



# A novel imidazole-based electrolyte additive for improved electrochemical performance of high voltage nickel-rich cathode coupled with graphite anode lithium ion battery



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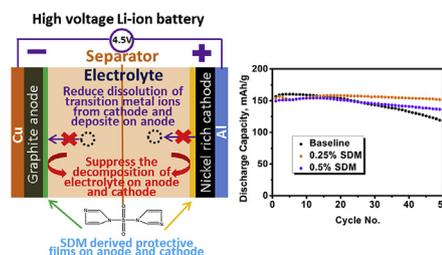
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## HIGHLIGHTS

- SDM is investigated as an electrolyte additive for graphite/LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cell.
- The cycling performance is enhanced with appropriate amount of SDM addition.
- The surface layer derived from SDM on the cathode is more stable and robust.
- Dissolution of Mn, Co, and Ni can be reduced by adding SDM.

## GRAPHICAL ABSTRACT



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## ABSTRACT

1,1'-sulfonyldiimidazole (SDM) has been investigated as a novel carbonate-based electrolyte additive for high voltage nickel-rich cathode chemistry, graphite/LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cells. Upon cycling at high voltage for 50 cycles, graphite/LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cells with SDM containing electrolyte have superior cycling performance than the cells with baseline electrolyte, specifically, 96.9% and 73.1% capacity retention, respectively. Moreover, cells with 0.25 wt. % SDM have lower impedance and better elevated temperature storage performance as well. The functional mechanism of electrolyte containing SDM on improved cycling performance is elucidated with ex-situ analytical techniques, including scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and fourier transform infrared spectroscopy (FTIR), etc. The surface analysis result reveals that SDM has been involved into the surface film forming on the LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cathode and graphite anode as well, which can simultaneously provide protection for both cathode and anode upon cycling to high voltage, leading to enhanced cyclability of the high voltage (4.5 V vs. Li/Li<sup>+</sup>) graphite/LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cells with the presence of SDM.

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## 1. Introduction

Lithium ion batteries (LIBs) have been used widely as dominant power source for portable electronic devices and also have

attracted growing interest for the application in electric vehicles and hybrid electric vehicles [1–5]. In order to meet the demands of these applications, further improvement in energy density of LIBs are required [6–8]. The energy density of LIBs can be improved by enhancing the specific capacity and the operating voltage of individual cells [9]. Among various cathode materials, layer-structured Ni-rich cathodes (Ni content  $\geq 0.5$ ), such as  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ ,  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$  and  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  have been considered as prospective cathode candidates for high energy density LIBs [10–13]. Extra capacity could be attained by charging the cells to high voltage ( $\geq 4.5$  V vs.  $\text{Li}/\text{Li}^+$ ) with the use of Ni-rich cathodes [14–17]. Unfortunately, high voltage is always accompanied by serious oxidative decomposition of the traditional  $\text{LiPF}_6$ /carbonate electrolyte [18–21], and these decomposed products lead to continuous growth of an undesirable surface film on the cathode, which is impeditive and erratic, resulting in bad cycling performance and poor coulombic efficiency [22]. It has been reported in the literatures that transition metal cations tend to dissolve from the Ni-rich cathode and subsequently move toward the graphite anode during cycling and aging process. This can destroy the formed solid electrolyte interface (SEI) on the graphite surface, resulting in additional lithium loss and capacity fading upon cycling [16,23–25].

Surface modification of Ni-rich cathodes with  $\text{Al}_2\text{O}_3$ ,  $\text{AlF}_3$ ,  $\text{SiP}_2\text{O}_7$  and  $\text{LiAlO}_2$  have been verified as an effective approach for improving the cycling performance of Ni-rich cathodes at high voltage [26–30]. But the surface modification usually involves complicated synthetic processes and high manufacturing cost [31].

Graphite is the preferred anode material and has been widely used for state-of-the-art LIBs due to its excellent advantages: relatively high capacity, low cost and environmental friendliness [32–36]. However, the layered structure of graphite anode is vulnerable and may be damaged when co-intercalation of electrolyte solvent occurs [37]. Therefore, a robust and protective SEI should be built up on the graphite anode. It has been reported that electrolyte additives such as vinylene carbonate (VC), fluoroethylene carbonate (FEC), 4-fluorophenyl acetate (4-FPA), propane sultone (PS) and 1-fluoropropane-2-one (FA) are able to form a SEI film on the graphite anode [36,38–45]. The additive-derived SEI film protects the graphite and reduces further decomposition of the electrolyte.

The concept by forming stable SEI via incorporation of additives to inhibit electrolyte reduction has been expanded to cathode surface film forming as well [46]. According to some recent studies, cathode film forming additives, including methylene methyl disulfonate (MMDS), tris (trimethylsilyl) borate (TMSB) and tris (trimethylsilyl) phosphate (TMSP), have been used to improve the cycling performance of the cells with Ni-rich cathode upon cycling at high voltage. These film forming additives tend to incorporate into cathode surface film forming process, resulting in a robust surface film on Ni-rich cathodes [47–50].

Several electrolyte additives reported recently are able to simultaneously form protective surface film on cathode and anode, and this unique functionality demonstrates more convenient and effective approach to improve the electrochemical performance of LIB. Li et al. reported that the cycling performance of the graphite/ $\text{LiMn}_2\text{O}_4$  cell at elevated temperature can be significantly improved with the use of prop-1-ene-1,3-sulfone (PES) [37], which can simultaneously form protective film on the graphite electrode and the  $\text{LiMn}_2\text{O}_4$  electrode. Xu et al. reported lithium difluoro (oxalato) borate ( $\text{LiDFOB}$ ) was considered as an effective additive for graphite/ $\text{LiFePO}_4$  cell with the formation of an oxalate-borate derived film on both anode and cathode, as well [51].

In this study, we report a novel electrolyte additive, 1,1'-sulfonyldiimidazole (SDM), to improve the electrochemical performance

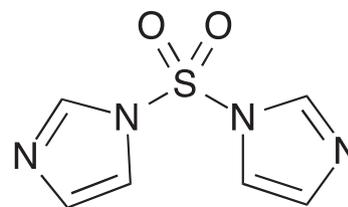
of graphite/ $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  cell upon cycling at 4.5 V vs.  $\text{Li}/\text{Li}^+$ . SDM possesses unique functionality by offering simultaneous protection to the graphite anode and  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  cathode upon cycling at high voltage, 4.5 V vs.  $\text{Li}/\text{Li}^+$ . Electrochemical methods combination with ex-situ surface analyses have been used to elucidate the effects of SDM containing electrolyte on the improved performance of graphite/ $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  cell upon cycling at 4.5 V vs.  $\text{Li}/\text{Li}^+$ .

## 2. Experimental section

1.0 M lithium hexafluorophosphate ( $\text{LiPF}_6$ ) dissolved in a solution of 3:5:2 ethylene carbonate (EC)/ethyl methyl carbonate (EMC)/diethyl carbonate (DEC) (wt.%) (baseline electrolyte) was obtained from Dongguan Kaixin Battery Materials Co., Ltd., China, and used without further purification. 1,1'-sulfonyldiimidazole (SDM, assay  $\geq 99.5\%$ ) was purchased from Fujian Chuangxin Technology Co., Ltd., China, and used without further purification. Electrolytes with SDM contain 0.25 or 0.5% by weight. Molecular structure of SDM is shown in Scheme 1. The composite  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  cathodes obtained from Foshan Advanced Electronics Energy Co., Ltd., China, containing 97.5% active material, super P (1.0%) and PVDF (1.5%). The composite graphite anodes obtained from Foshan Advanced Electronics Energy Co., Ltd., China, consisting of 95.5% graphite, super P (1.0%), CMC (1.5%) and SBR (2.0%). Graphite/ $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  2025-type coin cells with Celgard 2400 as separator were assembled in an argon glove box for electrochemical performance measurements.

The electrochemical charge/discharge behavior of  $\text{Li}/\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  cells and graphite/ $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  cells were explored on a Land cell test system (Land CT2001A, China) according to the following procedure: cells cycled at 25 °C were first charged to 4.5 V at a constant current (0.2 C for full cells and 0.5 C for half cells) followed by a constant voltage charge ( $V = 4.5$  V) until the current decreased to 10% of the applied charging current, and then the cells were discharged to 2.75 V with the same constant current. The  $\text{Li}/\text{graphite}$  cells were charged and discharged between 0.01 and 2.5 V at 0.2 C. Cyclic voltammetry was performed on Solartron-1480 (England) in the potential range of 0.01–2.5 V at a scanning rate of 0.1  $\text{mV s}^{-1}$ . The electrochemical impedance spectroscopy (EIS) were carried out under discharged state, with the amplitude of 5 mV, and the frequency ranging from  $10^5$  Hz to 0.01 Hz by using a PGSTAT-30 electrochemical station (Autolab Metrohm, Netherlands). Self-discharge measurements of the graphite/ $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  cells were performed according to the following protocols: cells were charged to 4.5 V with a constant current of 0.2 C, followed by a constant voltage ( $V = 4.5$  V) charge with a cut-off current of 10% of applied charging current, and then the cells were stored at open circuit voltage for 25 days at elevated temperature (55 °C).

The cycled graphite/ $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  cells were disassembled in a glove box filled with high purity argon. Both the cycled graphite anode and  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  cathode were rinsed with anhydrous dimethyl carbonate (DMC) three times to remove the residual EC



Scheme 1. Molecular structure of SDM.

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