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Enhanced electrochemical performance and thermal stability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ using the electrolyte with sulfolane

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A sulfide-based SEI layer was formed on the surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode by using a sulfolane-carbonate solvent mixed electrolyte, leading to the improvement of the electrochemical performance. Moreover, the thermal stability of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode was also significantly improved with the presence of the SEI. ARC (Accelerating Rate Calorimetry) test shows that the self-heating rate of the delithiated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material in the sulfolane-carbonate electrolyte was suppressed.

In order to satisfy the increasing demand of next generation of electronic devices, Li-ion batteries with more safety, longer lifespan and higher energy densities are required. To improve the energy densities of Li-ion batteries, cathode materials with high operating voltages, such as spinel LiMn_2O_4 , have been widely researched.¹⁻³ But the cycling behaviour of LiMn_2O_4 is poor owing to Jahn-Teller distortion of Mn^{3+} and structure collapse. Hence, the Ni-substituted partially spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with stable structure and improved cycling life has been paid great attentions since it was first reported.⁴ Compared with commercialized LiCoO_2 , $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ possesses higher potential plateau (4.7 V vs. Li^+/Li) and energy density (650 Wh/Kg), which is expected as an alternative cathode for next generation LIBs. However, the promising cathode for Li-ion batteries still suffers from poor rate and cycling performance, especially from safety concern. The weak compatibility between the charged $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode and present carbonate-based commercial electrolyte is a critical issue, which severe side reactions would emerge on the interface at such a high operating voltage.⁵ The common electrolyte based on carbonate ester solvents can be oxidized easily and decomposed on the active cathodes surface, which results in an undesirable battery performance and safety issue.⁶ Moreover, Mn^{2+} derived from the Mn^{3+} disproportionation can be easily dissolved into the electrolyte, resulting in a low coulombic efficiency and rapid capacity fading.

A lot of work were developed to overcome the shortcomings, for instance, metal ion substitution⁷ and surface modification⁸ are both efficient ways to improve the stability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode. But the introduction of metal oxide and metal fluoride would reduce the mass of active material as well as the electron conductivity of

cathode.⁹ Actually, the thermodynamic stability of electrolyte plays an important role in improving the battery performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Since the HOMO of present electrolyte based on carbonate solvent is below the voltage of $\text{Ni}^{4+}/\text{Ni}^{3+}$ redox couple in the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode.¹⁰ It is a crux to develop a larger voltage window of electrolyte or a passivation layer on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ surface to block electron transfer from electrolyte HOMO to the cathode and protect the electrolyte from oxidation. For example, some novel organic aprotic solvents, such as ionic liquid and sulfolane, can provide an appropriate voltage window to satisfy the demand of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode, due to their high decomposition potential, thermal stability and relative permittivity.^{6, 11} However, the high viscosity and low ion conductivity of these solvents still retard the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode to achieve an acceptable rate performance. Meanwhile, a favourable passivation solid electrolyte interface (SEI) forming on the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode surface not only contributes to the stability of electrolyte and safety characteristic of cell, but also obstructs the dissolving of Mn^{2+} , thus improves the cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode.^{12, 13}

Herein, a novel sulfolane-carbonate mixed electrolyte (named as E1 electrolyte) was introduced for the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode and compared with the carbonate electrolyte (E0). A stable SEI layer containing sulfide component forms on the surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode in the E1 electrolyte, resulting in the improved rate capability and cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells. The cathode material also exhibits the excellent thermal stability with E1 electrolyte with the existence of SEI, which is the key issue for the practical application of LIBs.

The cathode material of spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ used in this work was prepared via a solid state reaction.¹⁴ As illustrated in the scanning electron microscopy (SEM) image of Fig. 1, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ shows an octahedron micro-structure with particle size of 1-5 μm . According to the X-ray diffraction (XRD) pattern and Raman spectra in the ESI†, the as-prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode is assigned to a cubic spinel structure with a space group of $\text{Fd}\bar{3}\text{m}$ (JCPDS card 01-080-2162). It is believed that disordered $\text{Fd}\bar{3}\text{m}$ phase performs better electrochemical properties than the ordered $\text{P4}_3\text{2}$ phase, due to the presence of a small amount of Mn^{3+} .¹⁵

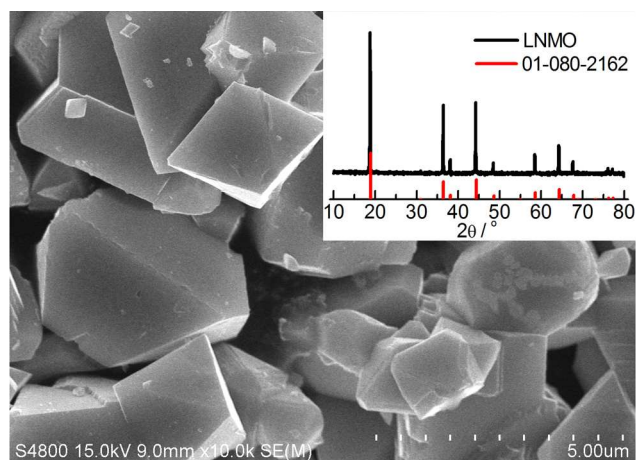


Fig 1: The SEM image and Powder XRD pattern of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel prepared by solid state reaction

The electrochemical performance of the spinel in two electrolytes was also investigated. As shown in Fig. 2a, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ shows typical electrochemical behavior in both electrolytes. The similar specific capacity of 113 mAh/g can be achieved at 0.1 C in both electrolytes. While at a high rate of 10 C, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material still delivers 97 mAh/g in E1, with a 8% increase than in E0 electrolyte. In addition, the obvious polarization of discharge curve in E0 electrolyte at 0.1 C shows that the spurious reactions tend to occur and result in the polarization resistance as well as large impedance,¹⁶ though it disappears gradually with the subsequent cycles. Conversely, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in E1 electrolyte shows an

enhanced rate-capability with less polarization. That means the presence of sulfolane not only increases the delivering capacities of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with less spurious reactions but also improves its energy densities under high rate conditions (Fig. 2b).

Further electrochemical impedance spectroscopy (EIS) investigation was carried out to understand the influence of sulfolane on electrochemical behavior of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode. The pristine EIS results of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}$ half cells after 50 cycles at 1C and the equivalent circuit were shown in Fig. 2c, in which the R_s is the solution resistance, R_{SEI} reflects the resistance of Li^+ migration through the surface film, and the R_{ct} is attributed to the charge transfer resistance across the surface film/active mass interface.¹⁷ Similar values of R_s in the two electrolytes can be observed, and both the Li^+ diffusion rates in the bulk material calculated by W_o at low frequency are about $10^{-12} \text{ cm}^2/\text{s}$.¹⁸ Though the R_{SEI} in the E1 electrolyte is a little bit larger, the R_{ct} , however, is 1.6 times less than that in E0 electrolyte (see Table S1†). It is evident that the charge transfer reaction is faster in the E1 electrolyte than in E0 electrolyte due to the lower R_{ct} , thus an improved rate performance and less polarization can be achieved. Meanwhile, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material also displays a high initial capacity of 103 mAh/g at 5C and exhibits a 98% capacity retention ratio (99 mAh/g) after 100 cycles in E1 electrolyte (Fig. 2d). However, the specific capacity of cathode decreases from 95 mAh/g to 77 mAh/g after 100 cycles in E0 electrolyte. The capacity retention ratio is only 81%. All above results confirms that sulfolane has the ability to enhance the charge transferring on the bulk surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material and form a favorable SEI that can also retard the dissolving loss of Mn^{3+} during charging/discharging to achieve a cycling stability.

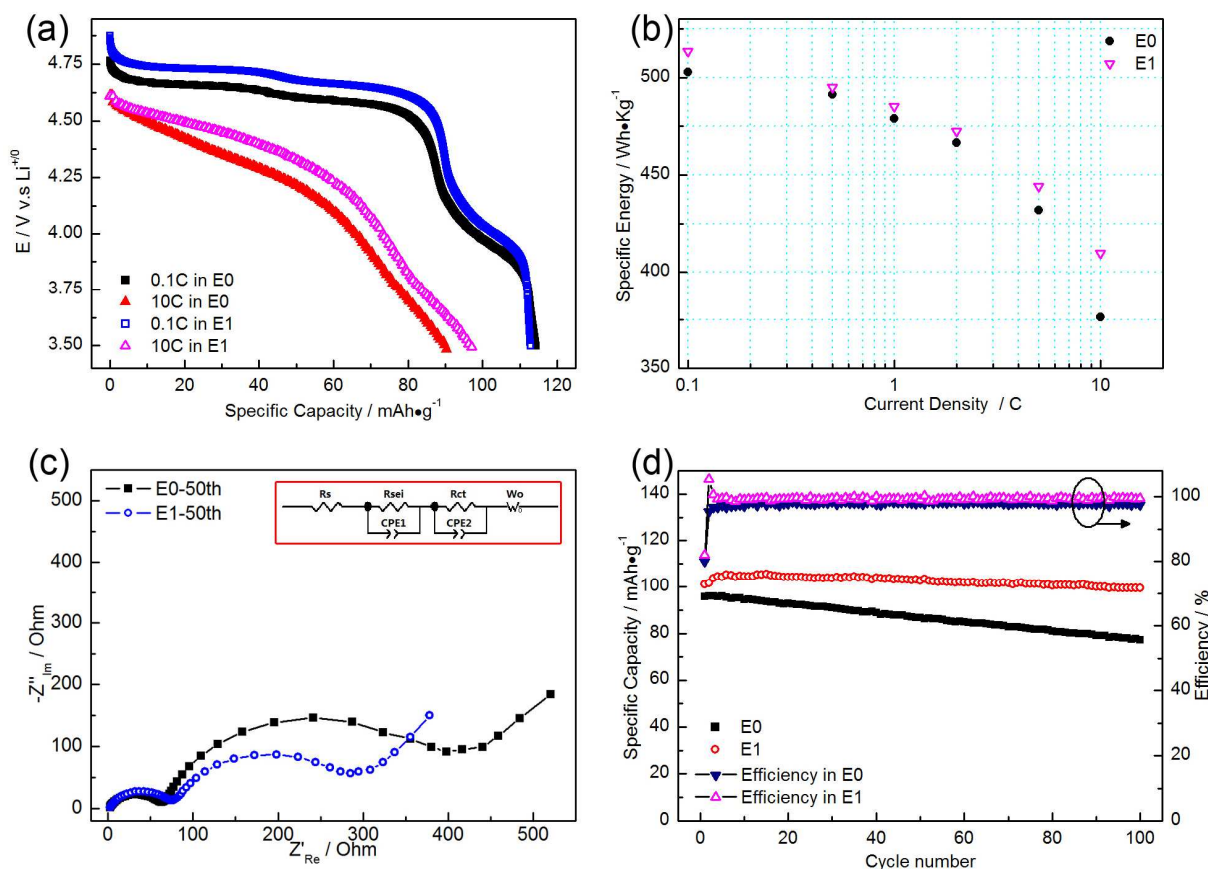


Fig 2: The discharge curves (a) and specific energies (b) of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at different current densities; (c) EIS of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}$ half cells after 50 cycles at 1C, insert is the corresponding equivalent circuit; (d) cycle and efficiency at 5C in two electrolytes.

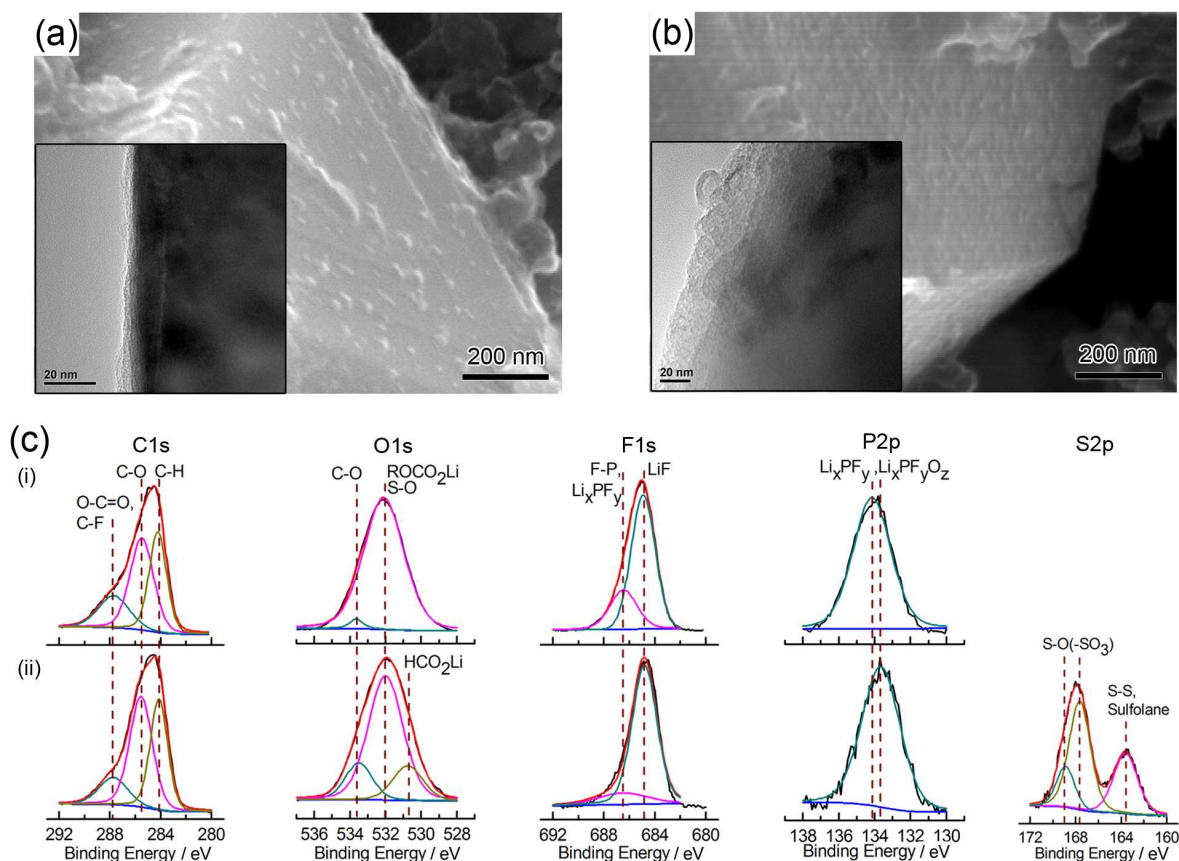


Fig 3: The SEM and TEM images of cathodes after 100 cycles at 1C in E0 electrolyte (a) and E1 electrolyte (b); (c) XPS spectra on the surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes after 100 cycles at 1C in (i) E0 electrolyte and (ii) E1 electrolyte.

As we can see from the SEM and TEM (transmission electron microscopy) images of surface morphologies of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes after 100 cycles at 1C in the two electrolytes (Fig.3a and Fig.3b), the thickness of SEI layer is only a few nanometers in the E0 electrolyte, while it is about 20 nm thick in the E1 electrolyte. And the latter is more uniform and compact, which explains why a more stable cycling performance of cathode can be obtained. Though the SEI forming in the sulfolane-carbonate mixed electrolyte is thicker, it does not impair the rates performance of the cathode. On the contrary, a smaller R_{ct} in the sulfolane-carbonate mixed electrolyte indicates that the SEI might contribute to modify the interface of cathode where a faster charge transfer process can be obtained.

Then the component of the special SEI and the contribution of sulfolane on the steady SEI were investigated by XPS analysis. As shown in Fig. 3c and Table S2[†], the similar peaks of C1s, F1s and P2p spectra of the cathodes after cycling in two different electrolytes can be observed. The C1s peaks at 285.5 eV and 287.8 eV corresponding to C-O and C=O environment of carbon respectively, along with the presence of C-O (532.0 eV) and ROCO₂Li (533.5 eV) in the O1s spectra, are associated with the carbonate electrolyte decomposition.^{19,20} Besides, the LiF (684.8 eV) and LiPF₆ (686.5 eV) in the F1s spectra as well as the Li_xPO_yF_z appearing at 133.4 eV in the P2p spectra are considered the products composition of electrolyte metamorphosis with the presence of trace water.^{21,22}

However, by contrasting the O1s and S2p spectra, we can point out the diverse constituents on the surfaces of the two cathodes in different electrolytes. For the O1s spectra of cathode after cycling in E1 electrolyte, a weak peak appears at 530.7 eV which is consistent with the presence of HCO₂Li, while it is nonexistent on the cathode

surface after cycling in E0 electrolyte. Moreover, the S2p spectra on the surface of cathode after cycling in E1 electrolyte indicates the key components of SEI layer differ from that of controlling cathode, which could be the RSO₃⁻ (169.0 eV and 167.6 eV) and R₁SSO_xR₂ (163.5 eV).^{23, 24} Generally, most sulfide-based solid electrolyte exhibits high lithium ion conductivity and wide electrochemical window,²⁵ which well explains why the faster charge transfer process occurs even with the existence of the thicker SEI formed in the sulfolane-carbonate mixed electrolyte, thus improving the battery performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material.

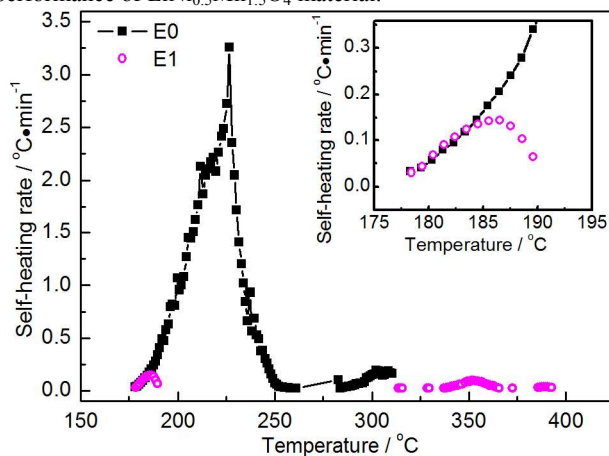


Fig 4: The ARC ((Accelerating Rate Calorimetry)) results of delithiated cathode material with two electrolytes.

Moreover, a stable SEI layer on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ bulk phase at high oxidation state would also ensure a better thermodynamic behavior, thus avoiding suffering from the safety issue during charging process. The thermal hazards of delithiated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material in two electrolytes were evaluated by an Accelerating Rate Calorimetry. As shown in Fig. 4, the exothermal onset temperature of both samples at about 170 °C corresponds to the decomposition of LiPF_6 and the reaction between electrode and electrolyte within interface.^{26, 27} Obviously, the max heating rate decreases from 3.258 °C/min in E0 electrolyte to 0.144 °C/min in E1 electrolyte. The second self heating processes at about 300 °C are associated with the decomposition of carbonate solvents, and this step delays until 350 °C in the E1 electrolyte. Hence the exothermal process of delithiated cathode at high potential with E1 electrolyte occurs more mildly. As a result, the thermo runaway of delithiated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material can be slowed down effectively which should be ascribed to the formation of the stable SEI layer in sulfolane-based electrolyte.

Conclusions

In our work, a sulfolane-carbonate mixed electrolyte was employed for the high voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode. With the presence of a special sulfide-containing SEI forming in the sulfolane-based electrolyte, not only the rate performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is significantly enhanced, but also a high cycling performance is obtained in comparison with that using the carbonate electrolyte. Moreover, such SEI film increases the thermal stability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode in sulfolane-based electrolyte. This strategy offers a new approach to stabilizing the surface and improving the electrochemical performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Details of experimental procedures, electrochemical windows of two electrolytes, rate performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode at different current rates, tables mentioned in the paper and the ARC of two electrolytes. See DOI: 10.1039/c000000x/

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