Electrocatalyst Activity in Various Li-O₂ Battery Electrolytes

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The Li-O₂ cell, with a theoretical energy density of ~3500 Wh/kg versus ~380 Wh/kg for standard lithium-ion cells [1], is an attractive technology for improving upon the current generation of rechargeable batteries. However, design issues such as safety, oxygen management, and cathode cyclability must be addressed before practical application can be achieved. Fundamental activity comparisons are necessary to select materials which improve cycle life and round trip efficiency. The selection of cathode catalysts to promote the oxygen reduction (ORR) and oxygen evolution (OER) reactions cannot be divorced from the selection of electrolyte due to distinct catalyst-electrolyte interactions.

In this work we explore these interactions with a fundamental comparison of the two most promising electrolytes for the Li-O₂ cell. DME- and DMSO-based electrolytes are compared on the basis of stability within normal voltage ranges, kinetics, and reaction selectivity.

The evaluation of noble metal catalysts for Li-O2 reactions requires a systematic method for comparing activity and onset potentials. Rotating disc electrode (RDE) cyclic voltammetry (CV) experiments eliminate many of the confounding factors that make comparisons in full cells imprecise and unconvincing. We use CV to elucidate the inherent activity of Au, Pt, and Pd catalysts in both DME- and DMSO-based electrolytes and demonstrate that the interplay between catalyst and electrolyte should have a profound effect on material selection. The selection of these catalysts was informed by previous studies that have shown Au to be one of the best catalysts for OER and Pt and Pd to have high activity towards ORR in a DME-based electrolyte [2,3]. However, we are the first to provide activity comparisons which combine both ORR and OER and a DMSO-based electrolyte. We find that Au appears to be more active and has a higher onset potential for ORR than Pt or Pd in DMSO which is opposite to the order of onsets in a DMEbased electrolyte. Reaction selectivity for OER is also influenced by the combination of Au, Pt, or Pd and electrolyte solvent. Based on our results, DMSO represents a more stable electrolyte that enhances the activity of noble metal catalysts and decreases the overpotential of Li-O₂ reactions.

To validate our approach, the same standard catalysts were deposited on a Ni-foam scaffold and evaluated in standard Li-O₂ cells under a pressurized O₂ atmosphere. CV and galvanostatic cycling experiments are provided for further activity comparisons that relate the function of catalyst and electrolyte.



Figure 1. CV of noble metal catalysts in 0.1M LiClO₄/DMSO electrolyte.



Figure 2. CV of noble metal catalysts in 0.1M LiClO₄/DME electrolyte.

References:

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