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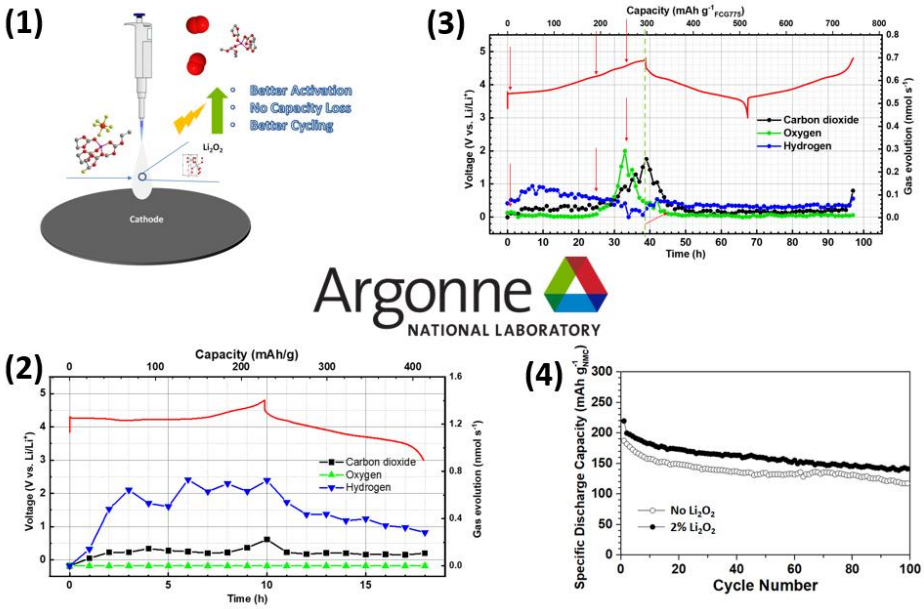
Probing the Prelithiation of Lithium Peroxide for Silicon Anode

Enhancing the energy density of lithium-ion batteries necessitates the development of high-energy-density chemistry. Silicon (Si) anodes, with their high specific capacity (3580 $mAhg^{-1}$), stand out as a promising candidate for the next generation of energy storage solutions. Despite numerous efforts to advance Si anodes, their practical application is impeded by challenges such as rapid capacity degradation and significant volumetric expansion. A critical issue with silicon anodes is their substantial first-cycle irreversibility, which results in a considerable loss of recoverable lithium from the cathode materials in a full cell. Pre-lithiation presents an attractive approach to address active lithium losses and boost practical energy density.

Despite lithium peroxide's (Li_2O_2) lower theoretical capacity (1168 $mAhg^{-1}$) compared to lithium oxide (1793 $mAhg^{-1}$), its potential as a lithium source remains compelling, as its capacity still far exceeds that of NMC (200 $mAhg^{-1}$). Our studies on the chemical stability of Li_2O_2 and its activation process on the cathode have shown that Li_2O_2 is more compatible with conventional electrolytes and cathode laminate slurries compared to lithium oxide. Furthermore, Li_2O_2 is non-hygroscopic and does not cause gelation during electrode slurry preparation, unlike the highly hygroscopic lithium oxide (Li_2O), which can induce gelation. However, the activation of Li_2O/Li_2O_2 is not particularly efficient, and the cathode material experiences capacity loss post-activation. In our pursuit of practical pre-lithiation for Si cells, we conducted a detailed study to understand the activation mechanism and address technical challenges such as low activation rates and gassing issues associated with this technique. By optimizing activation conditions and implementing our new spread-coating technique (Figure 1), we successfully mitigated capacity loss by minimizing the impact of dioxygen gas release and Li_2O_2 evacuation on the cathode.



We utilized Differential Electrochemical Mass Spectrometry (DEMS, HPR-40 DEMS) to determine the threshold potential for dioxygen release, the major by-product of Li_2O_2 activation. The target gases for the DEMS test were carbon dioxide, oxygen, and hydrogen. Figure 1 shows that no O_2 was detected in the pure NMC cathode, even when the cell was charged to 4.8 V. During the first charge cycle of the NMC cathode, the decomposition of electrolyte impurities and residual lithium carbonate on the cathode surface generated CO_2, while H_2 gas originated from the reaction of the metallic

lithium anode with electrolyte impurities and PVDF binders. In the DEMS study (Figure 2) of the FCG with 5% Li_2O_2 composite cathode, O_2 release commenced at approximately 4.2 V, along with a significant release of CO_2. The peak release of O_2 was detected at around 4.6 V, and CO_2 release began simultaneously with O_2 generation, peaking at 4.8 V. The detection of a large amount of O_2 gas during the charging process of the composite cathode clearly demonstrates the successful activation of Li_2O_2 for dioxygen gas release and recyclable lithium.

When applied in Si||NMC full cells, the Li_2O_2 spread-coated cathode exhibited a highly promising activation rate and significantly enhanced specific capacity and cycling stability compared to uncoated full cells (Figure 4). Overall, our work demonstrates the promising potential of Li_2O_2 as a lithium reservoir to counter first-cycle capacity irreversibility and enable stable cycling of Si cells.

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Hiden Product:
HPR-40 DEMS