Towards Highly Efficient Lithium-Ion Batteries: Focusing on Electrolytes

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Abstract. Lithium-ion is various advantages and is required by batteries such as high power, so lithium-ion plays a crucial role in lithium-ion batteries. The electrolyte is one of the core materials of lithium secondary battery and primary battery capacity, improves the mobility between the mobile anode and cathode, and plays the role of medium material. The lithium-ion battery's electrolyte, a crucial component, transports ion conduction current between the positive and negative electrodes. Choosing the right electrolyte is also essential for achieving high energy and power densities, long cycle lives, and good safety performance of the lithium-ion secondary battery. First, understand the lithium-ion battery charge and discharge of the working principle of the chemical equation, and the lithium-ion battery is split into four key components, respectively: positive and negative electrode, diaphragm, and electrolyte, then the electrolyte analysis, the electrolyte is composed of organic solution, conductive salt, and additives. Finally, a new type of sulfate additive, ethyl sulfate, is found and studied at the electrolyte level by literature search. By using the constant current charge-discharge test, cyclic voltammetry, scanning electron microscopy, energy scattering spectroscopy, and electrochemical impedance spectroscopy, researchers are examining the effects of additive ethyl sulfate (DTD) on the performance of lithium-ion batteries and the interfacial performance of graphitized carbon microspheres (MCMB) electrode/electrolyte (EIS).

Keywords: Lithium-ion battery; electrolyte; energy storage.

1. Introduction

As electrical appliances are used increasingly, the demands on batteries are more likely to be safer, larger, faster to charge, smaller, lighter and thinner. The lithium-ion battery in many batteries is one of the main directions of battery development, so the use of the lithium-ion battery is also very wide; For example, the capacity of lithium-ion battery uses solar streetlamps, UPS backup power supply, mobile power supply, laptop phone battery, lighting system, energy storage system, medical equipment, financial equipment, smart home, etc. Power lithium-ion battery uses electric vehicles, moped, power tools, electronic cigarettes, model aircraft, etc.

Secondly, lithium-ion battery, as one of the main directions of modern battery development, also has many advantages: large capacity, high working voltage, strong charge retention ability, long cycle life, high safety, safe and fast charge and discharge, no environmental pollution, no memory effect, small size, lightweight, high energy and so on.

Of course, people also found that lithium batteries have many problems, such as overcharge, over-discharge, overcurrent, charging imbalance, and the impact of ambient temperature on battery life. These problems can cause serious damage to the battery and can even cause the battery to explode. People also put forward higher and higher requirements and new challenges for lithium batteries, mainly including high energy density [1], high power density, high safety, long life [2], extreme environment adaptation, low cost, and other aspects of the development needs.

Lithium-ion battery research has increased due to the continued advancement of science and technology and the growing importance of energy and environmental issues. Due to their benefits, such as high voltage, high energy density [1], high safety, and low self-discharge rate, lithium-ion batteries are a promising new energy source. Therefore, lithium-ion batteries have a great application prospect and huge market demand. The research on high-performance lithium-ion batteries has great scientific significance and economic benefits.

Lithium-ion batteries are batteries that use a non-aqueous electrolyte solution. The operation of lithium-ion batteries, which are secondary (rechargeable), depends on the movement of lithium ions between the positive and negative terminals. Electrolytes, on the other hand, are compounds that can conduct electricity on their own when dissolved in an aqueous solution or a molten state. And electrolytes are bonded by ionic bonds or polar covalent bonds.

2. Working Mechanism of Lithium-Ion Battery

Lithium-ion battery refers to two different secondary battery systems that can be reversibly embedded and removed from lithium-ion compounds as the positive and negative terminals of the battery, respectively. While the positive electrode is in the low-potential Li-rich state and the negative electrode is in the high-potential Li-poor state during the charging process, Li^+ is detached from the positive compound and embedded in the negative electrode's lattice. Li^+ separates from the negative electrode during discharge and enters the positive electrode, which is incredibly rich in lithium. When charging and discharging, an equal number of electrons are transferred from the external circuit and move between the positive and negative poles with Li^+ to maintain the charge balance. This causes oxidation and reduction reactions at the positive and negative poles. A certain potential is maintained [3]. The electrode and battery reaction formula can be written as follows if $Li_yM_nY_m$ stands for the negative electrode material and $Li_zA_vB_w$ for the positive electrode material:

Negative electrode reaction:

$$Li_yM_nY_m + xLi^+ + xe \leftrightarrow Li_{x+y}M_nY_m \quad (1)$$

Positive electrode reaction:

$$Li_zA_vB_w \leftrightarrow Li_{z-x}A_vB_w + xLi^+ + xe \quad (2)$$

Battery reaction:

$$Li_yM_nY_m + Li_zA_vB_w \leftrightarrow Li_{x+y}M_nY_m + Li_{z-x}A_vB_w \quad (3)$$

The battery reaction is as follows [3] if a carbon material with a graphitized structure is used as the negative electrode and a lithium-rich compound $LiMO_2$ with a layered structure is utilized as the positive electrode:

Negative electrode reaction:

$$6C + xLi^+ + xe \leftrightarrow Li_xC_6 \quad (4)$$

Positive electrode reaction:

$$LiMO_2 \leftrightarrow Li_{1-x}MO_2 + xLi^+ + xe \quad (5)$$

Battery reaction:

$$6C + LiMO_2 \leftrightarrow Li_{1-x}MO_2 + Li_xC_6 \quad (6)$$

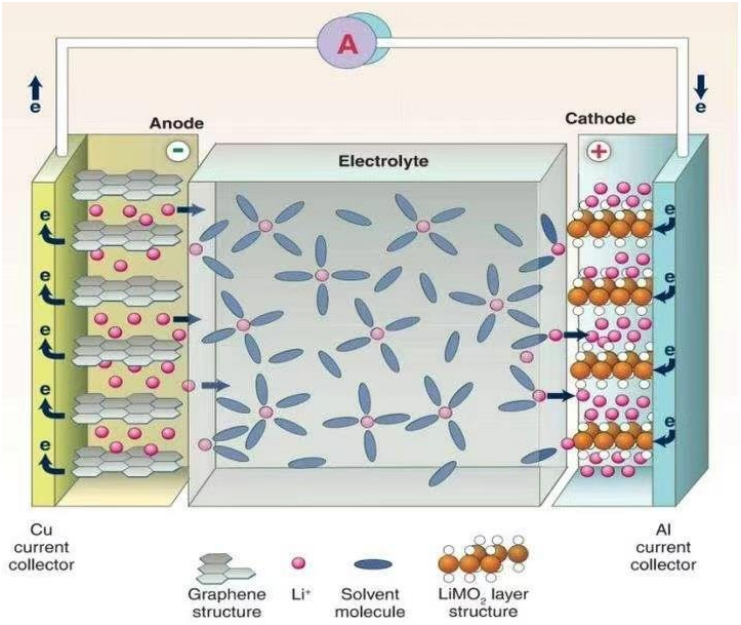

Fig. 1 Lithium-ion battery charging and discharging schematic diagram [2]

According to this principle, a lithium-ion battery is a charging and discharging principle (Fig. 1).

Because the battery in the reversible cell can output the useful work is equal to the largest battery reaction of Gibbs free energy change of △G. Therefore, the maximum output power of the battery depends on the selection of the battery anode materials, battery reaction Gibbs free energy change of △G for Li in the difference between the positive and negative electrode of the chemical potential, thus, lithium-ion battery electromotive force E can press type calculation:

$$E = -\triangle G/(nF) = (\mu_{Li}^{Negative} - \mu_{Li}^{Positive})/F \quad (7)$$

Which, $\mu_{Li}^{Negative}$ and $\mu_{Li}^{Positive}$ represent the chemical potential of lithium ions on the surface of negative and positive electrode materials; F is Faraday's constant, which is 96500 C per mole. Thus, to obtain a higher battery electromotive force and fully demonstrate the advantages of lithium-ion batteries, it is necessary to select appropriate electrode materials to improve the chemical potential difference between the two electrodes [3].

3. Composition of Lithium-Ion Battery

The four different components of the lithium-ion battery are the positive and negative electrode, the diaphragm, and the electrolyte. To enable the charge and discharge functions, the primary purpose of positive and negative electrode materials is to liberate and embed lithium ions [4]. Second, the diaphragm is a crucial component of lithium-ion batteries. An interface layer with the characteristics of a solid electrolyte, this passivation layer is an electronic insulator but a superb conductor of lithium. Through this passivation layer, Li can be embedded and released without restriction. Therefore, the short name for this passivation film is solid electrolyte interphase (SEI) film. The electrolyte comes last. The battery's electrolyte is a crucial component as well. So, the lithium salts, organic solvents, and additives make up the organic liquid electrolyte used in lithium-ion batteries [5].

4. Composition of Electrolyte

4.1. Organic Solvent

The organic solvent is the main part of the electrolyte, which mainly provides media and conditions for lithium-ion migration. There are three main categories of organic solvents: protic, aprotic and

inert. Because the negative electrode of lithium-ion battery has a potential close to that of lithium and is very reactive, non-aqueous and aprotic organic solvents must be used [6].

4.2. Conducting Salt

The conductivity of the electrolyte can be improved by adding soluble conductive salt because of the poor conductivity of the organic solvent. Lithium salt with good performance should have the following characteristics (1) easy to dissolve in organic solvents and dissociate to ensure the conductivity of the electrolyte. (2) Better thermal stability. (3) Better oxidation stability. (4) Environmentally friendly [6].

4.3. Additive

Lithium-ion batteries can perform better if the electrolyte is supplemented with a few additives. In contrast, the SEI film-forming additive is a polar aprotic solvent used in lithium-ion batteries that reacts at the electrode/electrolyte interface during charging and discharging to create a passivation film that covers the electrode surface [7]. Since SEI film is insoluble in the organic solvent, the electrode's cycle performance and service life are greatly enhanced [4].

5. Effect of DTD on the Performance of Lithium-Ion Batteries

DTD is a new type of sulfate additive, ethyl sulfate. Aiming at whether this new additive can improve the efficiency of lithium-ion batteries [8], the commonly used electrolyte 1 M $LiPF_6$/EC+DMC+EMC (volume ratio 1:1:1) was selected from commercial lithium-ion batteries. The quantum chemistry principle calculated the frontier orbital energies of electrolyte solvent and DTD [9]. By testing methods, it was possible to examine the effects of DTD on the interface properties of the electrode and electrolyte, as well as the performance of lithium-ion batteries [10].

5.1. Effect of DTD on MCMB Electrode

5.1.1 Theoretical Basis

Electrochemical stability is very important for lithium-ion battery electrolyte solvents. Currently, many researchers use frontier orbit theory to calculate the electrochemical stability of solvents. According to the frontier orbital theory, the most active and first acting frontier molecular orbital (FMO) is the molecular orbital that controls molecules' ability to gain, lose, and transfer electrons, as well as how intermolecular reactions are oriented in space [9]. A molecule's oxidation is better the higher its lowest unoccupied molecular orbital number. And the reduction is better than the lower, the highest occupied molecular orbital [10].

Table 1 shows the calculation results of frontier molecular orbital energies after molecular optimization of commonly used solvents and additives. As can be seen from the table, the LUMO energy (ELUMO) of DTD is much lower than that of solvent. According to the frontier orbital theory, the molecule's LUMO orbital corresponds to the molecule's reduction potential, so the additive DTD has a stronger ability to gain electrons than the solvent and is easier to reduce on the surface of the MCMB electrode.

Table 1. Frontier orbital energies for frequently used solvents and DTD [10]

Reagent	E_{HOMO}/eV	E_{LUMO}/eV
EC	-6.90330566	-0.2952288
DMC	-6.4625296	-0.401608
EMC	-6.3720896	-0.3255024
DTD	-7.1820784	-1.5021744

5.1.2 Charge and discharge testing with constant current

The discharge capacity cycle curve of a room-temperature MCMB/Li half-cell charged and discharged at a rate of 0.2 C is shown in Fig. 2.

The figure illustrates how the additive concentration significantly affects battery performance. When DTD is not added, the battery discharge is unstable for the first few weeks. The battery's cycle stability is improved, and its discharge capacity is stable after adding DTD. DTD density should not be too high at the same time. Adding a DTD with a volume fraction of 0.1% does not increase the battery discharge capacity. Adding a DTD with a volume fraction of 0.01% to the electrolyte makes it possible to significantly increase the cell's reversible discharge capacity (from 300 mAh/g to 350 mAh/g) and enhance the cycle performance of the MCMB electrode. Based on the above results, a DTD with a volume fraction of 0. 01 % was selected for the study [10].

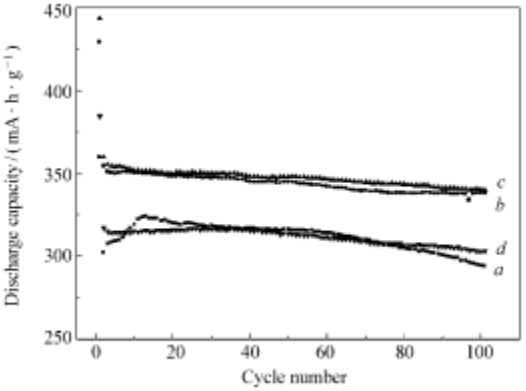

Fig. 2 Plot of capacity retention for MCMB/Li cells at 0.2 C rate and ambient temperature. The cut-off voltages for the cell's charge and discharge were 3.0 V and 0.05 V, respectively. [10]

5.1.3 Cyclic Voltammetry

During the first two weeks, Fig. 3 displays the cyclic voltammetry curves of the MCMB electrode with and without the DTD electrolyte system. The figure demonstrates that a reduction current peak occurs at an electrode potential of about 0.6 V during the initial negative potential scanning operation when DTD is not introduced. This is consistent with the SEI film development and the reduction and degradation of solvent components in the electrolyte. Indicating that the SEI layer that had developed on the surface of the stone and ink electrode had prevented the dissolution of electrolytes during the first cycle, no reduction current peak was seen at about 0.6 V during the second negative scanning procedure [10].

After adding 0.01% DTD, the MCMB electrode displayed distinct cyclic voltammetry behavior in the electrolyte. A modest reduction current peak developed when the electrode potential was about 1.4 V during the first negative potential scan, and it should be attributable to the decrease of additive DTD on the MCMB electrode and the development of the SEI layer. With the decrease of the cathode potential, the reduction current of the cathode increases gradually, and the current reduction peak of the solvent decreases obviously at about 0.6 V. This indicates that DTD participates in the formation of SEI film through reductive decomposition, which can partially inhibit solvent decomposition. During the second negative scan, the cathodic reduction current peak of about 1.4 V disappeared, indicating that the SEI film on the surface of the MCMB electrode had been completely formed after the first scan. In conclusion, The results of the previous molecular orbital calculation are confirmed. According to the results, DTD is involved in forming SEI film on the MCMB electrode, and the base electrolyte solvent is preferred for the reduction decomposition to occur.

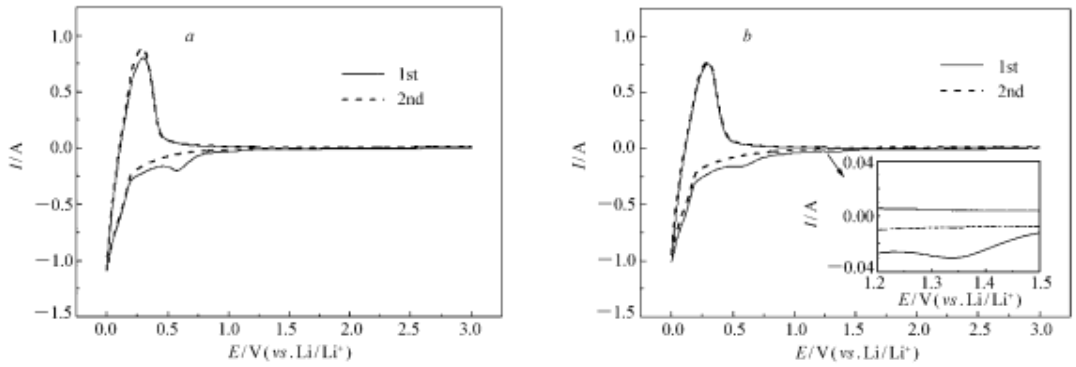

Fig. 3 MCMB electrode cyclic voltammograms at 0.5 mV/s in various electrolytes [10]

5.1.4 SEM Characterization and EDS Analysis

The CV test of the MCMB electrode sheet after two weeks of cycling is depicted in Fig. 4 using an SEM image. The morphologies on the two polar plates are noticeably different, as shown in Fig. 4. When the MCMB electrode circulates in the electrolyte without additives, a rough and uneven film forms on its surface. However, the film formed on the surface of the MCMB electrode becomes relatively smooth and uniform after being circulated in the electrolyte with DTD. The findings demonstrate that the addition of DTD enhances the morphology of SEI film on the MCMB electrode surface, primarily due to DTD's preference over the reduction decomposition of electrolyte solvent, which modifies the composition of SEI film. [10].

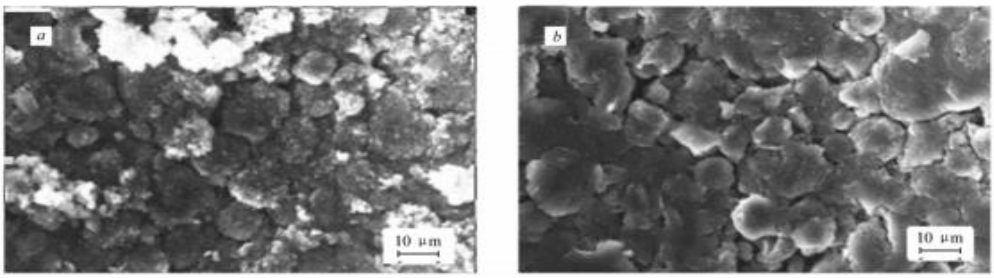

Fig. 4 Surface morphologies of MCMB electrodes as seen in SEM images [10]

The composition of the SEI film on the electrode surface was examined using EDS to determine whether DTD is involved in its formation. After two cycles of CV testing in electrolytes, both with and without DTD added, the MCMB electrode sheet's EDS energy spectrum is shown in Fig. 5. C, O, and F elements can be seen in both energy spectra by comparing the two figures. The peak of the S element was seen after the addition of DTD, demonstrating that the additive DTD helped form the SEI film on the surface of the MCMB electrode through reduction decomposition. Indicating a slower rate of decomposition of the electrolyte salt $LiPF_6$, at the same time, the peak intensity of the F element became weaker, and the peak of the P element vanished. The change of SEI film composition can improve the film performance and increase the specific capacity and cycling performance of the MCMB electrode.

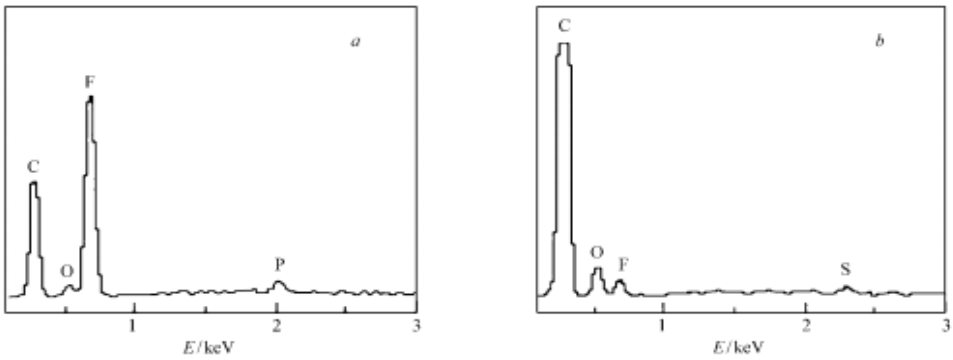

Fig. 5 EDS analysis of MCMB electrode surface [10]

5.1.5 Electrochemical Impedance Spectroscopy

The impedance of a battery has a considerable impact on its electrochemical performance. Graphite electrodes often have two semicircles in their electrochemical impedance spectra. The semicircle in the high-frequency region corresponds to the impedance of SEI film, the semicircle in the medium-frequency region, and the semicircle in the origin of the charge transfer process at the electrode/electrolyte interface, while the straight line in the low-frequency region represents the Warburg impedance, which is the impedance caused by Li^+ diffusion in the graphite electrode [10].

The first-time discharge Nyquist plots of the MCMB and Li half-cells at various voltages (2.5, 1.5, 0.6, and 0.05 V) are shown in Fig. 6. It can be seen from Fig. 6A and Fig. 6B that the total battery resistance in the electrolyte containing DTD is significantly smaller than that in the electrolyte without DTD, indicating that the addition of DTD additive is beneficial to improving the kinetic properties of the electrode/electrolyte interface reaction. Results show that with the reduction of voltage without additive membrane impedance is increased, and add the DTD membrane impedance is gradually reduced, showing that the MCMB electrodes formed on the surface of a thin layer and stable SEI film, thus reducing the electrode in the process of Li^+ migration resistance, is advantageous to the reversible lithium process embedded.

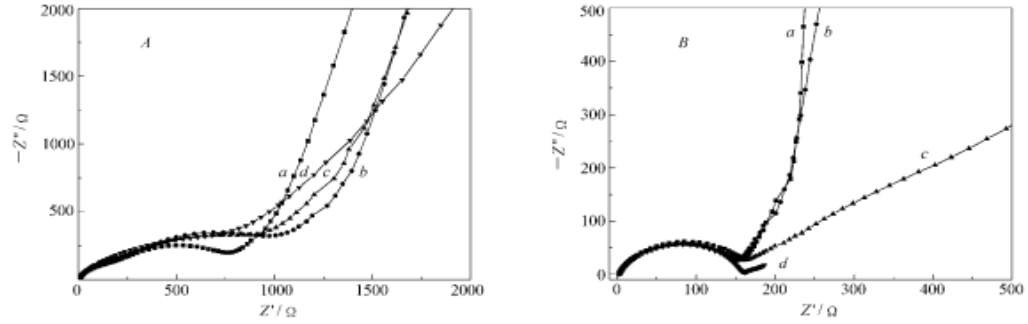

Fig. 6 MCMB/Li cell Nyquist plots for various voltage measurements [10]

5.2. Effect of DTD on LiMn2O4 Electrode

Fig. 7 shows the cyclic voltammetry curves of $LiMn_2O_4$ electrode in the first 5 weeks without and with a volume fraction of 0. 01 % DTD electrolyte system. As can be seen from the figure, the position of the REDOX peak did not change significantly before and after the addition of DTD, but the degree of electrode polarization decreased after the introduction of DTD, indicating that the additive had little effect on the positive electrode. The charge and discharge curves show this as well. The $LiMn_2O_4$/Li half-cell charged and discharged at a rate of 1 C at room temperature is shown in Fig. 8 as having a discharge-specific capacity cycle curve. Fig. 8 shows that although the $LiMn_2O_4$ electrode's cycling performance has improved slightly due to the addition of DTD, the improvement is not particularly noticeable. [10].

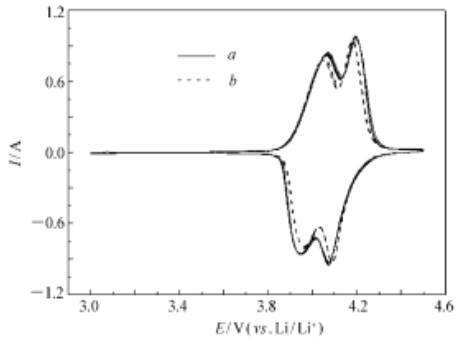

Fig. 7 LiMn2O4 electrode cyclic voltammograms at 0.5 mV/s in various electrolytes [10]

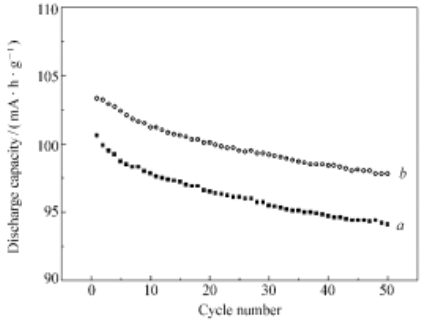

Fig. 8 Plot of capacity retention in $LiMn_2O_4$/Li cells at 1 C/C rate and ambient temperature. The cut-off voltages for the cell's charge and discharge were, respectively, 3.5 V and 4.5 V. [10]

Fig. 9 shows the SEM of the $LiMn_2O_4$ electrode CV test after 5 weeks of cycling. From the comparison of Fig. 9a and Fig. 9b, it can be seen that the surface morphology of the $LiMn_2O_4$ electrode did not change significantly after circulating in the electrolyte with a volume fraction of 0.01 % DTD. The results indicate that the addition of DTD has little effect on the SEI film on the surface of the $LiMn_2O_4$ electrode. In conclusion, DTD has no adverse effect on $LiMn_2O_4$ electrode performance.

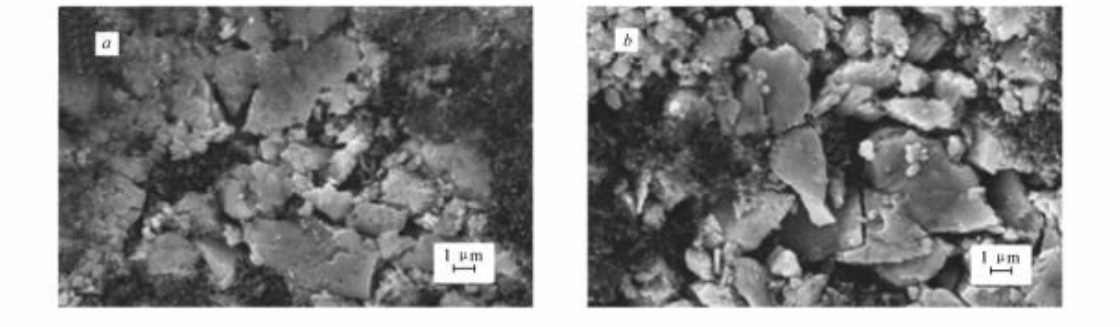

Fig. 9 SEM images of surface morphologies of $LiMn_2O_4$ electrodes [10]

6. Conclusions

According to the lithium-ion battery's operating theory and step-by-step analysis, some electrolyte components irreversibly decompose during the battery's initial charging and discharging process. A passivation film is a solid electrolyte phase interface film that forms on the electrode surface (SEI film). The performance of this movie directly impacts lithium-ion battery performance. Additionally, a brand-new sulfate additive called ethyl sulfate was discovered in the electrolyte layer. It has been discovered that this new additive significantly raises the performance of lithium-ion batteries in mixed electrolytes. According to the results, adding a volume fraction of 0.01% DTD to the electrolyte increased the reversible discharge capacity of the MCMB/Li battery from 300 mAh/g to 350 mAh/g, decreased the battery's overall impedance, and enhanced cycle stability. In the first reduction process,

which involved creating a solid electrolyte phase interface film (SEI film) on the surface of the MCMB electrode, DTD was electrochemically reduced at 1.4 V (VS Li/Li^+), according to a CV test. Additionally, DTD has no detrimental effects on the performance of $LiMn_2O_4$ electrodes.

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