双掺杂调控电荷自平衡机制及其协同界面修饰对超高镍正极材料高电压循环稳定性研究

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超高镍正极材料通过提升镍含量、降低钴用量乃至实现无钴化，可有效提升材料性价比与能量密度，但其商业化应用仍受限于一系列关键瓶颈：晶体结构稳定性差、微裂纹、循环寿命快速衰减等问题突出，严重制约了超高镍正极的大规模产业化应用。当前，较为成熟的改性思路，主要包括元素掺杂、包覆改性、形貌优化等策略，为开发结构更稳定、电化学性能更优异的超高镍正极材料提供了重要研究基础与技术方向。

本论文围绕电荷自平衡、双掺杂、界面调控等多种改性策略的协同融合，开展超高镍正极材料的系统性研究。首先，通过高价阳离子掺杂对二次粒子微观结构进行修饰，实现一次粒子的合理重组；其次，引入电荷相对较低的 Al 元素，平衡高价阳离子掺杂引发的镍离子低价态转变趋势；最后，双掺杂体系中 Al 元素带来的结构稳定性，与另一种掺杂元素协同作用，共同提升材料的结构稳定性。综上所述，本论文探究了多种双掺杂组合方案，如图 1 所示，所制备的多种材料放电容量均超过 230 mAh g^{-1}，显著优于当前商业化高镍正极材料，且展现出优异的高电压循环稳定性与电化学可逆性。

本论文研究的科学价值主要体现在以下几点：其一，突破单一改性方法的局限，实现电荷自平衡、双掺杂、界面调控等多种改性策略的协同融合，构建多维度协同改性体系，解决单一改性难以兼顾材料结构稳定性与电化学性能的瓶颈；其二，通过多策略协同作用实现材料性能的显著提升，突破传统超高镍正极材料循环衰减快、稳定性差的技术痛点；其三，聚焦超高镍正极材料在新能源储能领域的实际应用需求，优化后的材料具备良好的产业化应用潜力，为高性能储能电极材料的设计与开发提供理论支撑和技术参考。

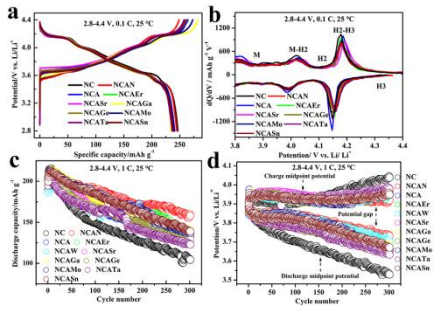

Fig. 1 (a) Initial charge and discharge voltage profile. (b) The CV profiles in first cycle. (c) Cycling performance at 1 C in the range of 2.8-4.4 V. (d) Evolution of electrochemical polarization voltages during different charge-dicharge cycling.

关键词： 锂离子电池；超高镍正极材料；协同改性；高电压；循环稳定性

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Regulation of Charge Self-Balance Mechanism by Double Doping and Its Synergistic Interface Modification on the High-Voltage Cyclic Stability of Ultra-High Nickel Cathode Materials

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Among all the intercalation compounds, ultrahigh-Ni (Ni > 0.9) layered oxides are the most probable commercially available cathode materials, with the high specific capacity and high discharge plateau, for the next-generation high energy lithium-ion batteries. However, with increasing Ni content in the oxides, fast decay of both the discharge capacity and mid-point potential during cycling is unavoidable due to the structural instability, which is the critical obstacle for the commercialization of ultrahigh-Ni oxides, including apparent microcracks and intrinsic phase transitions. In this work, we systematically combine the charge self-balancing, double doping, interface regulation and other modification strategies to prepare the ultrahigh-Ni layered oxide by co-precipitation method. The as-prepared ultrahigh-Ni cathode design can be attributed to following fundamental principles: (i) Strong bonding to oxygen: Al^{3+} and high-valence dopants, for example, Nb^{5+}, Mo^{6+}, and W^{6+}, doping in transition metal (TM) cation sites (tetrahedral interstices and octahedral sites) reinforces the robust bonds with O. (ii) the formation of more Ni^{2+} along with the high-valence dopants doping are to maintain charge imbalance, increasing cation mixing. The introduction of Al can help overcome the drawback of increased cation mixing caused by high-valence dopants doping. (iii) Radially oriented structure: Doping with high-valence dopants is favorable to reassemble primary grains, resulting in the dense microspheres with radially oriented morphologies. Such microstructure modification can greatly suppresses the microcracks through dissipating the strain caused by the serious H2-H3 phase transition. Correspondingly, the dual-doping ultrahigh-Ni oxides demonstrate superior capacity retention at 1C rate over 300 cycles with an upper cutoff potential of 4.4V (vs Li/Li^{+}). Consequently, this work provides an efficient strategy to design and stabilize ultrahigh-Ni layered oxides for high energy lithium-ion batteries.