

Effects of Vinyl Ethylene Carbonate Additive on Elevated-Temperature Performance of Cathode Material in Lithium Ion Batteries

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The addition of 2% vinyl ethylene carbonate (VEC) into LiPF₆/EC + DMC electrolyte can significantly improve the cyclic performance of a LiNi_{0.8}Co_{0.2}O₂/Li cell at elevated temperatures such as 50 °C. In situ electrochemical mass spectrometry (EMS) was used to investigate the gas evolution spectroscopy in the cell during a charge/discharge process with and without VEC additive. Fourier transform infrared (FTIR), ultraviolet–visible (UV–vis), and liquid nuclear magnetic resonance (NMR) spectroscopies were also carried out to investigate the reactions between various electrolyte components and VEC without the electrochemical reaction. We propose the possible polymerized products based on the spectroscopy and the acting mechanism of the VEC additives.

Introduction

Lithium ion batteries have been commercialized for almost 20 years and play an important role in everyday life. The voltage of this kind of battery is much higher than those of other battery technologies, which leads to high specific energy density and power density. However, this advantage also results in the potential safety problems associated with decomposition of nonaqueous electrolytes and the reaction between electrode and electrolyte, which may affect the cyclic stability and safety of the batteries. One solution to this problem is to use electrolyte additives to help delay these reactions. Ideally, the additive should decompose before the other electrolyte components during the electrochemical process, forming a protective solid electrolyte interphase (SEI) and preventing subsequent decomposition of the remaining electrolyte.

Recently, it has been shown that adding a few percent of unsaturated carbonates to the nonaqueous electrolytes could significantly improve their electrochemical performance. For example, vinylene carbonate (VC) is one of the widely used additives since it could form a stable SEI film on the surface of the carbon anode.^{1–3} However, VC is not a stable compound, which may restrict its application.^{3,4} Thus, because it has a more stable structure than VC, vinyl ethylene carbonate (VEC) has attracted more attention in these years. Considering its electron-rich double bond and higher reduction potential than those of other electrolyte components, some researchers concluded that addition of VEC would help enhance the electrochemical performance of lithium ion batteries, especially in propylene carbonate (PC) based electrolytes.^{5–10} It would take different reductive routes in different current densities,⁶ since the solvent molecules undergo one-electron reduction at low current density and two-electron reduction at high current density.⁵ The main reductive products at low and high current density are ROCO₂Li and Li₂CO₃, respectively.^{6,7} Due to the lack of a barrier to

reaction observed in the computational study, VEC should be more readily reduced than ethylene carbonate (EC) or PC at the reduced concentrations (1–5 wt %) to form the passivating Li₂CO₃ layer because the direct two-electron reduction of VEC is thermodynamically favorable.⁸ Though there are several mechanisms of reduction, it is commonly accepted that addition of VEC to PC-based electrolyte not only can prevent the exfoliation of carbon anodes, but also can form stable SEI films. However, up to now, most investigations of VEC were focused on its function on the surface of carbon anode electrode, and the experiments were always conducted at room temperature. Knowledge of the effect of VEC at high temperature and on the cathode electrode is still lacking. In fact, this is a question which deserves to be investigated thoroughly.

As we know, the decomposition of electrolytes causes gas evolution in an electrochemical cell. This change will decrease the cyclic stability, increase the internal pressure in the batteries, and cause a safety hazard. However, if a stable SEI can form in the first cycle on the surface of electrodes, it may prevent further reductive electrolyte decomposition and reduce the amount of gas evolution during the electrochemical process. Therefore, monitoring the in situ change of gas evolution (such as CO₂) under different conditions should help us understand the effects of additives on SEI formation, if any.

A method that has been proven to be very useful for studying the gas evolution during the charge/discharge process is electrochemical mass spectrometry (EMS). It has been used in many lithium ion battery systems for in situ gas evolution, such as electrolyte behavior,^{11,12} SEI formation,¹³ and oxygen release from lithium excess layered cathode material.¹⁴

In this paper, we report an investigation on the improvement of the electrochemical performance of LiNi_{0.8}Co_{0.2}O₂ cathode electrode in commercial 1 M LiPF₆/EC/DMC (DMC, dimethyl carbonate) electrolyte with addition of VEC at both room temperature and 50 °C. It is shown that adding 2% VEC to LiPF₆/EC + DMC electrolyte can significantly improve the cyclic performance of LiNi_{0.8}Co_{0.2}O₂/Li cell at elevated temperature. This is attributed to the formation of a stable SEI layer on the surface of the electrode, which will cover the surface of

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the electrode, preventing subsequent decomposition of the remaining electrolyte, and thus improve the electrochemical performance of the batteries. It is believed that such information will help us understand in depth the functional mechanism of unsaturated carbonate additive in the nonaqueous electrolytes on cathode materials.

Experimental Section

$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ compounds were synthesized by the $\text{Ni}(\text{OH})_2$ spheres solid state reaction method as previously reported.¹⁵ The electrolytes were prepared by mixing $\text{LiPF}_6/\text{EC} + \text{DMC}$ (1:1 volume ratio) with 0%, 2%, or 5% VEC (Huizhou ShanShan Company, battery grade) according to the volume ratio. The positive electrode was prepared by blade-coating the slurry, which was composed of 85 wt % $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, 10 wt % carbon black, and 5 wt % poly(vinylidene difluoride) (PVDF) on an aluminum foil current collector. The charge/discharge cycles were performed by a coin cell at a current density of 36 mA/g either at room temperature (about 25 °C) or at 50 °C; the lithium metal was used as the counter electrode. After reaching a potential of 4.3 V vs Li/Li^+ in the first galvanostatic step, the electrode charging was continued at 4.3 V potentiostatically until the current dropped below 9 mA/g. Then, the lithium reinsertion was performed galvanostatically at a constant specific current of 36 mA/g to a cutoff potential of 3.0 V. The subsequent charge/discharge cycles were performed under the same conditions.

The EMS setup consists of a quadrupole mass spectrometer (Aeolos QMS 403 C, Netzsch, Germany) and a custom-designed electrochemical cell. The cell body was made from polytetrafluoroethylene, and an O-ring was used to seal the cell. A nonwetable porous membrane was added as a solvent barrier between the cell and the vacuum system of the mass spectrometer. The counter electrode was made by blade-coating the mesocarbon microbeads (MCMB, Huizhou Shanshan Company, battery grade) base slurry or pressing metallic lithium on a copper current collector. The MCMB slurry was composed of 85 wt % MCMB, 5 wt % carbon black, and 10 wt % PVDF. All EMS tests were carried out potentiodynamically either at room temperature or at 50 °C. The cutoff voltages for the cyclic voltammetry (CV) were 3.0 and 5.0 V with a scan rate of 0.2 mV/s.

Fourier transform infrared (FTIR) experiments were performed by a Nicolet Avatar 3600 FTIR spectrometer (USA). The electrolyte was directly dropped on a KBr window and covered by another KBr window, sealed in an Ar glovebox by paraffin wax. The UV-vis results were carried out by a Shimadzu UV-2100 instrument (Japan) with the wavelength between 800 and 200 nm, and the pure $\text{LiPF}_6/\text{EC} + \text{DMC}$ electrolyte was taken as the blank sample. The decomposition products were characterized by ^{13}C and ^{31}P nuclear magnetic resonance spectroscopy (NMR, Bruker 400 MHz instrument, CDCl_3 solvent). ^{13}C NMR resonances were referenced to CDCl_3 at 77.0 ppm,¹⁶ and ^{31}P NMR resonances were referenced to LiPF_6 at -145.0 ppm.^{17,18}

Results and Discussion

Comparison of Electrochemical Performance of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ Cathode Material with or without Addition of VEC. Figure 1 shows cyclic performances of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode material in the $\text{LiPF}_6/\text{EC} + \text{DMC}$ electrolytes with or without 2% VEC added either at room temperature or at 50 °C. At room temperature the discharge capacity drops from 180 mA h/g of the first cycle to 137.4 mA h/g of the 100th cycle without VEC

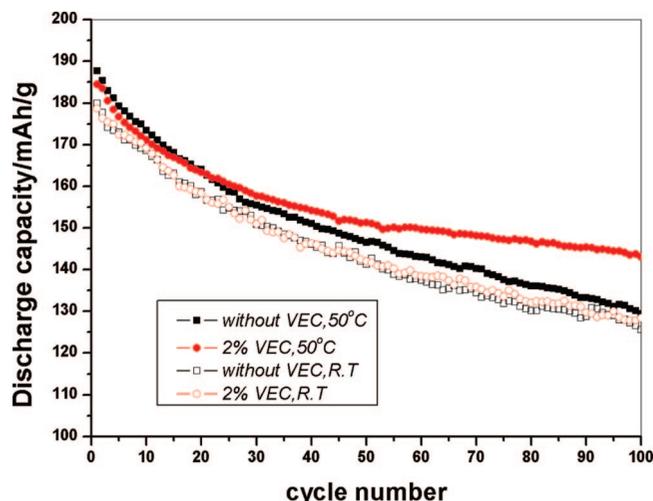


Figure 1. Cyclic performances of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode material in $\text{LiPF}_6/\text{EC} + \text{DMC}$ electrolytes with or without 2% VEC added either at room temperature or at 50 °C. Lithium metal was used as the counter electrode.

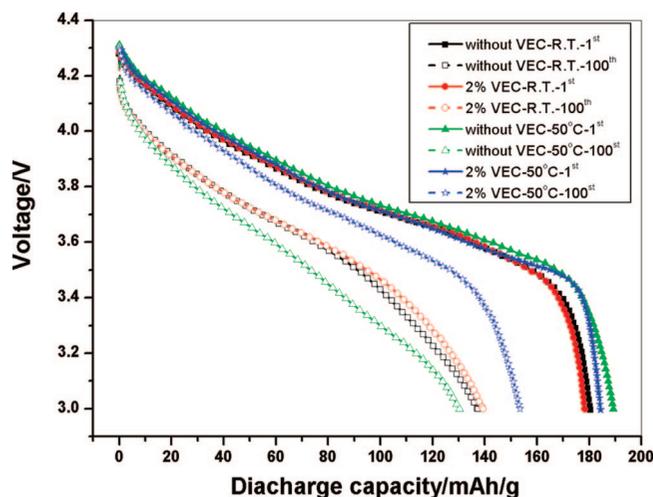


Figure 2. Discharge curves of first and 100th cycles for $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode material in $\text{LiPF}_6/\text{EC} + \text{DMC}$ electrolytes with or without 2% VEC added either at room temperature or at 50 °C.

additive; the capacity retention is about 76.3%. If 2% VEC is added to the electrolytes, the capacity drops from 178.8 mA h/g of the first cycle to 139.4 mA h/g of the 100th cycle, maintaining 78.0% of the original capacity. Therefore, for the coin cell tested over the potential of 3.0–4.3 V and at a current density of 36 mA/g, addition of 2% VEC does not bring remarkable improvement to the cyclic stability at room temperature. On the contrary, when the temperature is increased to 50 °C, the improvement becomes obvious. The capacity retention increases from 68.8% for a cell without VEC to 84.8% for a cell with 2% VEC added. Though the first discharge capacity (180.6 mA h/g) of the coin cell with 2% VEC electrolyte (189.7 mA h/g) is lower than that without VEC, the 100th cyclic discharge capacity is much higher (with 2% VEC, 153.2 mA h/g; without VEC, 130.8 mA h/g). If we compare discharge capacities of the first and 100th cycles (Figure 2), obvious improvement is also observed. At 50 °C, though the first cyclic discharge plateaus were similar for all tested cells, the 100th cyclic discharge plateau of the 2% VEC cell decreased much less than that of the cell without VEC. It can be seen that the improvement in the cyclic performance of the electrode materials under the participation of VEC only occurs at high temperature.

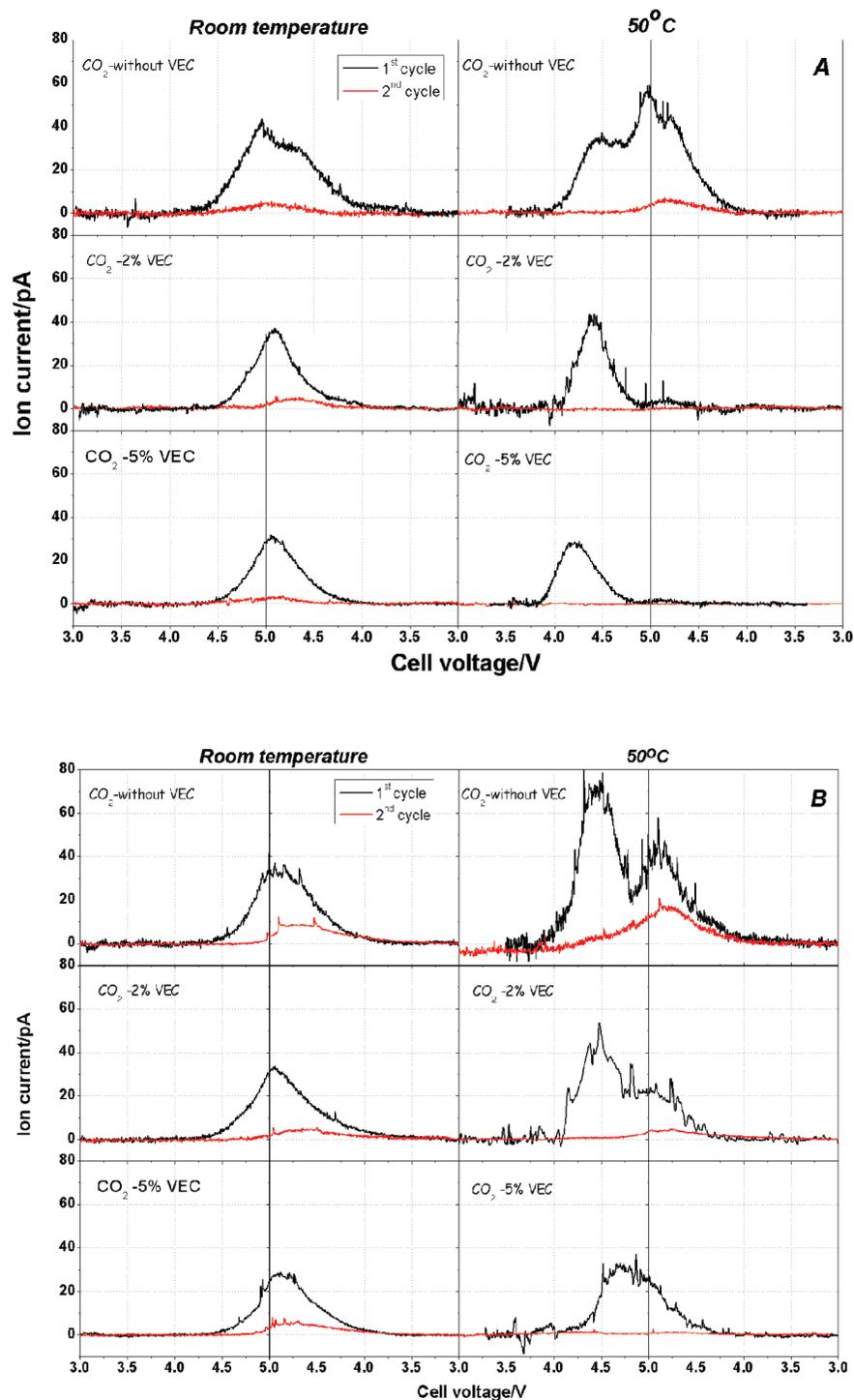


Figure 3. EMS measurement of CO_2 gas evolution on $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode and $\text{LiPF}_6/\text{EC} + \text{DMC}$ electrolyte in the first (black) and second (red) cycles at room temperature and 50°C , without VEC, and with 2% or 5% (volume ratio) VEC added to the electrolyte. The counter electrodes are metallic lithium (A) and MCMB (B).

Electrochemical Mass Spectrometry Results in Different Testing Situations. Many researchers have proved that the addition of VEC can help to form a stable SEI layer on the surface of an anode electrode, and the improvement of the cathode materials at high temperature by VEC may also be attributed to the formation of some kind of SEI layer on the cathode surface, even though the composition and structure of the layer should be different. If such a change occurs, the SEI prevents subsequent decomposition of the electrolytes, and the gas evolution during the electrochemical process may be different. To monitor such changes, in situ EMS measurements of the corresponding systems were carried out. The results are

shown in Figure 3. In order to be consistent with coin cell testing, we first took metallic lithium as the counter electrode (Figure 3A). (i) It can be seen that the onset voltage of CO_2 evolution at 50°C is lower than that at room temperature (i.e., ~ 4.5 V for room temperature, ~ 4.0 V for 50°C), indicating that the reaction or reduction of electrolyte may start at a lower voltage at higher temperature. (ii) According to the area under these curves, the content of CO_2 evolution is obviously decreased if VEC is added at 50°C , but this phenomenon is invisible at room temperature. (iii) The peaks for CO_2 evolution disappear in the second cycle at 50°C after VEC is added, while they exist at room temperature all the time. All of these

observations indicate that a stable SEI layer may be created in the first cycle under the participation of VEC at elevated temperatures such as 50 °C.

In addition, there are two CO₂ evolution peaks emerging in the EMS spectrum for 50 °C, revealing two different changes occurring during the electrochemical process. However, which evolution peak corresponds to the cathode side is not clear. In order to make sure of the origin of the evolution peaks, we replaced lithium by MCMB as the counter electrode (Figure 3B). Considering the reaction between CO₂ and lithium, which might reduce the amount of readily formed CO₂,¹⁹ changing the counter electrode to another material that is inert to CO₂ would lead to a different result. It is obvious that the first peak located at about 4.5 V is much wider and more intense (in the forward scanning process) than that with the lithium counter electrode, while the second peak changes little. Therefore, we consider that the peak at the lower voltage range may come from the electrolyte decomposition on the anode, and the one at higher voltage may belong to the electrolyte decomposition on the cathode. At the same time, after addition of VEC to the electrolytes, the two peaks merge into one, especially with 5% VEC at 50 °C whenever lithium or MCMB is used as the counter electrode. Two possible explanations may be considered for this difference. First, it suggests that the content of CO₂ evolution is too small to be detected on the cathode under the participation of VEC at high temperature. Second, it is also possible that VEC decomposes before other electrolyte components; the CO₂ evolution shifts to the lower voltage and mixes with the signal peak of the anode electrode which appears at lower voltage. These proposed processes cannot be differentiated with our current method. They should be proved with other spectroscopic methods, which we will explain in our future work.

FTIR and UV–Vis Results of Electrolytes at Different Storage Temperatures with or without VEC Added. Since the improvement for the electrochemical cycle is obvious only at 50 °C, the temperature will be a very important control parameter for VEC additive. During the experiments, we found that when we added VEC into LiPF₆/EC + DMC electrolyte, the mixture turned from transparent colorless to yellow when stored at 50 °C for 1 day (or more) even without charge/discharge. However, this phenomenon was not observed in pure VEC and LiPF₆/EC + DMC electrolyte. That is, the VEC may react with other components of the electrolyte if the temperature increases to 50 °C. Therefore, we investigated a series of electrolytes without the presence of the electrode by some spectral instruments, including FTIR, UV–vis, and NMR.

Figure 4 shows the FTIR spectra of LiPF₆/EC + DMC electrolytes with and without 5% VEC at different storage conditions in the frequency region of 3200–2800 cm⁻¹. The features at 3010 and 2930 cm⁻¹ are attributed to the methylene (–CH₂–) asymmetric and symmetric modes in a saturated heteroatom ring, e.g., in EC and VEC. The feature at 3094 cm⁻¹ is attributed to the vinylene group (=CH₂) asymmetric stretch in VEC. Aliphatic methylene (–CH–) asymmetric mode would be found at 2930 cm⁻¹, and aliphatic methyl (–CH₃) asymmetric stretch would be found at 2960 cm⁻¹. We note that the peak at 3094 cm⁻¹ is visible in spectrum B, but absent in spectrum A. At the same time, the peak in the region near 2960 cm⁻¹ (the unique group in DMC)⁷ in spectrum A almost disappears. Both observations indicate that the VEC might polymerize with DMC at 50 °C.

Considering that the color of the electrolyte and additive mixture changed during storage, UV–vis spectrometric mea-

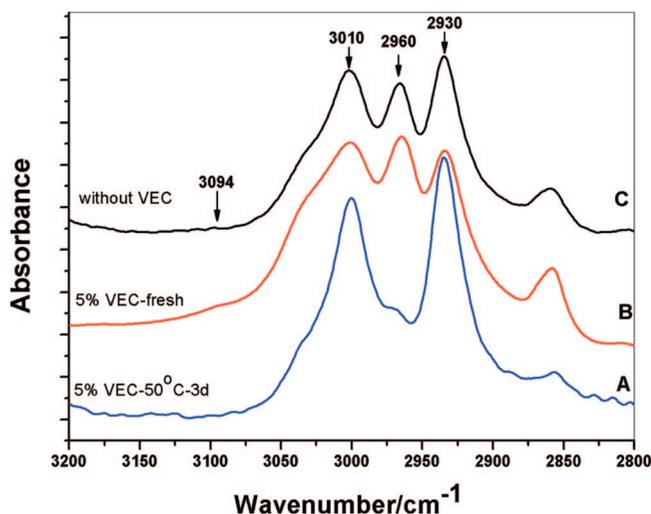


Figure 4. FTIR spectra for LiPF₆/EC + DMC electrolytes with and without 5% VEC at different storage conditions.

surement was also carried out. The results are shown in Figure 5. For the LiPF₆/EC + DMC + 5% VEC electrolyte stored at 50 °C (red dotted line in Figure 5a), the absorbance does not remain zero in the region of 700–400 nm, which results in the color change. The main peak located at about 215 nm shifts to higher wavelength (about 225 nm), and the peak located at 270 nm becomes more visible. Thus, we proposed that some long-chain polymers or conjugated macromolecules may be created through the reaction among these electrolyte components. Subsequently we tested the pure organic solvent and EC/VEC and DMC/VEC mixed solvents, respectively. From Figure 5c, we can see that there is no obvious change in the curves of the EC + VEC solution (Figure 5c): the shapes of the curves are almost the same as those for pure EC except for the little peak at 260 nm, which contributes to 5% VEC additive. This means that EC and VEC can keep their stability when mixed as the solution. However, the situation is different for the DMC + VEC mixture (Figure 5d): the highest peak shifts from 213 to 222 nm, and another peak shifts from 268 to 272 nm. In the spectra for LiPF₆/EC + DMC/VEC electrolyte, both peaks shift to higher wavelengths. Though the reaction products are still unclear, the creation of long-chain polymers or conjugated double bond molecules through the reaction between DMC and VEC at 50 °C could be proven, which is consistent with FTIR results.

NMR Results of Electrolytes at Different Storage Temperatures with or without VEC Added. As we know, for a solution with LiPF₆ dissolved in organic solvents, the LiPF₆ may decompose and react with organic solvent, especially at higher temperature. The fact that the VEC additive can improve the cyclic stability of the cell indicated that VEC may have some effect on the decomposition process in the electrolyte. ¹³C and ³¹P NMR were performed to evaluate this hypothesis. The ³¹P NMR traces of the electrolytes in different conditions are shown in Figure 6. For the fresh electrolyte, only the seven splitting peaks with identical separation due to the magnetic effects of six coordinated F atoms are observed. However, in the spectra for stored electrolytes, besides the original ³¹P signals of PF₆⁻, new peaks appear at the low field of the shift region. This means that P-containing compounds other than LiPF₆ also exist in the electrolyte, which most probably come from the decomposition of LiPF₆. For the sample with 5% VEC additive and stored at room temperature for 1 day, there are two groups of chemical shifts are observed: one locates at –34.3 ppm has

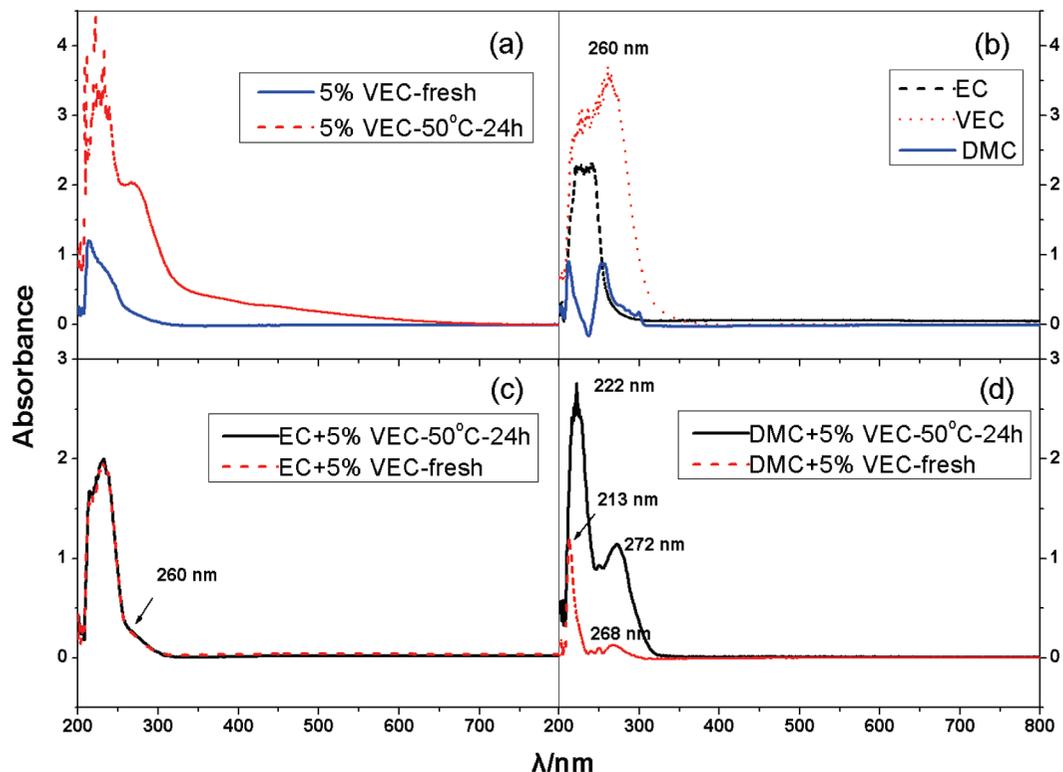


Figure 5. UV-vis spectra for electrolyte components and their mixtures freshly prepared and after storage at 50 °C for 24 h. (a) LiPF₆/EC + DMC + 5% VEC electrolyte. (b–d) Pure or mixed organic solvents.

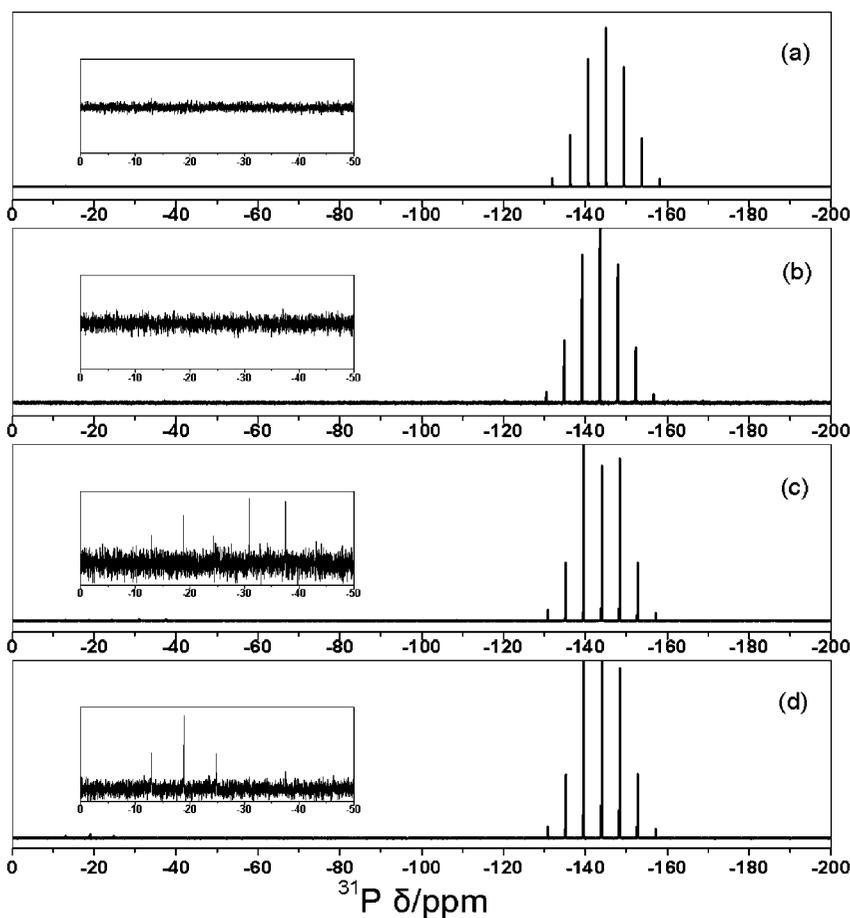


Figure 6. ³¹P NMR spectra of LiPF₆/EC + DMC electrolyte: (a) without VEC, (b) tested as soon as 5% VEC is added, (c) tested after 1 day at room temperature stored with 5% VEC added, and (d) tested after 1 day at 50 °C stored with 5% VEC added.

four splitting peaks, and the other locates at -18.9 ppm with three splitting peaks (Figure 6c). Four splitting peaks are due

to the magnetic effects of three coordinated F atoms indicating the decomposition product of OPF₃, and the three coordinated

Carbon Labeling

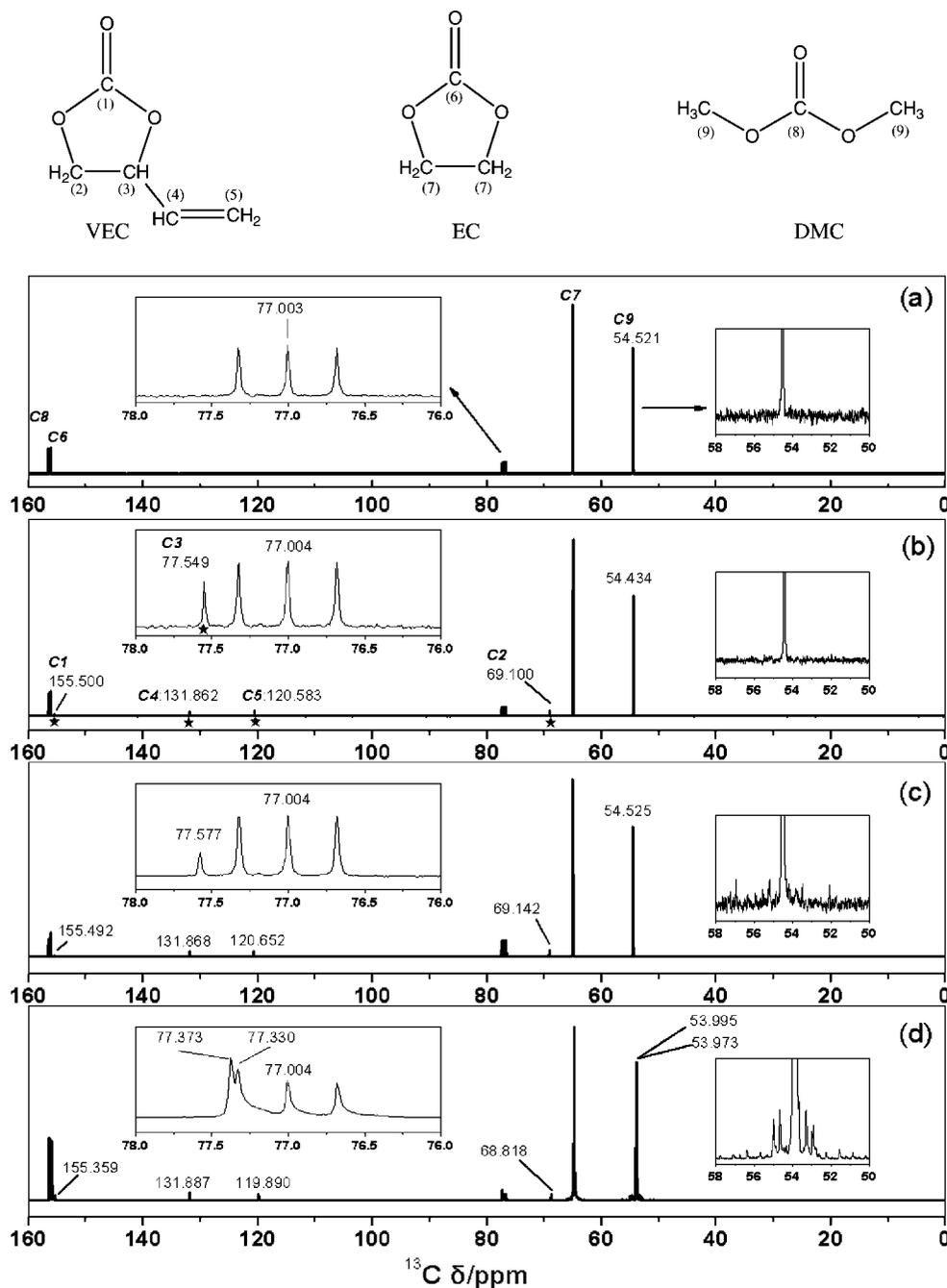


Figure 7. ^{13}C NMR spectra of $\text{LiPF}_6/\text{EC} + \text{DMC}$ electrolyte: (a) without VEC, (b) tested as soon as 5% VEC is added, (c) tested after 1 day at room temperature stored with 5% VEC added, and (d) tested after 1 day at 50 °C stored with 5% VEC added. ★: peaks for carbons of VEC.

F atoms indicate the decomposition product of OPF_2OR .^{17,18,20} Since the relative intensities of four splitting peaks become weaker and the three splitting peaks become stronger in the spectra of the sample stored at 50 °C for 1 day, we proposed that the OPF_3 is one of the important transition products of LiPF_6 decomposition which will finally turn to OPF_2OR during the process of the reactions with VEC. Therefore, VEC is easier to react with LiPF_6 and its decomposition products, so it can help to suppress the subsequent reactions between OPF_3 and DMC/EC , especially at elevated temperature.

Figure 7 shows the ^{13}C NMR traces of the electrolytes in different conditions. Based on chemical shifts of the standard spectra, the carbons of the organic components in the electrolyte can be labeled as shown in Figure 7. There are two obvious

differences in the spectra between the electrolyte stored at 50 °C and others. One is that the positions of C5 and C3 move to lower chemical shifts. Since both belong to VEC, we think that VEC is more ready to react with LiPF_6 than EC and DMC at elevated temperature. Comparing with the results of ^{31}P spectra, the C3–O bond in the VEC may break down and react with the transition product OPF_3 from the decomposition of LiPF_6 , and then turn to OPF_2OR eventually. At the same time, as many studies on VC additives show, the C=C (C5 position) bond in VEC may also increase its activity to produce polyvinyl ethylene carbonate at elevated temperature.²⁰ In a word, decomposition of LiPF_6 is severe at elevated temperature and leads to an intermediate product OPF_3 ;¹⁸ if some VEC is added to $\text{LiPF}_6/\text{EC} + \text{DMC}$ electrolyte, it could react with the OPF_3 in advance

and suppress the subsequent reactions between OPF₃ and DMC/EC.^{18,20} These kinds of products of OPF₂OR and polyvinyl ethylene carbonate will have significant effects on the formation of the stable SEI layer on the surface of the electrode.

The second difference is that the single peak of C9 splits into two peaks and moves to lower chemical shifts (from 54.5 to 54.0 ppm) in Figure 7d, which indicates the reaction between DMC and other components at elevated temperature. This phenomenon is consistent with the results of FTIR experiment which we have explained in the previous section. Otherwise, the NMR peaks can only split when they connect with an odd number of protons or neutrons, so if the DMC only polymerizes with VEC, the splitting peaks should not be observed. DMC can react with LiPF₆ or its decomposition compounds and have products including the C–P bond which leads to the splitting peaks at about 54 ppm. C9 will be electronically negative after the C–H bond break. Therefore, it is impossible to form a bond between C9 and F atoms since the charge on the F atom is always negative. In addition, some groups with two splitting peaks are also viewed around the peak of C9. They emerge as one peak in the spectra for room temperature, and become stronger in the spectra at 50 °C. This is another indication of the presence of products with C–P bonds. After these reactions, some long-chain polymers or conjugated macromolecules are present and cover the surface of the electrode, and prevent subsequent decomposition of the remaining electrolyte during the charge/discharge process.

Conclusion

Adding 2% VEC to LiPF₆/EC + DMC electrolyte can significantly improve the cyclic performance of LiNi_{0.8}Co_{0.2}O₂ cathode material at elevated temperatures such as 50 °C. The discharge capacity retention increases from about 68.8% to 84.8% after 100 cycles. According to EMS measurement, the content of CO₂ evolution is obviously decreased, and the peak of CO₂ disappears in the second cycle if VEC is added at 50 °C, indicating the creation of a stable SEI layer on both the anode and cathode electrodes under the participation of VEC. Based on FTIR, UV–vis, and NMR results, it is demonstrated that VEC can react with OPF₃ in advance to form OPF₂OR, which is a necessary transition product of the decomposition of LiPF₆, suppressing the consequent reactions between OPF₃ and DMC/EC. At the same time, the reactions among DMC, VEC, and LiPF₆ occur at 50 °C. The possible reaction sites

have been analyzed by NMR. Both will result in formation of long-chain compounds and polymers, which will be very helpful to build up a stable SEI layer on the surface of electrodes, which prevents subsequent decomposition of the remaining electrolyte during the charge/discharge process and improve the electrochemical performance of the batteries.

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