Bifunctional Electrocatalytic Effect for Oxygen Reduction and Evolution in Li-O₂ Batteries: RRDE and DEMS Insights

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Alkaline Li-air batteries could make a major breakthrough in battery technology. However, a key challenge is the development of a bifunctional catalyst which enhances the sluggish kinetics of both ORR and OER. In alkaline solution, Ag is known to be the best non-precious electrocatalyst for oxygen reduction. However, Ag is not catalyzing oxygen evolution. Spinels such as Co_3O_4 and various Perovskites have been shown to be good catalysts for oxygen evolution but are not very good for oxygen reduction. We have recently reported that a particular carbon-free mixture of a Ag catalyst with Co_3O_4 nanoparticles leads to a catalyst which not only combines the good performance of Ag for the ORR with that of Co_3O_4 for the OER, but shows a better activity than its components with good stability.[1, 2]

Here, we will present further insights and demonstrate that this effect is also observed for various perovskites. The synergistic effect is also observed when Co_3O_4 or the perovskites are deposited on smooth Ag and Au electrodes. We determined the free Ag surface area by Pb-underpotential deposition. XPS analysis has shown that the presence of Ag⁺ in contact with Co_3O_4 facilitates the redox switching of Co_3O_4 . This could be the reason for the enhanced catalytic activity of the mixture.

Using differential electrochemical mass spectrometry (DEMS) and ¹⁸O- isotope labeling it has shown in our previous work that the lattice oxygen is participating in the OER at oxides.[3-6] This procedure is applied to Co_3O_4 and the mixed catalyst as well and showed higher amount of oxygen exchange at the mixed catalyst.

Cycling performance in DMSO at gold has been quantitatively studied.[7] Here, investigations of OER and ORR in an aprotic electrolyte based on a blend of tetraglyme and DMSO at gold electrode has been done using RRDE and DEMS techniques. Insights into the mechanism has also been considered.

Acknowledgement: Funding of this project by the BMBF (LuLi - project 03X4624A) is gratefully acknowledged.

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