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 (Eₐ) 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.

 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 Eₐ 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 ~2.1 V, but still high.

The concentration of B in H₂-evolving electrodes is very high (~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 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 Eₐ 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 ~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 Eₐ at each U.

Figure 1. C₁₀H₁₆ cluster model with H₂⁺ and hydronium ion with two coordinated H₂O as discussed in the text.

Figure 2. Calculated activation energies as functions of electrode potential: * for H₂⁺; 0 for substitutional B

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

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References