

Roles of Interstitial Hydrogen and Substitutional Boron During H₂ Evolution on Diamond Electrodes.
Model DFT Calculations

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On high-quality relatively defect-free boron-doped diamond electrodes hydrogen evolution in acid commences at about 1.25 V on the hydrogen scale.¹ Unlike platinum, H₂ formation is unlikely to involve recombination of adsorbed hydrogen atoms because C-H bonds are twice as strong as Pt-H bonds. The most likely mechanism would be discharge of a hydronium (H₃O⁺) ion over a surface C-H bond. However, an earlier theoretical study indicated a high activation energy (E_a) for this mechanism.² Might impurities or defects lower some surface C-H bond strengths to create active sites for the latter mechanism?

Recent experiments indicate that H is present in the very near surface region of CVD diamond.³ We have examined this theoretically using B3LYP hybrid density functional theory and a 6-31G basis set, and a cluster model, to explore the possibility of there being additional H in the surface region. We find that two H atoms are stable in the normal C-H terminated (111) surface when one is in an interstitial site of the first subsurface C-C bond and the other is bonded to the top C atom of the pair as shown by the black cluster atoms in Fig. 1. This H₂^{*} complex has the H of the antibonding site on top of the surface and this new surface C-H bond has a strength of 3.89 eV, which is weaker than the 4.70 eV value calculated for a normal surface C-H bond.

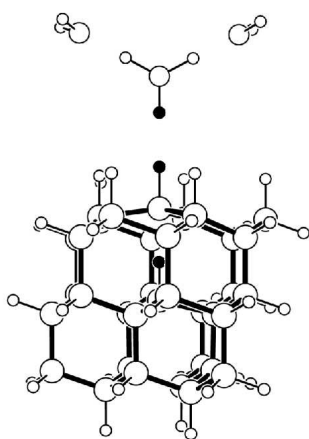


Figure 1. C₃₅H₃₆ cluster model with H₂^{*} and hydronium ion with two coordinated H₂O as discussed in the text.

Activation energies for the discharge of H₃O⁺ over this weakened C-H bond were calculated at several potentials (U) using the model of Fig. 1. This was accomplished using the method of Lagrange multipliers at each of the potentials. The E_a results in Fig. 2 are lower than those over a normal C-H bond, for which the actual path is reduction of H⁺(aq) to H• at \sim -2.1 V, but still high.

The concentration of B in H₂-evolving electrodes is very high (\sim 10²⁰ cm⁻³) and substitutional B atoms may be at sites just beneath the surface. This was modeled as

shown in Fig. 3. Because B is electron deficient, an extra

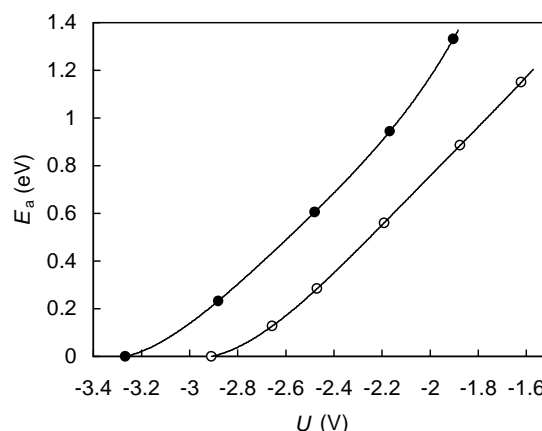


Figure 2. Calculated activation energies as functions of electrode potential: • for H₂^{*}; o for substitutional B

H can bond to a radical surface antibonding site. This bond strength is only 2.36 eV, making it a good candidate for H₂ evolution. The calculated E_a vs U curve in Fig. 2 reflects this weak bond. Though the activation energies are probably still high, it is noted that the potential range of H₂ evolution is well negative of the \sim 1.0 eV flat band potential,¹ which that means the double layer will have excess cations and their field will increase the electron affinity of the reduction center, effectively shifting both curves in Fig. 2 to the right, lowering the E_a at each U .

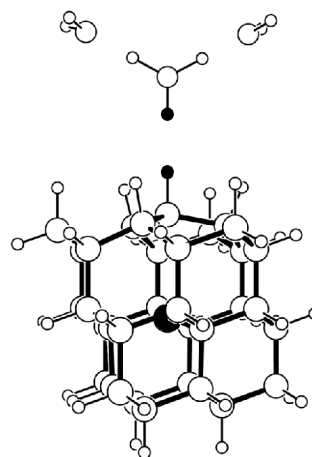


Figure 3. As in Fig. 1, but with black substitutional B at the center.

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