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Catalytic activity of nanostructured carbon electrodes for electrosynthesis of H_2O_2 through water oxidation: Predictions from first principles

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Introduction

Hydrogen peroxide (H_2O_2) is widely used in many industrial areas and applications, particularly in the chemical industry and synthesis processes, electronic industry, textile industry, metallurgy, as detergent, for pulp and paper bleaching, in wastewater treatment, environmental protection and in other applications. Currently, the main industrial methods for producing hydrogen peroxide have major drawbacks. *E.g.* an indirect method of anthraquinoline oxidation cannot be considered a green method because it involves the sequential hydrogenation and oxidation of an anthraquinone precursor dissolved in a mixture of organic solvents that generates substantial waste and its transportation causes possible hazards. Way of obtaining H_2O_2 using reactions wherein H_2O_2 is a by-product do not allow synthesizing of the necessary volumes of H_2O_2. Direct synthesis from H_2 and O_2 is a dangerous and expensive method because hydrogen/oxygen mixtures are explosive over a wide range of concentrations. Electrochemical water oxidation by means of two-electron water oxidation reaction (2e WOR) is an attractive alternative for commercial production of H_2O_2. Extraction of H_2O_2 from water is a shine example of green chemical technology. This process can be used to treat wastewater or obtain drinking water, since H_2O_2 is a strong oxidant that disinfects and efficiently mineralizes contaminants without leaving a trace.

In our study the carbon-type graphene nanostructured electrodes for 2e WOR were studied from first principles by means of density functional theory. Calculated free energy of 2e WOR intermediates' adsorption and calculated overpotential required for successful 2e WOR are used as descriptors for comparing carbon-type thin films, their possible morphologies and reconstructions. The results are presented in free energy diagrams for graphene, bilayer graphene, and in part for diamond and B-doped diamond. Our study provides deeper understanding of the catalytic properties of the carbon allotropes on 2e WOR.

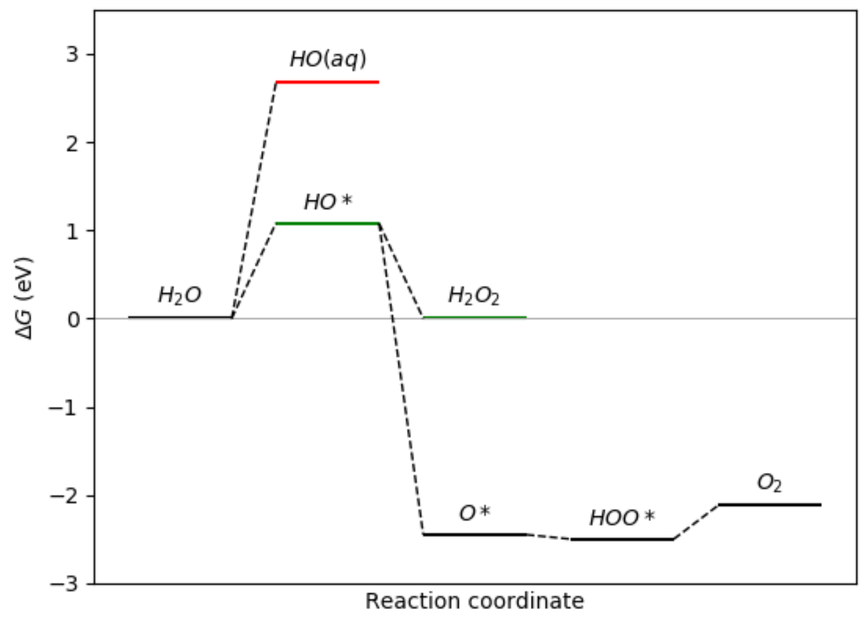
Results:

Free energies for OER

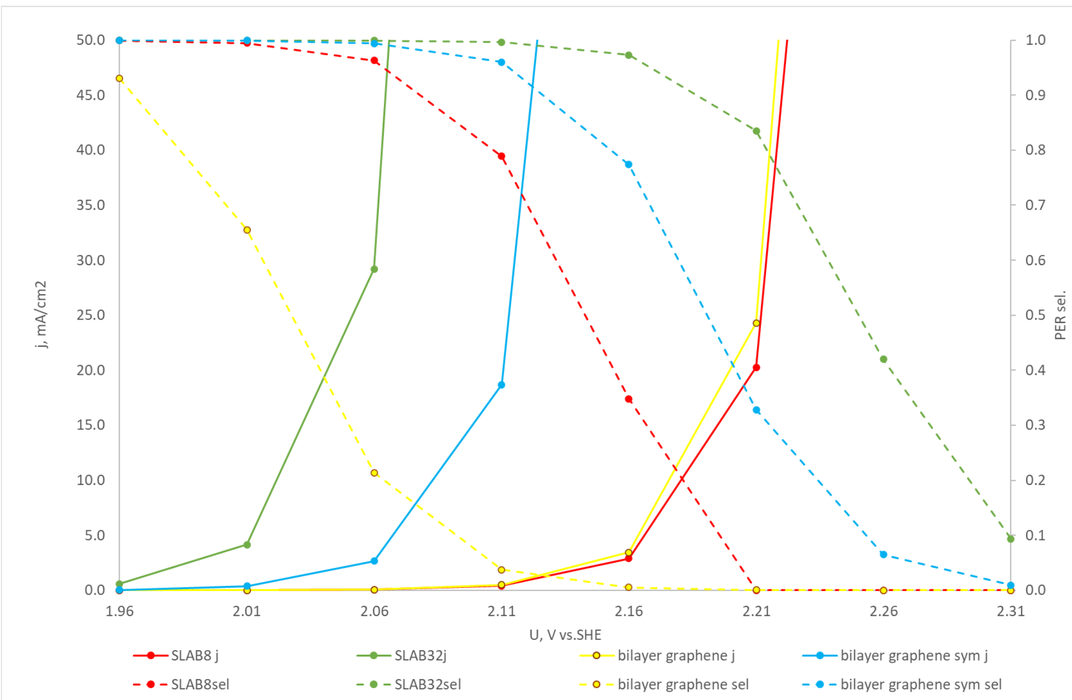
	dG^0, eV	dG (U=1.23V), eV
HO*	2.84	1.61
O*	1.07	**-1.39**
HOO*	2.78	-0.91
O_2	4.92	0.00

Free energies for PER (peroxide formation reaction)

	dG^0, eV	dG (U=1.76V), eV	dG(reaction), eV
HO*	2.84	**1.08**	1.08
HO(aq)	4.43	2.67	
Peroxide	3.52	0.00	-1.08



We have studied single- and double-layered graphene as the catalysts for peroxide electrosynthesis. The every possible coverage and/or configuration of adsorbate atop adsorption sites were analyzed. Here we present the reaction energy diagram for one eights coverage as the most energetically favorable catalysts. Calculated Gibbs free energies of reactions at corresponding theoretical equilibrium potentials, 1.23 eV vs. standard hydrogen electrode for OER and 1.76 eV for PER, are listed in the tables. As it is well seen from the diagram, both 4e and 2e reactions are up-hill, assuming the need of overpotential.



Free energy referring to the thermodynamic part of free activation energy

$$G_{max} = k_B T\, ln(10)\left(\log\left(\frac{k_B T z e \Gamma_{act}}{h}\right) - \log(j)\right) \qquad j = \frac{k_B T z e \Gamma_{act}}{h} \cdot \exp\left(\frac{-G_{max}}{k_B T}\right)$$

For graphene slab 8, to reach the current density of $j = 1\ mAcm^{-2}$, $G_{max}PER = 0.71$ eV is required, which corresponds to applied U = 2.03 V vs. SHE, η_{PER} = 0.27 V vs. SHE. At this potential PER selectivity = 98%.

In case of graphene the maximal PER free energy is less than maximal OER free energy. That means we can calculate selectivity of PER versus OER using listed relations. PER selectivity is estimated with respect to overpotential at PER (η_{PER} vs. SHE). Selectivity toward peroxide evolution (2e reaction) begins with applied overpotential starting from 0.25 V.

In the left figure is shown the dependence of both current density (solid lines) and selectivity toward peroxide production (dashed lines) on the overpotential for the graphene structures under study.

For instance, to reach current density of 1 milli Ampere per square centimeter the overpotential of 0.27 Volts is necessary. At this overpotential PER selectivity is close to 98 percent.

Taking into account the most endothermic and the most exothermic steps of both OER we can estimate the slope of the Volcano diagram for carbon related catalysts.

Most of our calculations for both diamond and BDD catalyst are currently in progress. However, from the preliminary data we can predict downhill OER and PER reactions for diamond-like terminated surfaces, that may explain the higher selectivity toward peroxide evolution of BDD catalysts.

Conclusions

The only up-hill 4-electron oxygen evolution reaction (OER) and 2-electron peroxide evolution reaction (PER) can be theoretically predicted for graphene-like catalyst meaning the need of overpotential;

Down-hill reactions are expected for diamond-type surfaces, e.g. boron-doped diamond (BDD), which are the most promising materials for 2e WOR catalyst.

Acknowledgement:

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