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Effect of surface modification using a sulfate-based surfactant on the electrochemical performance of Ni-rich cathode materials

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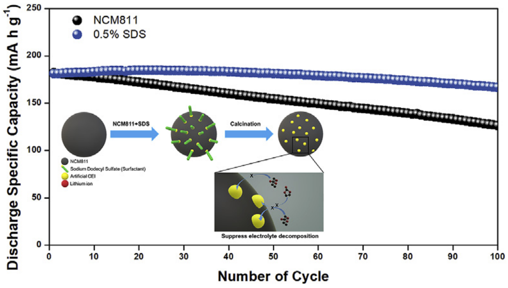
HIGHLIGHTS

- The surface of the Ni-rich NCM cathode is modified by thermal treatment of SDS.
- Thermal treatment of SDS provides SO_x-based artificial CEI layer on NCM cathode.
- SO_x-immobilized artificial CEI layer improves surface stability of NCM cathode.
- SO_x-based artificial CEI layer effectively mitigates decomposition of electrolyte.
- The cycling retention of SDS-modified Ni-rich NCM cathode is improved.

GRAPHICAL ABSTRACT



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ABSTRACT

Ni-rich layered oxides (Ni-rich NCM) have received much attention owing to their high specific capacity, but poor cycling performance attributed to their inferior surface properties is still considered to be a bottleneck preventing the expansion of the wider adoption of these materials in lithium-ion batteries (LIBs). In this work, we propose one-step efficient surface modification process which utilizes an organic surfactant (SDS) with a sulfate functional group in order to improve the surface stability of Ni-rich NCM materials. The surface modification provides a sulfate-embedded cathode-electrolyte interphase (CEI) layer on the Ni-rich NCM surface, which includes a SO_x functional group. All of cells employing SDS-treated NCM cathode exhibit higher specific capacity retention after 100 cycles. Among these, the cell cycled with the 0.5% SDS-treated Ni-rich NCM cathode exhibited specific capacity retention of 91.9%, which is a remarkable increase compared with the cell cycled with bare NCM811 (69.6%). Additional analyses of the cycled electrodes indicated that the better cycling performance of the SDS-treated NCM811 cathode is attributable to the stabilization of the NCM811 surface; less electrolyte decomposition was observed in a cycled SDS-treated NCM811 cathode when analyzed by SEM, EIS, and XPS.

1. Introduction

Ensuring a high level of electrochemical performance together with a certain level of safety has become a critical issue as

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increasing demands for large-scale devices such as electric vehicles (EVs) and energy storage systems (ESSs) [1–3]. Accordingly, advanced cathode materials with a high specific capacity or a high working potential have received a considerable amount of attention as alternative cathode materials because the energy density of the cell is directly proportional to the specific capacity and working potential of the electrode material [4,5]. Achieving a high energy density in cells is a challenging issue at this time because it significantly determines the specifications for large-scale applications, such as fuel mileage levels (for EVs) or operation times (for ESSs). Among the many attractive candidates, a layered lithium nickel cobalt manganese oxide ($Li[Ni_xCo_yMn_z]O_2$, NCM) has been the main subject of research owing to the intrinsic electrochemical properties of this material [6–10]. Note that the specific capacity of a NCM cathode material can be increased by increasing the Ni composition in the layered oxide structure; a Ni-rich NCM cathode material composed of a high Ni composition ($x \geq 60\%$) can realize a specific capacity of more than 170 mA h g^{-1}, meaning that this material can be considered as one option for replacing conventional lithium cobalt oxide ($LiCoO_2$), which offers a specific capacity of approximately 150 mA h g^{-1}.

Ni-rich NCM cathode materials are now gradually being utilized in LIB applications; however, the poor surface stability levels of these materials should be improved in order to ensure high cycling performance of the cell. This is mainly attributed to the decomposition of the electrolyte: the electrolytes easily decompose on the surface of a Ni-rich NCM cathode, after which the accumulated decomposed adduct material seriously increases the interfacial resistance of the cathode, which causes rapid fading of the cycle life of the cell [11–13]. Note that electrolyte decomposition on the surface of the Ni-rich NCM cathode always occurs through an electron transfer reaction between the electrode and the electrolyte; many attempts to reduce the surface reactivity of Ni-rich NCM cathodes have been made, such as surface coatings with inorganic materials [14–18] and use of an organic material as a functional electrolyte additive [19–25] to enable the creation of a cathode-electrolyte interphase (CEI) layer on the Ni-rich surface.

In this work, we propose a surface-functionalized Ni-rich NCM cathode material which is realized through an efficient surface coating process with sodium dodecyl sulfate (SDS) as the surfactant (Fig. 1). SDS has amphiphilic characteristics; it is composed of a hydrophobic body (dodecyl functional group) with a hydrophilic tail (sulfate (SO_4) functional group). Note that the SO_x chemical moiety is considered to be an effective chemical functional group to improve the surface stability of cathodes because it only allows ion migration while inhibiting the electron transfer reaction at the interface between the electrode and the electrolyte, thus suppressing electrolyte decomposition during the electrochemical process, as it acts as a CEI layer [26–28]. In detail, partial negative charges develop at the oxygen atoms of the SO_x functional group as a result of the resonance structure ($S^+–O^-$). The partial negative charges can improve the kinetic behavior of Li^+ by means of the ion hoping mechanism [29,30], implying that embedding the SO_x functional group could effectively improve the cycling performance of a Ni-rich NCM cathode. In addition, the spontaneous presence of hydrophilic and hydrophobic functional groups in the molecular structure of SDS would allow fine control of the CEI morphology by controlling the SDS arrangement on the surface of the Ni-rich NCM cathode. Note that SDS as a surfactant plays a key role in the spontaneous organization of molecular units into ordered structures. If SDS forms a secondary cluster via a self-assembly process, the clusters remain stable on the surface due to steric and electronic repulsions between the clusters [31–33], resulting in an increase in the coating uniformity of the CEI layers. In addition, SDS is a typical commercial surfactant; it is very inexpensive and readily available anywhere. In other words, the use of SDS as a precursor for a surface coating process would be beneficial in terms of processability because it is scalable and economical. With these material strategies in hand, surface functionalized Ni-rich NCM was synthesized by an efficient one-step thermal treatment process and its physicochemical and electrochemical properties were then evaluated.

2. Experimental details

SDS was dissolved in 50 mL of *N*-methyl-2-pyrrolidone (NMP, Sigma Aldrich) and the resulting solution was then stirred for 2 h at room temperature. $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ powder (NCM811, Ecopro) was added to the transparent solution and dispersed for 1 h. The solution was then filtrated and the resulting powder was subjected to a thermal treatment at 600 °C for 3 h. After material synthesis, its surface morphology was characterized by scanning electron microscopy (SEM, FEI) and the chemical functional groups were analyzed by Fourier transform infrared spectrometry (FT-IR, Bruker). The analysis of the bulk structure of NCM811 was conducted by X-ray diffraction (XRD, PANalytical).

For the preparation of the NCM811 cathode, 90 wt% (SDS-treated) NCM811 powder, 5 wt% of poly(vinylidene fluoride), and

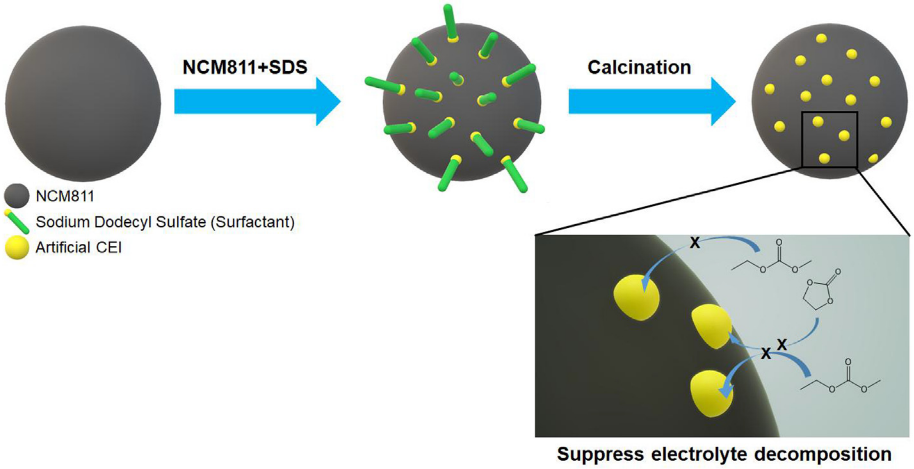

Fig. 1. Scheme for surface modification of NCM811 cathode by SDS.