materials.<sup>1</sup> 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<sup>2</sup> with Tafel slopes in the range of 55 - 59 mV/decade.<sup>2</sup> Amorphous cobalt boride in the form of Co-B<sup>3</sup> and Co<sub>2</sub>B<sup>4</sup> 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<sup>5,6</sup> The high electrocatalytic activity of the amorphous transition metal borides (TMB<sub>x</sub>, with x < 2) was attributed to their electronic structure that transferred electrons from boron to *d*-orbitals of the transition metals.<sup>7</sup> The electron rich *d*-orbitals of metal atoms are considered to be highly active for HER.

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