

Understanding Chlorite, Chlorate and Perchlorate Formation when Generating Hypochlorite using Boron Doped Diamond Film Electrodes

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Chlorine is a commonly used disinfectant in drinking water, wastewater, cooling towers, swimming pools, and spas. Due to the hazards and costs of shipping and storing chlorine gas, on-site generation (OSG) of hypochlorous acid (HOCl) from salt solutions has become increasingly attractive. OSG of HOCl has most commonly employed electrodes consisting of RuO₂ films coated on titanium substrates. In attempts to improve efficiency and prolong electrode life, boron-doped diamond (BDD) film electrodes are being explored as potential anode materials for OSG of hypochlorite for disinfection. BDD electrodes have shown promise in these applications and allow oxidant generation at higher current densities and higher Faradaic efficiencies relative to traditional electrodes. However, recent studies have documented that significant quantities of unwanted byproducts, such as: chlorite (ClO₂⁻), chlorate (ClO₃⁻), and perchlorate (ClO₄⁻) may be produced in OSG systems using BDD electrodes.

This research used density functional theory for investigating reactions on BDD electrodes that contribute to unwanted byproduct formation during hypochlorite generation. Clusters containing 10 or 34 carbon atoms were used to simulate the diamond electrode surface, as illustrated in Figure 1. The simulations included reactions with hydrogen terminated surfaces, and with surface sites produced by anodic polarization, namely: ≡C·, =C·H≡C·O·, and =C·HO. The activation energies for oxidation of chlorine oxyanions via direct electron transfer and via reaction with hydroxyl radicals were calculated. Figure 2 illustrates the potential dependence of the activation energy for the oxidation reaction: HOCl → OCl· + H⁺ + e⁻. Oxidation of all chlorine oxyanions became activationless at potentials less than 2.4 V/SHE.

Oxychlorine radicals (ClO·, ClO₂·, ClO₃·) were found to chemically adsorb to both secondary and tertiary carbon atoms on the BDD surface, as illustrated in Figure 3. These chemisorbed intermediates could react with

hydroxyl radicals to regenerate the original chlorine oxyanion (ClO⁻, ClO₂⁻, ClO₃⁻), and produce ≡C·O· and =C·HO sites on the BDD surface. The ≡C·O· and =C·HO sites also reacted with oxychlorine radicals to form chemisorbed intermediates, which could then be converted to higher oxidation states (ClO₂⁻, ClO₃⁻, ClO₄⁻) via reaction with hydroxyl radicals.

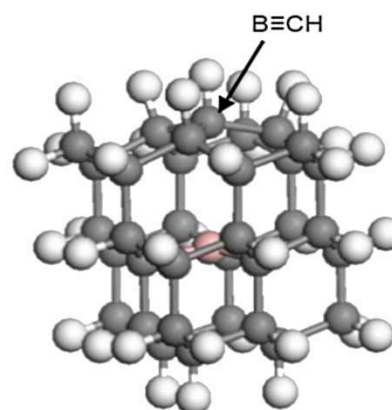


Figure 1. 34-carbon structure used for simulating boron-doped sites near the diamond surface. The structure is C₃₄BH₃₆, and the B≡CH site is indicated. Atom key: carbon, grey; hydrogen, white; boron, pink.

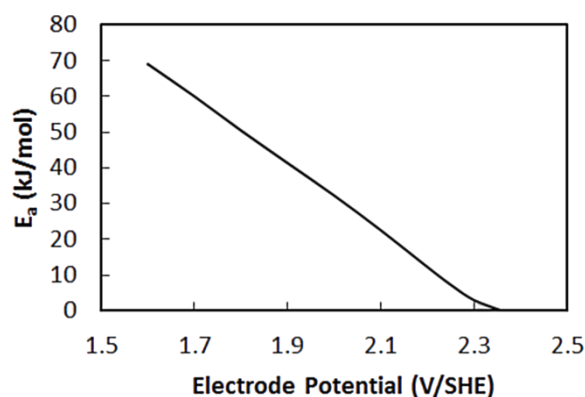


Figure 2. Activation energy as a function of electrode potential for HOCl oxidation.

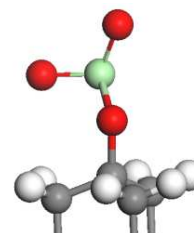


Figure 3. Chemically adsorbed ClO₃· on a tertiary carbon atom on the simulated diamond surface. Atom key: carbon, grey; hydrogen, white; oxygen, red; chlorine, green.