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YAL SOCIETY CHEMISTRY

# Journal Name

# ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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# A bifunctional electrolyte additive for H<sub>2</sub>O/HF scavenging and enhanced graphite/LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cell performance at a high voltage

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A novel strategy for selecting an additive based on understanding the influence of different functional groups on electrochemical characteristics is adopted. *N,N*-diethylamino trimethylsilane (DEATMS) is tested as a bifunctional electrolyte additive to scavenge  $H_2O$  and neutralize HF in the electrolyte and enhance the behaviour of graphite/LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cells operating at a high voltage (4.5 V vs. Li/Li<sup>+</sup>) or elevated temperature (55 °C). With 2% DEATMS, no LiPF<sub>6</sub> hydrolysis species is found after storage at 55 °C for 6 days, even with a moisture content of 2000 ppm in the electrolyte. In addition, the graphite/LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cells containing DEATMS show cycling performances superior to those of the cells without DEATMS upon cycling for 100 cycles at a high voltage (85.5% vs. 72.0%) or high temperature (81.2% vs. 70.6%). The sacrificial oxidation of DEATMS on the cathode surface restricts direct contact between the electrolyte and cathode, improving the electrochemical performance. The *ex situ* surface analysis of the electrodes after cycling indicates that both the electrolyte decomposition and Mn dissolution are inhibited by the deposition of DEATMS oxidation products.

# Introduction

Because of their high operating voltage, high energy density, excellent cycling performance and good rate capability, lithium-ion batteries (LIBs) are the most popular power supplies for portable electronics and will likely dominate large-scale energy storage applications for electric vehicles (EVs), hybrid electric vehicles (HEVs) and energy storage systems (ESSs).<sup>1-3</sup> The equation  $\Delta E = \int_{0}^{\Delta Q} V \cdot q dq$ , where E is the energy, V is the voltage and q is the charge, shows that increasing the operating voltage can improve the capacity density of high energy density LIBs for transportation applications. Therefore, high-voltage cathode materials have attracted more attention. In addition to investigating 5 V novel cathodes, such as LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> (4.7 V vs. Li/Li<sup>+</sup>),<sup>4-6</sup> Li<sub>2</sub>CoPO<sub>4</sub>F (5.1 V vs. Li/Li<sup>+</sup>),<sup>7,8</sup> and LiNi<sub>x</sub>Co<sub>1-x</sub>PO<sub>4</sub> (4.8-5.1 V vs. Li/Li<sup>+</sup>),<sup>9</sup> enhancing the operating voltage of nickel-rich layered oxide cathodes (LiNi<sub>x</sub>Co<sub>y</sub>Mn<sub>1-x-y</sub>O<sub>2</sub>, x ≥ 0.5) has also attracted attention from

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academia and the battery industry<sup>10-12</sup> because the practical capacities are proportional to the charging voltages. Among nickel-rich layered oxide cathodes, LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> (NCM523) is attractive due to its moderate combination of a good electrochemical stability and high capacity at high voltages.<sup>13, 14</sup> Unfortunately, when the charging potential reaches over 4.4 V vs. Li/Li<sup>+</sup>, the conventional electrolyte is anodically unstable, and many parasitic reactions can occur.<sup>15,</sup> <sup>16</sup> At high cut-off voltages, the electrolyte suffers from continuous oxidative decomposition, and the decomposed products collect on the cathode surface. The products and irreversible oxygen evolution result in deterioration of the cell performance because of the increasing internal pressure and resistance.<sup>17, 18</sup> Furthermore, high oxidation state transition metal cations (Mn<sup>4+</sup> and Ni<sup>4+</sup>) oxidize the carbonate solvent, and their reduced species undergo a disproportionation reaction, resulting in the dissolution of the transition metal cations in the electrolyte, especially  $Mn^{2+}$ .<sup>19, 20</sup> These cations tend to pass through the separator and be reduced on the graphite surface, which destroys the formed solid electrolyte interphase (SEI) layer and leads to the additional loss of active lithium.<sup>21-23</sup> Finally, electrolyte oxidation can release heat, which may cause a fire risk.<sup>24</sup> As a result, an efficient method to stabilize the interface between the electrolyte and cathode is needed for LIBs cycled at high voltages ( $\geq$  4.4 V) with an NCM523 cathode.

Several measures for enhancing the performance of cathodes at high voltages have been proposed, e.g., surface coatings of inorganic oxides ( $Al_2O_3$ ,  $SiO_2$ , MgO, and  $ZrO_2$  etc.)<sup>25,</sup>

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

<sup>26</sup> or organic polymers (PI<sup>27</sup> and PEDOT:PSS<sup>28</sup> etc.), using novel organic solvents with a high anodic stability or adding additives to the electrolyte. A surface coating prevents direct contact between the active material particles and the electrolyte, which restricts the oxidative decomposition of the electrolyte. However, large-scale industrial application of this technique is difficult and involves extra processing costs. Although some novel organic solvents have been reported to be stable over 5 V (vs.  $\text{Li}/\text{Li}^+$ ), such as nitriles,<sup>29, 30</sup> sulfones,<sup>31</sup> fluorinated carbonates<sup>20, 32</sup> and ionic liquids,<sup>33</sup> these alternative solvents have other problems, such as a lack of SEI formation on the graphite anode, high viscosity, or high cost. The use of electrolyte additives to prevent electrolyte instability at high voltages is cost-efficient and industrially easy to implement.

There are two main types of high-voltage additives that have been widely investigated by scientists. One type is "coordination-type" additives that contain two or more cyano groups (-CN). Succinonitrile (SN) is one of the earliest researched "coordination-type" additives, and Kim et al.<sup>34</sup> first reported an improvement in the thermal stability of graphite/LiCoO<sub>2</sub> cells because of the complex that formed between the surface metal atoms of Li<sub>x</sub>CoO<sub>2</sub> and the cyano groups of SN. Other dinitriles, such as glutaronitrile (GLN),<sup>35</sup> adiponitrile (ADN),<sup>36</sup> suberonitrile (SUN)<sup>37, 38</sup> and sebaconitrile (SEN),<sup>39</sup> have also been widely investigated as high-voltage additives in academia and the battery industry. The other type of high-voltage additive is "preferentially oxidized-type" additives with highest occupied molecular orbital (HOMO) levels higher than those of the carbonate solvents, and these additives can be preferentially oxidized on the cathode surface. Representatives of this type of high-voltage additive include conductive polymer monomers, such as thiophene,<sup>4</sup> and ethylene dioxythiophene (EDOT),<sup>41</sup> cyclic compounds, such as 1,3-propanesultone (1,3-PS),<sup>42</sup> prop-1-ene-1,3-sultone (PES),<sup>43</sup> and methylene methanedisulfonate (MMDS),<sup>44, 45</sup> and specific phosphites, phosphates and borates, 46 such as tris(trimethylsilyl) phosphite (TMSPi),<sup>47</sup> tris(trimethylsilyl) phosphate (TMSP),<sup>48</sup> and tris(trimethylsilyl) borate (TMSB).<sup>49-51</sup> These additives tend to be preferentially oxidized on the cathode surface, and their oxidation products can form a stable film or deposits on the cathode surface over the active sites of the cathode to prevent direct contact between the electrolyte and cathode. By this mechanism, the electrolyte decomposition and side-reactions between the electrolyte and cathode are significantly reduced.

The commercial LIBs electrolyte usually consists of LiPF<sub>6</sub> dissolved in a mix of carbonate-based solvents. Nevertheless, LiPF<sub>6</sub> has disadvantages such as thermal decomposition at high temperatures and a high reactivity with moisture. These problems are mainly caused by the decomposition of LiPF<sub>6</sub>, as shown in Eq. 1:<sup>52-54</sup>

$$LiPF_6 \rightleftharpoons LiF + PF_5 \tag{1}$$

The equilibrium favours the left under normal conditions. Nevertheless, in the presence of H<sub>2</sub>O, PF<sub>5</sub> reacts with H<sub>2</sub>O and Eq. 1 slants towards the right, producing an ionic insulator, i.e., LiF. The reaction of PF<sub>5</sub> with H<sub>2</sub>O, which generates POF<sub>3</sub>

Page 2 of 11

and HF, and the reaction of POF<sub>3</sub> with H<sub>2</sub>O to produce POF<sub>2</sub>(OH) and POF(OH)<sub>2</sub>, are illustrated in Eq. 2, 3 and 4:

$$PF_5 + H_2O \rightarrow POF_3 + 2 HF$$
(2)  
$$POE + H_Q \rightarrow POE (OH) + HE$$
(2)

$$POF_{3} + H_{2}O \rightarrow POF_{2}(OH) + HF$$
(3)

$$POF_{2}(OH) + H_{2}O \rightarrow POF(OH)_{2} + HF$$
(4)

These solid products LiF, POF<sub>2</sub>(OH), POF(OH)<sub>2</sub> and POF<sub>3</sub> will become part of the SEI layer and cause an increase in the cell impedance. Furthermore, the HF that is produced will erode the cathode surface and result in the dissolution of transition metal cations.<sup>55</sup> Since water hinders the performance of LIBs, eliminating moisture in batteries is important. One method to eliminate moisture is to use electrolyte additives, which can suppress PF<sub>5</sub> hydrolysis by strongly coordinating with PF<sub>5</sub>, such as hexamethylphosphoramide (HMPA)<sup>56</sup> and tris-2,2,2trifluoroethyl phosphite (TTFP),57 or by strongly coordinating with water molecules, such as lithium 2-trifluoromethyl-4,5dicyanoimidazole (LiTDI).58

Herein, we focus on a novel bifunctional additive that can scavenge H<sub>2</sub>O and neutralize HF in the electrolyte and enhance the electrochemical behaviour of a graphite/LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cell operating at a high voltage (4.5 V vs. Li/Li<sup>+</sup>) or elevated temperature (55 °C). We first examined the Si-N bond as the main chemical constituent in the additive structure because of its Lewis-base properties and H<sub>2</sub>O/HF-scavenger ability. Several silazanes containing a Si-N bond have been shown to scavenge H<sub>2</sub>O and neutralize HF in electrolytes and enhance the cycling and stability of LIBs, for instance, (HMDS),<sup>59</sup> hexamethyldisilazane heptamethyldisilazane (HTMDS)<sup>60</sup> and 1-(trimethylsilyl)imidazole (1-TMSI).<sup>61</sup> We also examined the trimethylsilyl group because it does not have a side effect on the properties of LIBs. In addition, the Si in the trimethylsilyl group reacts with fluorine and reduces LiF on the cathode surface.<sup>62, 63</sup> Lastly, we examined the diethyl group because of its higher positive inductive effect (+I effect) and ability to increase the HOMO energy of molecules, which ensures preferential oxidation on the cathode surface. Based on the above, we selected N,N-diethylamino trimethylsilane





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(DEATMS) as an additive, which is functionalized with a Si-N bond, trimethylsilyl group and diethyl group (Fig. 1a). The electrochemical behaviour of DEATMS and its influence on the performance of graphite/LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cells were investigated by combining theoretical calculations, linear sweep voltammetry (LSV) and cyclic voltammetry (CV), battery measurements with electrochemical impedance spectroscopy (EIS), ex situ Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), transmission electron microscope (TEM), field emission scanning electron microscopy (FE-SEM), and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Few additives have been reported to simultaneously: 1) scavenge H<sub>2</sub>O and neutralize HF and 2) be preferentially oxidized to improve the electrochemical performance of a cell. Moreover, our strategy for selecting an additive based on understanding the influence of different functional groups on the cell performance may be useful for the design and screening of electrolyte additives.

## Experimental

#### **Calculation methods**

The density functional theory (DFT) calculations were performed using the Gaussian 09 package.<sup>64</sup> The B3PW91/6-311++G(d, p) basis set was employed to optimize the equilibrium structures, since the B3PW91 HOMO/lowest unoccupied molecular orbital (LUMO) energy levels can be successfully related to molecular properties, such as the ionization potential and electron affinity, in a semiquantitative manner.<sup>47</sup> To investigate the effects of solvents, we used the conductor-variant polarized continuum model (CPCM). Herein, we selected a dielectric constant of 46.4 as a weighted mean value between the dielectric constant of ethylene carbonate (EC, 89.6) and dimethyl carbonate (DMC, 3.1) since the solvent contained EC: DMC = 1: 1. The Gibbs free energies were calculated at 298.15 K, and the Gibbs free energy changes of  $H_2O~(\Delta G_{HOH})$  and HF  $(\Delta G_{HF})$  with DEATMS were calculated to predict reactivity.

## Electrolyte and electrode preparation

The battery-grade lithium salt and solvents, LiPF<sub>6</sub>, EC and DMC, were kindly provided by Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd. The baseline electrolyte was prepared by dissolving 1 M LiPF<sub>6</sub> in a mixture of EC/DMC (1: 1 v/v). The 2% or 0.5% DEATMS-involved electrolytes were prepared by a mix of DEATMS (Aladdin, 98%) and the baseline electrolyte in a mass ratio. The moisture content of the baseline electrolyte is around 20 ppm as determined by the 831 KF Coulometer (Metrohm, Switzerland). To investigate the stability in the presence or absence of H<sub>2</sub>O, 2000 ppm (weight) deionized (DI) H<sub>2</sub>O was blended in the baseline electrolyte and the baseline electrolyte with 2 wt.% DEATMS (denoted 2% DEATMS). Similarly, to investigate the effect of using DEATMS as an HF scavenger, a 2000 ppm (weight) HF aqueous solution (40 wt.%, Xilong Scientific) was added to the baseline electrolyte and the 2% DEATMS electrolyte. The water or HF enrichment experiments were conducted in the glovebox to

reduce moisture contamination from the air. The NCM523 electrode was prepared by mixing 93.93 wt.% active material (Beijing Easpring Material Technology Co., Ltd), 2.33 wt.% Super-P (a carbon black conducting agent, IMERYS Graphite&Carbon), 0.93 wt.% KS-6 (a graphite conductive agent, IMERYS Graphite&Carbon) and 2.80 wt.% PVdF (polyvinylidene fluoride, Guangzhou Songbai Chemical Industry Co., Ltd) via mechanical stirring and coating the mixture on an Al current collector with a very high areal loading of  $11 \sim 13$ mg cm<sup>-2</sup>. The graphite electrode was fabricated from the active material (Shanghai Shanshan Tech Co., Ltd), Super-P, CMC (carboxymethyl cellulose sodium, Guangzhou Songbai Chemical Industry Co., Ltd) and SBR (styrene butadiene rubber, Guangzhou Songbai Chemical Industry Co., Ltd) in a weight ratio of 95.5: 1: 1.2: 2.3 on a Cu current collector via mechanical stirring with an areal loading of 6  $\sim$  8 mg cm<sup>-2</sup>. After the electrodes were dried under vacuum at 80 °C for 12 h, the graphite/LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> 2032-type coin cells were assembled in an argon-filled glovebox with an Asahi Kasei polyethylene (PE) membrane as the separator for the electrochemical behaviour tests.

#### **Electrochemical measurements**

To assess the anodic stability of the electrolytes in the presence or absence of DEATMS, LSV was carried out between the open circuit voltage (OCV) and 6 V vs.  $\text{Li/Li}^{+}$  at a scan rate of 0.1 mV s<sup>-1</sup> using a CHI660 electrochemical workstation (Chenhua, Shanghai) with a Pt working electrode and Li-metal counter and reference electrodes. The CHI660 was also used to conduct CV tests for a three-electrode cell with a graphite working electrode and Li-metal counter and reference electrodes.

The electrochemical charge/discharge behaviours of graphite/LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cells were tested on a Land CT2001A cell test system based on the protocol below: the current density was C/5 rate for the 1st cycle and followed by 100 cycles at 1 C for the constant current/constant voltage (CC/CV) charge and the constant current (CC) discharge mode at room (25 °C) or elevated (55 °C) temperature. The 1 C corresponds to 160 mA  $g^{-1}$  for cycling between 3 ~ 4.5 V and 145 mA  $g^{-1}$  for cycling between 3 ~ 4.3 V. The cut-off current of the constant voltage was 10% of the charging current. The EIS tests were performed under charged state, with the frequency ranging from 100 kHz to 0.1 Hz and the amplitude of 10 mV, by using a PGSTAT 302N electrochemical station (Autolab Metrohm, Switzerland). The self-discharge tests were carried out based on the following procedure: the current density was C/5 rate for the 1st cycle and followed by 10 cycles at 1 C for the CC/CV charge and the CC discharge mode at room temperature (25 °C). Afterwards, the cells were charged to 4.3 V for the CC/CV charge mode, and reserved at OCV for 7 days at 55 °C.

#### Material characterizations

The cycled cells were disassembled in an argon glovebox. Both the cycled anode and cathode were rinsed with DMC four times to remove the residual  $\text{LiPF}_6$  and EC deposited on the

DOI: 10.1039/C8SE00064F Journal Name

## ARTICLE

surface. Then, they were dried overnight and sealed under vacuum at 25 °C to avoid water and air contamination before the ex situ characterizations. Microstructure of the cathode particles after pre-cycling was analyzed with TEM (JEM-2100HR, JEOL, Japan). The surface morphologies of LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cathode and graphite anode were observed with FE-SEM (S-4800, Hitachi), and the chemical composition of the surface layer on them was analyzed by XPS with a PHI Quantum 2000 scanning ESCA (electron spectroscopy for chemical analysis) microprobe with Al Ka radiation (1486.6 eV) (Physical Electronics, Inc. US). The Raman spectra of  $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$  cathode were measured on a microscopic Raman instrument (Renishaw, UK) with a 0.5 mW helium/neon laser at 532 nm excitation. To analyse the metal dissolution behaviour at high temperatures, the electrolytes and anodes were extracted from graphite/LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cells cycled at 55 °C and analysed by a Plasma1000 ICP-AES (NSC, China). The ICP-AES samples were prepared with the procedure below: the anodes and remaining electrolytes cycled at 55 °C were soaked in anhydrous DMC (4 mL) for 15 days in an argon glovebox to dissolve the Mn ions in the DMC solution. Afterwards, the DMC solution was collected, treated with acid, and diluted to 10 mL with DI water for the ICP-AES analysis.

# **Results and discussion**

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## $\rm H_2O$ and HF scavenging in the electrolyte

The reactivity of DEATMS with H<sub>2</sub>O and HF and the Gibbs free energy changes of H<sub>2</sub>O ( $\Delta G_{HOH}$ ) and HF ( $\Delta G_{HF}$ ) with DEATMS were first investigated by DFT calculations. As shown in Fig. 1b, the estimated  $\Delta G_{HOH}$  and  $\Delta G_{HF}$  values are -14.4 kcal mol<sup>-1</sup> and -26.1 kcal mol<sup>-1</sup>, respectively, indicating that the Si-OH and Si-F bonds are energetically likely to form. The self-decomposition reaction of neutral DEATMS self-decomposition reaction is energetically unfavourable, namely, highly endoergic. This indicates that neutral DEATMS is more likely to scavenge water and neutralize HF than undergo the self-decomposition reaction.

To evaluate the impact of using DEATMS as a water scavenger, the moisture content of the electrolyte, in the presence or absence of DEATMS, was enriched by 2000 ppm to speed up the electrolyte hydrolysis, and the added molar ratio of DEATMS: H<sub>2</sub>O was slightly above 1: 1. As Fig. 2a shows, both the fresh baseline electrolyte and 2% DEATMS electrolyte are colourless. After the water enrichment and storage at 55 °C for one day, the baseline electrolyte was brown (Fig. 2b). As the storage time continued, the colour change became more obvious (Fig. 2c), and the baseline electrolyte was dark brown on the sixth day (Fig. 2d). However, the 2% DEATMS electrolyte remained colourless after 6 days of storage at a high temperature. This agreed with the result provided by Wilken et al.,<sup>65</sup> and their work showed that the colour change was indicative of LiPF<sub>6</sub> electrolyte degradation.

The fresh baseline electrolyte, 2% DEATMS electrolyte and their  $H_2O$ -enriched equivalents were characterized by  $^{31}P$  NMR

after 6 days in storage at 55 °C. As seen in Fig. 2e and Fig. 2f, the <sup>31</sup>P spectra of the fresh baseline and 2% DEATMS electrolyte contain a septuplet signal centred at -144.3 ppm, which belongs to the  $PF_6$  anion. After storage at 55 °C for 6 days, a new triplet signal centred at -15.9 ppm ( ${}^{1}J_{P-F} = 946$  Hz, attributed to OPF<sub>2</sub>OR-type compounds) and two new doublet peaks centred at -7.3 ppm  $({}^{1}J_{P-F} = 937$  Hz, attributed to OPF(OR)<sub>2</sub>-type compounds) and -7.5 ppm ( ${}^{1}J_{P-F} = 921$  Hz, attributed to OPF(OR)2-type compounds) emerged (Fig. S2, ESI<sup>+</sup>). To our knowledge, OPF<sub>2</sub>OR and OPF(OR)<sub>2</sub>-type compounds are common degradation products of LiPF<sub>6</sub>-based electrolytes.<sup>53, 54, 65</sup> Conversely, after 2% DEATMS was added to the baseline electrolyte, no LiPF<sub>6</sub> hydrolysis species were observed after storage at 55 °C for 6 days with the water enrichment, and only the PF<sub>6</sub> septuplet signal was presented in the <sup>31</sup>P spectrum, which indicated that LiPF<sub>6</sub> hydrolysis did not occur in the 2% DEATMS electrolyte. These NMR results were consistent with the lack of a significant colour change in the 2% DEATMS electrolyte.

To further investigate the effect of using DEATMS as an HF scavenger, a storage experiment with  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  powders and the HF-enriched electrolyte was conducted with and without DEATMS. The storage experiment illustrations are presented in Fig. 2g. All the components were assembled and sealed in an argon glovebox before storage, and the added molar ratio of DEATMS: (H<sub>2</sub>O + HF) was slightly higher than 1: 1. HF is known to be a major cause of the dissolution of transition metal cations on cathodes.<sup>55</sup> After storage at 55 °C for 3 days, a metal ion test (ICP-AES) was performed on the electrolyte supernatant after centrifugation (Fig. 2h). The concentration of Mn ions dissolved in the 2% DEATMS electrolyte (8.5 ppm) was much lower than that in the baseline electrolyte (200 ppm), which verified that DEATMS can effectively scavenge HF in the electrolyte.

The theoretical calculations and storage experiments after adding water or HF to the electrolyte proved that the electrolyte stability is adequately enhanced by the  $H_2O/HF$ scavenger properties of DEATMS. DEATMS is crucial to achieve a high stability electrolyte, particularly in the presence of high moisture levels or HF.

#### High-voltage battery performance at room temperature

The frontier molecular orbital energy, which reflects the ability to lose or gain electrons, is often used to forecast oxidation and reduction trends of molecules. Table 1 shows the HOMO/LUMO energies of EC, DMC, and DEATMS. The HOMO energy level of DEATMS is higher than that of the carbonate solvents, indicating that DEATMS is a better electron donor than the other molecules and should be preferentially oxidized on the cathode surface. Meanwhile, DEATMS possesses nearly the same LUMO energy as the carbonate solvents, and therefore, DEATMS may not participate in the reductive reaction on the anode surface. DEATMS is a potential additive for the cathode and should not decrease the performance of the anode material.

To investigate the anodic stability of DEATMS, LSV

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**Fig. 2** (a) Image of the fresh baseline (left) and 2% DEATMS (right) electrolytes. (b) Image of the baseline electrolyte with 2000 ppm  $H_2O$  (left) and the baseline electrolyte with 2% DEATMS and 2000 ppm  $H_2O$  (right) after storage at 55 °C for one day, (c) 3 days and (d) 6 days. (e) <sup>31</sup>P NMR spectra of the fresh baseline electrolyte and baseline electrolyte with 2000 ppm  $H_2O$  stored at 55 °C for 6 days. (f) <sup>31</sup>P NMR spectra of the fresh baseline electrolyte with 2% DEATMS and the baseline electrolyte with 2% DEATMS and 2000 ppm  $H_2O$  stored at 55 °C for 6 days. (f) <sup>31</sup>P NMR spectra of the fresh baseline electrolyte with 2% DEATMS and the baseline electrolyte with 2% DEATMS and 2000 ppm  $H_2O$  stored at 55 °C for 6 days. Insets are enlarged by the same factor. (g) Schematic illustration of the storage experiment after HF enrichment of the electrolyte. (h) The concentration of Mn ions dissolved from the NCM523 powders into the electrolyte after storage at 55 °C for 3 days with and without DEATMS.

experiments were conducted with a three-electrode cell using Pt as the working electrode. As shown in Fig. S3 (ESI<sup>+</sup>), the baseline electrolyte did not decompose until 5.0 V (vs. Li/Li<sup>+</sup>), but the starting oxidation potential of the DEATMS-containing electrolyte is approximately 3.5 V (vs. Li/Li<sup>+</sup>). It is noteworthy that the oxidation potential of baseline electrolyte acquired from LSV is evidently higher than that from the common sense, i.e., 4.4 V vs. Li/Li<sup>+</sup>. That is because unlike a real cathode, which is an interactive transition metal rich surface and possesses highly catalytic nature, an inert Pt working electrode usually gives higher value of oxidation potential.<sup>20,66</sup> As expected, DEATMS possesses a lower oxidation potential than the carbonate solvents, and thus, DEATMS will be preferentially oxidized on the cathode surface. The DEATMS oxidation products can deposit on the cathode surface and cover the cathode active sites, which can effectively prevent continuous electrolyte decomposition at a high voltage.

To further investigate the cathodic stability of DEATMS, CV experiments were conducted with a three-electrode cell using graphite as the working electrode. As shown in Fig. S4 (ESI<sup>+</sup>), the cathodic stability of the DEATMS-containing electrolyte is nearly the same as that of the baseline electrolyte, and no

significant differences were observed in the graphite electrode during the first three CV cycles for the cells with and without DEATMS. A reduction peak was observed at approximately 0.7 V before the Li intercalation reaction in the baseline and DEATMS-containing electrolyte and was ascribed to the reduction of EC to form the SEI layer on the graphite surface. The DFT calculations and CV results show that DEATMS will not participate in the reductive reaction on the anode surface and does not negatively affect the performance of the anode material.

To verify the different influences of DEATMS on the cathode and anode, the electrochemical properties of a  $Li/LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$  cell and Li/graphite cell with DEATMS as an electrolyte additive were tested. As shown in Fig. S5a (ESI<sup>+</sup>),

Table 1 HOMO and LUMO energy levels of EC, DMC and DEATMS.

Molecule	HOMO (eV)	LUMO (eV)
EC	-8.73	0.02
DMC	-8.47	0.06
DEATMS	-5.70	-0.05



**Fig. 3** Cycle performances of graphite/NCM523 cells with and without DEATMS operated in different voltage ranges between (a)  $3.0 \sim 4.3 \text{ V}$  and (b)  $3.0 \sim 4.5 \text{ V}$ . Voltage profiles for graphite/NCM523 cells cycled between  $3.0 \sim 4.5 \text{ V}$  with the (c) baseline electrolyte and (d) 0.5% DEATMS electrolyte. (e) EIS results for the graphite/NCM523 cells after 100 cycles in a voltage range of  $3.0 \sim 4.5 \text{ V}$  in electrolytes without and with 0.5% DEATMS.

the Li/LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cell with DEATMS showed a better cycling performance than the cell with the baseline electrolyte owing to the preferential oxidation of DEATMS. In contrast, the Li/graphite cells with different electrolytes showed nearly the same cycling stability, as presented in Fig. S5b (ESI<sup>+</sup>), which confirmed that DEATMS does not deteriorate the performance of the graphite anode.

To confirm whether DEATMS deposited on the cathode surface, the TEM images of pre-cycled LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cathodes are depicted in Fig. 4a-4d. After pre-cycling with the baseline electrolyte, a non-uniform surface layer with thickness from 0 ~ 60 nm is observed on the surface of cathode particles, which is derived from electrolyte decomposition at high voltage (Fig. 4c and 4d). This uneven surface layer cannot prevent the electrolyte from continuously decomposing as cycling progressed. While in DEATMScontaining electrolyte, the passivation layer is formed uniformly on the cathode surface with much thinner thickness than that formed in baseline electrolyte, approximately 5 nm (Fig. 4a and 4b). The constituents of the passivation layer on the pre-cycled LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cathode were further investigated by using XPS. As seen in Fig. S6 (ESI<sup>+</sup>), the N 1s peak intensity in the XPS spectra of the cathode with DEATMS is obviously higher than that with the baseline electrolyte. However, the Si 2p peaks in the XPS patterns of the cathode with DEATMS or the baseline electrolyte were not substantially

different. Because of the high valence of the Si atom and easy breakage of the Si-N bond, the Si-N bond may break during the oxidative decomposition of DEATMS. The -N group will deposit on the cathode surface due to the strong complex formation between the surface metal atoms and the lone electron pair of the N atom. Conversely, the saturated -Si will dissolve into the electrolyte. This conjecture is consistent with the above XPS results.

The electrochemical performances of graphite/LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cells under different conditions are shown in Fig. 3. When they were cycled between  $3.0 \sim 4.3$  V at 25 °C, the cells showed similar discharge capacity retentions and coulombic efficiencies after 100 cycles (Fig. 3a and Fig. S7a (ESI<sup>+</sup>)), which confirmed that DEATMS does not remarkably influence the behaviour of cells operating between  $3.0 \sim 4.3$  V at 25 °C. When the charging cut-off voltage was increased to 4.5 V (Fig. 3b and Fig. S7b (ESI<sup>+</sup>)), the cell with DEATMS had a high specific capacity of 148.1 mAh g<sup>-1</sup> after 100

Table 2 Fitted resistances for the cells after cycling between 3.0 ~ 4.5 V with and without 0.5% DEATMS.

Fitted resistand	ces (ohm)	$R_s$	R <sub>sei,an</sub>	R <sub>sei,ca</sub>	R <sub>ct</sub>	<b>R</b> <sub>sum</sub>
After 4.5 V	Baseline	2.1	14.1	3.0	28.6	47.8
cut-off cycling	DEATMS	2.3	5.1	9.5	20.7	37.6

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**Fig. 4** TEM images of the high-voltage pre-cycled NCM523 cathodes with (a, b) 0.5% DEATMS electrolyte and (c, d) the baseline electrolyte. SEM images of the (e) fresh NCM523 cathode and (f) cycled NCM523 cathodes at a high voltage with the baseline electrolyte and (g) 0.5% DEATMS electrolyte. (h, i and j) XPS profiles of the surface elements on the NCM523 cathode after 100 cycles at a high voltage with and without the DEATMS additive.

cycles and a high average coulombic efficiency with a capacity retention of 85.5% at a 1 C charging/discharging rate. In comparison, the baseline cell showed a specific capacity of 125.0 mAh g<sup>-1</sup> and a capacity retention of 72.0%. Moreover, the voltage profiles of the baseline cell dramatically changed during long-term cycling (Fig. 3c). The charging slope increasingly shifted to high values; however, the voltage slope of discharging shifted to low values during cycling. In contrast, both the average charge and discharge voltages of the DEATMS cell were extremely stable as cycling progressed, and the capacity retention was better (Fig. 3d).

This improvement can also be interpreted by the lower impedances of the DEATMS-containing cell after cycling. The impedances, which consist of the bulk resistance ( $R_{s}$ ), passivation layer resistance on the cathode ( $R_{SEI, CA}$ ), SEI resistance on the anode ( $R_{SEI, AN}$ ) and charge transfer resistance ( $R_{ct}$ ), <sup>67</sup> were analysed with an equivalent circuit diagram, as presented in Fig. 3e, and the fitting parameters are outlined in Table 2. A dramatic difference was not observed in the  $R_{s}$ . The  $R_{SEI, CA}$  of the DEATMS-containing cell was slightly higher than that of the baseline cell due to the deposition of DEATMS

oxidation products on the cathode surface. However, the  $R_{SEI,AN}$  (14.1  $\Omega$ ) and  $R_{ct}$  (28.6  $\Omega$ ) of the baseline cell were substantially larger than those of the DEATMS cell (5.1 and 20.7  $\Omega$ , respectively), which suggested that DEATMS may efficiently suppress the electrolyte decomposition on the anode surface and enhance the charge transfer between the electrodes and the electrolyte. Therefore, the overall cell resistance (the sum of  $R_{s}$ ,  $R_{SEI,AN}$ ,  $R_{SEI,CA}$  and  $R_{ct}$ ) of the baseline cell was much higher than that of the DEATMS containing cell.

The normalized Raman spectra of the cathodes in the pristine state and after cycling between 3.0 ~ 4.5 V are presented in Fig. S8 (ESI<sup>+</sup>). The pristine LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> electrode displays the A<sub>1g</sub> and E<sub>g</sub> bands for the v (MO<sub>6</sub>) vibrations (at approximately 600 cm<sup>-1</sup>) and  $\delta$  (O-M-O) vibrations (at approximately 500 cm<sup>-1</sup>), respectively.<sup>68</sup> During the charging step, a new band appeared at approximately 545 cm<sup>-1</sup> and showed a constant increase in intensity upon delithiation.<sup>69</sup> Singh et al. assigned this new band to the A<sub>1g</sub> band of Ni<sup>3+</sup>, which is present due to the oxidation of Ni<sup>2+, 70</sup> because the Raman spectra of LiNiO<sub>2</sub>, in which Ni is present in

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DOI: 10.1039/C8SE00064F Journal Name

the +3 oxidation state, show an  $A_{1g}$  band at 545 cm<sup>-1,71</sup> Normally, this new band will completely disappear due to the reduction of Ni<sup>3+</sup> during the discharge step. However, continuous structural degradation occurs on the surface of LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> during high-voltage cycling. The electrode polarization becomes more severe, preventing full lithiation of the cathode, even at 3.0 V, and causing a Li deficiency on the cathode surface.<sup>72</sup> Thus, some Ni<sup>3+</sup> must remain on the cathode surface at 3.0 V to achieve charge neutrality. As the LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> surface degradation increases, the intensity of the A<sub>1g</sub> band of Ni<sup>3+</sup> also increases, as shown in the Raman spectra. Clearly, the ratio of  $A_{1g\text{-Ni}}^{\phantom{1}3+}/A_{1g}$  on the cathode surface with the DEATMS electrolyte was significantly lower than that with the baseline electrolyte, which indicated that structural degradation of the LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> surface was suppressed in the presence of DEATMS.

The SEM images of the cathodes cycled with the DEATMScontaining electrolyte or the baseline electrolyte are shown in Fig. 4e-4g. As presented in Fig. 4e, the spherical particles of LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> are obvious on the fresh cathode, and the rope-like material is conductive carbon black. After cycling with the baseline electrolyte at a high voltage for 100 cycles, some of the LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> particles sustained severe degradation, and some cracks appeared on the surfaces of the particles (Fig. 4f). This phenomenon can be attributed to the dissolution of the transition metal from the cathode surface upon operating between 3.0 ~ 4.5 V.<sup>73</sup> Nevertheless, in the presence of the DEATMS-containing electrolyte, the structure of the LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> particles was well maintained (Fig. 4g). This indicated that the DEATMS oxidation products deposited on the cathode surface can preserve the cathode upon cycling at a high voltage.

To further understand the surface composition of the cathode operated at a high voltage, XPS was used to determine the constituents on the cathode surface. Fig. 4h-4j shows the XPS F 1s, P 2p and N 1s spectra of the LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> electrode surface after 100 cycles with the 0.5% DEATMS electrolyte or baseline electrolyte. The main peak in the F 1s spectra at 685.0 eV belongs to LiF, and the peak at 687.2 eV corresponds to the decomposition products of  $LiPF_6$  ( $Li_xPF_v$  and  $Li_xPF_vO_7$ , denoted P-F) overlapping with the signal of fluorine in PVdF.<sup>61</sup> The LiF peak intensity was stronger for the cathode with the baseline electrolyte than that with the DEATMS-containing electrolyte. LiF is attributed to the decomposition of LiPF<sub>6</sub> and could result in increased cell impedance. In the P 2p spectra, the peaks at 136.3 eV and 134.4 eV can be assigned to  $Li_x PF_y$  and  $Li_x PF_y O_7$ , which are due to LiPF<sub>6</sub> decomposition on the cathode surface.<sup>73</sup> The intensities of LiF,  $Li_x PF_v$  and  $Li_x PF_v O_7$  were weaker on the cathode surface containing 0.5% DEATMS than those for the cathode cycled with the baseline electrolyte, which showed that the decomposition of LiPF<sub>6</sub> on the cathode surface was suppressed in the DEATMS-containing electrolyte. The N 1s peak intensity in the XPS spectra of the cathode with DEATMS was higher than that for the cathode with the baseline electrolyte, which indicated that the DEATMS oxidation

products deposited on the cathode surface are stable and will not break away from the cathode surface, even after 100 cycles at a high voltage.

The SEM images of the graphite anodes in the pristine state and after operating between  $3.0 \sim 4.5$  V are shown in Fig. S9 (ESI<sup>+</sup>). The graphite particles were obvious before cycling, as shown in Fig. S9a. However, after 100 cycles at a high voltage with the baseline electrolyte, the particles were encased by a thick SEI film and had round edges and rough surfaces (Fig. S9b). This is due to the transition metal ions deposition from continuous the cathode. resulting in electrolyte decomposition. In contrast, the particles were still recognizable after cycling with the DEATMS-containing electrolyte and maintained sharp edges and smooth surfaces (Fig. S9c). These behaviours agree with the EIS data shown in Fig. 3e.

XPS was used to further comprehend the surface composition of the cycled graphite anodes. As seen in Fig. S10 (ESI<sup>+</sup>), the F 1s spectra of the anodes showed two main peaks. The peak at 685.0 eV corresponds to LiF, and the peak at 687.2 eV corresponds to other LiPF<sub>6</sub> decomposition products (denoted P-F).<sup>61</sup> In the P 2p spectra, the peak at 136.5 eV represents Li<sub>x</sub>PF<sub>y</sub>, while the peak at 133.2 eV can be assigned to Li<sub>x</sub>PF<sub>y</sub>O<sub>z</sub>.<sup>43</sup> The graphite anode with the DEATMS-containing electrolyte displayed weaker intensities for Li<sub>x</sub>PF<sub>y</sub>O<sub>z</sub> and LiF, and these results and the SEM images of the graphite anodes indicate that electrolyte decomposition on the graphite surface is also inhibited in the presence of DEATMS.

## Impact of DEATMS at an elevated temperature

To determine the effectiveness of the DEATMS oxidation products deposited on the cathode surface during high-temperature cycling, the graphite/LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cells were cycled at 55 °C for over 100 cycles with the baseline or DEATMS-containing electrolyte. The cell with DEATMS displayed a better capacity retention (81.2%) than the baseline cell (70.6%), which indicated that the addition of DEATMS dramatically improves the high-temperature property of graphite/LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cells operated at 55 °C (Fig. 5a and Fig. S11 (ESI<sup>+</sup>)).

Transition metal (especially Mn) ion dissolution from  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ , which is usually triggered by HF, is a vital element that is responsible for capacity fading at high temperatures. The amount of dissolved Mn in the electrolyte and the deposition on the graphite anode after 100 cycles at 55 °C were tested by ICP-AES, as shown in Fig. 5b. Fewer Mn ions were detected in the cell cycled with the DEATMS-containing electrolyte than the baseline cell. In other words, the deposited DEATMS oxidation products protected the  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  surface from HF attack, resulting in less Mn dissolution.

The electrolyte decomposition extent can be evaluated via testing the self-discharge of cells at a state of charge (SOC) of 100%. Hence, self-discharge tests were performed for the graphite/LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cells with and without DEATMS at



**Fig. 5** (a) Cycle performance and (b) dissolved Mn content in the electrolyte and deposition on the graphite anode of graphite/NCM523 cells with and without DEATMS cycled between  $3.0 \sim 4.3$  V at 55 °C. (c) The self-discharge curves of graphite/NCM523 cells without and with DEATMS after storage in a fully charged state for 7 days at 55 °C.

an elevated temperature. The change in the cell OCV as a function of the storage time is depicted in Fig. 5c. In contrast to the additive-containing cell, a rapid OCV drop was observed in the cell without DEATMS, which indicated rapid re-lithiation via self-discharge. Thus, the self-discharge rate of the cell with DEATMS at a 100% SOC is smaller than that of the cell without DEATMS due to suppressed electrolyte oxidation.

# Conclusions

In summary, N,N-diethylamino trimethylsilane (DEATMS) is first presented as a bifunctional electrolyte additive for scavenging H<sub>2</sub>O and neutralizing HF in the electrolyte and enhancing the behaviour of graphite/LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cells operating at a high voltage (4.5 V vs. Li/Li<sup>+</sup>) or elevated temperature (55 °C). According to the theoretical calculations, storage experiments after water or HF enrichment and <sup>31</sup>P NMR results, the electrolyte stability is adequately improved in the presence of DEATMS, and the decomposition of LiPF<sub>6</sub> is greatly suppressed due to the H<sub>2</sub>O/HF-scavenging characteristics of DEATMS. This can reduce the requirement for extensive drying during the manufacturing process and contribute to energy savings. DEATMS can be preferentially oxidized on the cathode surface to form a protective film, and DEATMS will not participate in the reductive reaction on the anode surface; i.e., it does not influence the performance of the anode material. The DEATMS oxidation products deposit on the cathode surface to effectively improve the interfacial stability, greatly mitigate the electrolyte decomposition, dramatically reduce transition metal dissolution from the cathode, and suppress the structural degradation of the  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  surface. Therefore, the behaviour of a graphite/LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cell operating at a cut-off voltage of 4.5 V or 55 °C is enhanced. DEATMS is a promising bifunctional additive that can be used for battery production. Moreover, the results of this work and our strategy for selecting an additive will contribute to the design and screening of suitable electrolyte additives for applications in high-voltage LIBs.

# **Conflicts of interest**

There are no conflicts to declare.

# Acknowledgements

This work was financial supported by National Natural Science Foundation of China (21603179), the Fundamental Research Funds for the Central Universities (20720170021), National Key Research&Development Plan (2017YFB0102000) and National Natural Science Foundation of China (21621091). The authors are grateful to Qing Lan for his kind help with NMR <sup>31</sup>P experiments, and wish to express their gratitude to Prof. Daiwei Liao for his valuable suggestions.

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# **Table of Contents Entry**



A novel strategy for selecting additives is adopted and a bifunctional additive is investigated for  $H_2O/HF$ -scavenging and enhanced cell performance.