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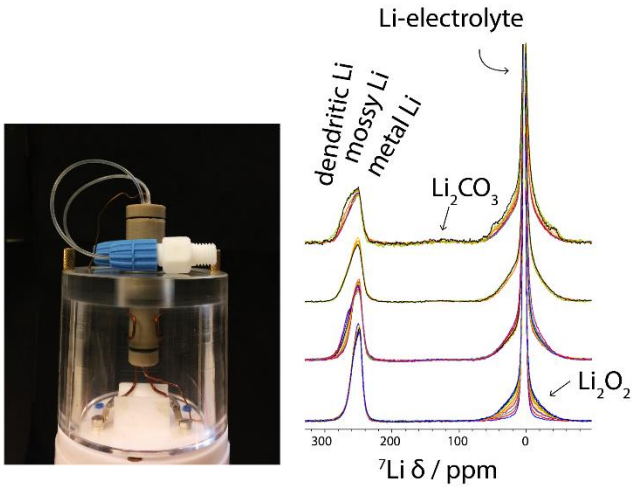
Rechargeable metal-O_2 batteries have attracted much attention in recent years as a possible alternative to the widely used lithium-ion batteries. This is particularly the case for lithium and sodium-oxygen batteries, due to their potential high energy density.[1] However, great challenges remain in the development of metal-O_2 batteries, including the stabilization of the discharge products, poor cyclability and the need for new cathode design. On a more fundamental aspect, one much completely grasps the understanding of the underlying electrochemical mechanisms taking placed inside the M-O_2 battery. Clear identifications of the discharge electrochemical pathways and their products (M-O_2, M_2O_2,…), as well as the reactivity of the electrolyte, are crucial. Discharge products have already been observed using many *ex situ* techniques such as XRD or Raman, however it may not provide a realistic view of the reactions and may lead to biased interpretation. Conversely, *In situ/operando* techniques[2] can capture the dynamic changes unequivocally in the cell environment during cycling and provide unprecedented information on intermediate phases that may be undetectable through *ex situ* analyses.

In the past few years, *ex situ* ssNMR emerged as a valuable tool for characterizing metal-O_2 cells on *ex situ* discharged and charged samples (Fig 4).[3,4] *Operando* ssNMR appears thus of considerable interest to monitor the structural and electronic changes in M-O_2 upon cycling and to obtain valuable insights on the transition of chemical phases. To this aim, we recently designed an *operando* cell dedicated to metal-O_2 batteries that enables for O_2 gas to react at the cathode without compromising the NMR experiments. The electrochemical performance in the Li-O_2 configuration is quite similar to what is expected in the literature and validates the design of the cell. We will detail the working principle of the cell, its performance, and present the evolution of NMR signals during cycling.



Operando ^{7}Li NMR on a Li-O_2 cell

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