

Critically Examining the Role of Nanocatalysts in Lithium-Oxygen Batteries: Viability towards Suppression of Recharge Overpotential, Rechargeability and Cyclability

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The metal and metal oxide catalysts that are widely employed in Li-O₂ cells to suppress the large recharge overpotential (typically >1V) have been consistently been mired with ambiguity regarding the possible exacerbation of side reactions. Specifically, the often-proposed merits of reduced overpotentials for the facile decomposition of the Li₂O₂ discharge product with catalysts may be largely superficial due to the possibility for enhanced parasitic side reactions. For instance, there is a common assertion that if the recharge potential is suppressed below 4 V, rechargeability can be improved with side reactions lessened, or even prevented. We show that this is not the case, even with ruthenium, which has been extensively reported to effectively suppress the recharge overpotential. Another shortcoming is the difficulty in comparing other catalysts reported in the literature in terms of the relative efficacy towards decreasing overpotential and increasing cyclability. This arises due to differences in experimental conditions, namely, catalyst size and loading, type of carbon, binder instability, and test conditions.

In our work, we have synthesized Ru, Pt, Pd, Co₃O₄ and Au nanoparticles supported on carbon nanotubes, which contain the same loading (40 wt%) with particle size of ~10 nm or less. Subsequently, we determined their corresponding Li₂O₂ decomposition efficiency, cycling stability and the predominant cell processes under the same experimental conditions. Our initial evaluations showed a notable suppression of recharge overpotential in the presence of catalysts. However, subsequent work to ascertain the overall cell processes reveal the suppression of recharge overpotential is not accompanied by reduction in side reactions leading to no notable improvement in rechargeability nor cyclability. Moreover, we show that highly efficient catalysts for Li₂O₂ decomposition also exhibit non-selectivity as evidenced by their enhancement in side reactions, which leads to the premature passivation of the electrode and compromise cyclability. Our work clearly highlights the importance of metrics outside of recharge overpotential and the necessity of pursuing approaches that enable reversible Li-O₂ electrochemistry.