

Oxygen reduction reaction in *p*- and *n*-doped conducting polymers: experiment and theory

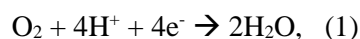
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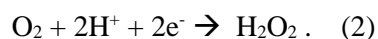
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The oxygen reduction reaction (ORR) typically limits the efficiency of oxygen-associated energy conversion in fuel cells and air-metal batteries. Today, expensive noble metal catalysts are commonly utilized to boost the ORR and the resulting conversion efficiency in those devices. Hence, there is an intensive research to find efficient electrodes, exhibiting a favorable electronic structure, for ORR based on non-critical raw materials/elements such as conducting polymers. ORR can proceed via two pathways, whether through the four-electron process when the oxygen reacts with protons and is reduced directly into water



or via the two-electron process leading to the formation of the hydrogen peroxide as an intermediate specimen



Here, we report the negatively doped conducting polymer poly(benzimidazobenzophenanthroline) (BBL) and positively doped conducting polymer poly(3,4-ethylenedioxythiophene), (PEDOT) as efficient ORR electrodes. We demonstrate experimentally that ORR on *n*-doped BBL proceed via four-electron process (1) leading to formation of water, whereas *p*-doped PEDOT supports the two-electron process (2) leading to production of peroxide.

In order to understand the experimental findings, the density-functional theory (DFT) calculations were performed where the change of the Gibbs free energies during all reaction steps were calculated, all transition states were identified, and the height of the corresponding reaction barriers were calculated. It is demonstrated that polymeric chains possess the catalytic activity, where no platinum catalyst or external dopants are needed to sustain the electrocatalysis. This remarkable property of polymeric chains is related to the formation of polaronic states, which leads to the decrease of the HOMO - LUMO gap and thus to the enhancement of the reactivity of the system.

It has been found that for the case of *n*-doped polymer (BBL), the path (1) is thermodynamically preferential, because it leads to a larger gain in the Gibbs energy as compared to path (2). Also, the path (1) is characterized by a lower reaction barrier. The predictions of the DFT modelling are hence in full agreement with experimental findings.

For the case of *p*-doped polymer (PEDOT) it has also been found that path (1) is thermodynamically preferential. However, the corresponding energy barrier is found to be much higher as compared to path (2). This explains why ORR in PEDOT follows path (2) despite the corresponding thermodynamics favors path (1). The calculated frequency of the vibration motion of the chemisorbed transition states was found to be in a good agreement with corresponding measurements using ATR-FTIR spectroscopy.