B-doped fullerene as a high-performance metal-free electrocatalyst for CO reduction reaction

Jun Nakamura

Department of Engineering Science, The University of Electro-Communications (UEC- Tokyo),
1-5-1 Chofugaoka, Chofu, Tokyo 182-8585, Japan

Developing highly efficient electrocatalysts for carbon monoxide reduction reaction (CORR) is highly attractive for CO conversion. Carbonaceous materials are considered promising electrocatalyst materials. This study aims to design and develop a high-performance electrocatalyst for CORR using first-principles calculations based on density functional theory (DFT). In this study, we investigated the dependence of the catalyst's curvature on the CORR electrocatalytic activity using different sizes of boron-doped fullerene ($C_{69}B$, $C_{75}B$, and $C_{83}B$). The computational hydrogen electrode model [1] is used to evaluate the catalytic properties of B-doped fullerene. The results reveal that CO molecules are stably adsorbed on $C_{69}B$, $C_{75}B$, and $C_{83}B$. The free energies of all possible reaction intermediates in the CORR under an acidic environment show that B-doped fullerenes can effectively facilitate the CORR process and further reduce CO to methane. All reactions proceed spontaneously by applying an external potential, the so-called overpotential. The overpotential was determined using the initial hydrogenation process, *CO →*CHO. The results suggest that $C_{69}B$, with a radius of 4.79 Å, is the best candidate for CORR with the minimum overpotential of 0.26 V and is better than the available metal-based catalysts in terms of overpotential. When the radius of curvature increases, the electrocatalytic property improves, while CO molecules are harder to adsorb. This research will pave the way for developing catalytic properties of surfaces with curvature [2].

[1] J. K.Nørskov et al., J. Phys. Chem. B **108**, 17886 (2004).
[2] A.F. Ridassepri, Y.Umejima, Jun Nakamura, J. Phys. Chem. C **128**, 9513 (2024).