Effect of vinylene carbonate on electrochemical performance and surface chemistry of hard carbon electrodes in lithium ion cells operated at different temperatures

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ABSTRACT: Due to wide uses of lithium ion batteries and emerging researches on sodium ion batteries, hard carbon (HC) as an anode material comes into sights of research fellows recently. HC anode delivers a considerable reversible capacity at room temperature and increasing capacities at elevated temperatures. However, the electrolyte and solid electrolyte interphase (SEI) formed on the electrode surface tend to become instable at elevated temperatures, though the appreciable reservoir ability of HC is alluring. Herein, we report that vinylene carbonate (VC) is a desirable electrolyte additive for HC electrodes especially at elevated temperatures. The influence of VC on electrochemical performance and surface chemistry of HC electrodes at both 25 °C and 50 °C is investigated in detail using Cyclic voltammograms (CVs), electrochemical impedance spectroscopy (EIS), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). In the presence of VC additive, a stable SEI film is formed upon cycling, which contains increased amounts of Li_2CO_3 and decreased F species contents. It demonstrates that the SEI formed in the presence of VC helps suppress salt anion (PF_6^-) decomposition as well as SEI transformation occurred at 50 °C.

Keywords: vinylene carbonate; hard carbon; temperature performance; SEI layers

1. INTRODUCTION

Lithium ion batteries (LIBs) are the power source not only for popular consumer electronics but also for upcoming and electric vehicles. Various forms of carbon have previously been employed as anode materials [1-4]. Natural graphite is preferred as an anode material because of its low cost, high Coulombic efficiency, and high capacity [2]. However, the prevailing commercial anode material is far from meeting the requirements for high energy/power density because of its limited power performances. In order to meet the increasing demands for LIBs with high rate capability and long battery life, scientific researchers around the world have made great efforts to find optimal candidates for anode materials [5-9]. Recently, hard carbon (HC) has been demonstrated to be one of the most promising anode materials for Li-ion or Na-ion batteries, due to its superior reservoir ability and rate performance compared to graphite [10-13]. Furthermore, enhanced capacities [14] and reliable safety (no solvent intercalation and lithium plating) [15-18] at elevated temperatures make HC an attractive candidate for special applications operated at high temperatures, such as above 50 °C. However, at elevated temperatures, the unstable nature of solid electrolyte interphase (SEI) formed on the electrode surfaces in conventional organic electrolytes obscures the lightness of HC anodes. Also, rapid degradation of electrolyte at elevated temperature directly leads to the capacity fading of HC electrodes during cycling.

Accordingly, the changes appearing in the SEI films are more pronounced at elevated temperatures [19-21]. There are two prime reactions that occur at elevating battery temperatures. First, transformation of SEI films occurs. Here, the components like lithium alkyl carbonates and semicarbonates convert to more stable components like Li_2CO_3 . The second process occurring at high temperatures is the reaction of active material with the SEI, or SEI with the electrolyte, or active material with the electrolyte, thus leading to poor cycling stability [22]. This shows that effective and thermal stable SEI is mandatory for good performance of LIBs.

To improve the stabilization and performance of SEI films at elevated temperatures, vinylene carbonate (VC) as a successful electrolyte additive has been widely used for

graphite anodes of cells [23-27]. VC is proved to be an effective SEI-forming additive in EC/PC based electrolytes. It is surmised that the SEI formed in the presence of VC could help suppress both solvent and salt anion decomposition, and therefore could help increase the thermal stability of the graphite electrodes. Aurbach et al. reported that VC has positive influences on improving the cyclability and reducing the irreversible capacity on both cathode and anode at elevated temperatures [24]. Dahn et al. found that VC can improve the coulombic efficiency, reduce charge/discharge endpoint slippage at 50 °C and 60 °C, and prolong cycle life [25, 28]. Also, Liu et al. declared that VC assists the formation of thermally resistant oligomeric phosphate ester layer on the graphite surface which is responsible for improved cycle stability of the cells at elevated temperatures [26].

Although the contribution of VC to the graphite anodes has been widely established, its actual functions on HC electrodes operating at room temperature and elevated temperatures are rarely reported yet. In this study, the influence of VC additive on both electrochemical performance and surface chemistry of HC electrodes operated at 25 °C and 50 °C was investigated in detail, using techniques including Cyclic voltammograms (CVs), electrochemical impedance spectroscopy (EIS), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Despite the fact that numerous emerging techniques, including solid-state MAS NMR spectroscopy and MALDI-TOF mass spectrometry [29], small-angle neutron scattering [30], real time mass spectrometry (DART-MS) [26], time-of-flight secondary ion mass spectrometer (TOF-SIMS) [31] etc., have been developed for analyzing SEI, FTIR and XPS are still the most widely used methods for the SEI films characterization, due to their high surface sensitive ability. Information from these two techniques together provides a good picture of the SEI. Combining electrochemical analyses with surface chemistry characterization, we aim to clarify the contribution of VC to the formation of SEI layers on the HC electrodes cycled at 25 °C and at 50 °C, respectively.

In addition, graphite electrodes only release a reversible capacity not higher than 372 mAh g⁻¹ even at high temperatures (i.e. 80 °C) [22]. Interestingly, a fairly large

reversible capacity of 675.0 mAh g⁻¹ at a current density of 0.1 mA cm⁻² was delivered by HC electrodes at 80 °C [14]. Also, similar findings on high-temperature performance of HC anode were obtained earlier in our group and were submitted elsewhere. Herein, we utilize the opportunity presented by appealing high temperature performances of HC electrodes for electrochemical and spectroscopic analyses of the SEI films formed in the presence of VC additive.

2. EXPERIMENTAL SECTION

2.1 Synthesis. Precise procedures for preparation of hard carbon from epoxy novolac resin were reported previously [32]. Generally, coal tar pitch is adopted as a source of carbon coating to modify the electronic conductivity of hard carbon. In this text, hard carbon and coal tar pitch (softening point: ~90 °C) were mixed in N-methylpyrrolidinone (NMP) (Sinopharm, China) at 120 °C with the weight ratio of 10:1. The as-prepared mixture was kept at 180 °C for several hours to evaporate NMP, followed by heating at 1000 °C for 1 h under an argon atmosphere. The obtained composite powders were labeled as HC for short.

2.2 Electrochemical measurement. The electrochemical measurements were carried out with 2016 coin cells using lithium metal as the counter electrode. The HC electrodes were prepared by a slurry coating procedure. The slurry was composed of active materials (HC), conductivity agent (carbon black) and binder (polyvinylidene fluoride) in a weight ratio of 80:10:10 dissolved in NMP. The slurry was then spread uniformly onto a copper foil and dried in a vacuum oven at 120 °C for 12 hours. The solution of 1 M LiPF₆ in ethylene carbonate (EC), propylene carbonate (PC) and dimethyl carbonate (DMC) (2:1:7) served as the blank electrolyte. Vinylene carbonate (VC) (Sinopharm, China) was added into the blank electrolyte at 1%, 3% and 5% by volume, which was labeled as VC-1, VC-3 and VC-5 respectively. The cells were galvanostatically charged and discharged at various current densities from 20 mA g⁻¹ to 2 A g⁻¹ between 0 and 2.0 V (vs. Li/Li⁺) on the Land battery testing system at 25 °C or 50 °C. The cells tested at 50 °C is pre-cycled 3 times at 25 °C with a current density of 20 mA g⁻¹. The high temperature environment was supported by a low-constant temp bath (DC-2006, Shanghai LNB Instrument Co., Ltd). Cyclic

1 voltammograms (CVs) were obtained at a scan rate of 0.1 mV s^{-1} and electrochemical
2 impedance spectroscopy (EIS) measurements were performed by employing an AC
3 voltage of 5 mV amplitude in the frequency range from 0.01 to 100 kHz at the
4 CHI660 electrochemical station (Chenhua Instrument Co., Shanghai). After 3 cycles
5 at 25 °C, 100 cycles at 25 °C and 100 cycles at 50 °C, respectively, the cells were
6 discharged to 0.1 V and tested on the electrochemical station to collect the impedance
7 data at 25 °C. The mass loading of active materials was around 2.5 mg in the cells.

14 **2.3 Surface characterization.** After electrochemical tests, the cells in the state of
15 Li^+ de-insertion were disassembled in the Argon-filled glovebox, after which, the HC
16 electrodes were washed with few drops of dimethyl carbonate to remove remaining
17 electrolyte species on the samples. After drying under vacuum for 5 h, the washed
18 electrodes were put into transfer vessel and then transported to the analyzing chamber
19 without exposure to the atmosphere for surface measurements. The organic
20 components of the SEI layers were characterized by Fourier Transform infrared
21 spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). XPS experiments
22 were carried out on a Thermo Fisher Scientific ESCALAB 250Xi spectrometer with
23 Al K α radiation in a cryo-pumped vacuum chamber with a measurement pressure
24 below 10^{-9} mbar and a base pressure less than 10^{-10} mbar. The XPS spectra were
25 analyzed and fitted using XPS-peak software (Version 4.1). A mixture of Lorentzian
26 and Gaussian functions was used for the least-squares curve fitting procedure and a
27 linear background was subtracted before the spectra were deconvoluted. The surface
28 morphologies of HC electrodes before and after 100 cycles at 25 °C and 50 °C were
29 observed by a field emission scanning electron microscopy (FESEM, Hitachi S-4800,
30 Japan).

3. RESULTS AND DISCUSSION

3.1 Effect of VC on the electrochemical performance at 25 °C

31 In order to investigate the contribution of VC additive to the electrochemical
32 performance of HC electrodes, we added 1%, 3% and 5% VC by volume to blank
33 electrolyte respectively. Fig. 1a and Fig. S1 present representative cyclic
34 voltammograms (CVs) of the initial two cycles at a sweep rate of 0.1 mV s^{-1} between
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0 and 2.0 V. It can be seen that the CV curves especially for the discharge branches in the first cycle are very different from those of the subsequent cycle. In Fig. 1a, the well-defined waves at 0.75~1 V are found in all samples during the first Li intercalation process but disappeared in the subsequent cycle (Fig. S1), which is usually attributed to the occurrence of some irreversible reactions associated with formation of SEI layers. It should be noted that the peak position of SEI film formation tends to shift to higher potential with VC content increasing, which demonstrates that VC is reduced prior to the reduction of EC/PC solvent [25]. However, there are no obvious differences among reversible cathodic/anodic current peaks observed from VC free to VC-5. The presence of subtle cathodic current peaks near 0.3 V can be attributed to irreversible side reactions of lithium with surface functional groups or absorbed species [33]. In both the first and second cycle, the distinct cathodic current peaks near 0 V during discharge and the distinct anodic peaks at 0.1 V during charge correspond to the Li adsorption and desorption in both sides of single sheets or walls of nano-pores, respectively, in accordance with previous reports on hard carbon based anodes [11, 15, 34-36].

Figure 1 (a) The 1st cycle profiles of CVs for VC free and VC containing samples at a sweep rate of 0.1 mV s⁻¹ between 0 V and 2.0 V. (b) The first charge-discharge voltage profiles of VC free, VC-1, VC-3 and VC-5 at a current density of 20 mA g⁻¹. (c) Rate performance at different current densities and (d) cycling stability at 400 mA g⁻¹ in the 0-2 V range for VC free, VC-1, VC-3 and VC-5.

The first galvanostatic charge-discharge curves of the HC electrodes in VC free and VC containing electrolytes at a current density of 20 mA g⁻¹ are shown in Fig. 1b. The charge-discharge profiles are composed of sloped curves and short plateaus, which is consistent with typical profiles of hard carbon anodes. The charge-discharge profiles of the VC containing samples remain the same shape as that of VC free but are shifted upwards. Also, it should be noted that a large proportion of the discharge capacity is released at a voltage range of 0-0.1 V. The initial discharge capacities of VC free, VC-1, VC-3 and VC-5 are approximately 584, 616, 574 and 560 mAh g⁻¹, and charge capacities are 413, 395, 361 and 328 mAh g⁻¹, resulting in an initial Coulombic efficiency of ~70.7%, 64.1%, 62.9% and 58.6%, respectively. It can be seen that the VC free has relatively larger reversible capacity and higher initial Coulombic

1 efficiency than VC containing samples. In other words, the first cycle irreversible
2 capacity increases as amount of VC increases. This demonstrates more lithium ions
3 are consumed irreversibly in the first discharge and decreasing lithium ions
4 de-/intercalate with the VC content increasing. These results keep in line with results
5 obtained by other researchers [25]. The initial irreversible capacity loss is usually
6 ascribed to: i) the inevitable formation of SEI and decomposition of electrolyte, in
7 good agreement with the above CV results, which also proves that VC in electrolytes
8 mainly involves in formation of SEI films. ii) Irreversible reactions between
9 heterogeneous atoms in carbon matrix (i.e. H atom) and lithium ions [37, 38]. In the
10 experiment, electrode material applied has the same proportion of heterogeneous
11 atoms, which hardly contributes to the increases of the initial irreversible capacity.
12 After the first charge-discharge process, the reversible capacities of HC electrodes
13 operated in varied VC concentrations experience a slight decrease in the following
14 two cycles (see Fig. S2). It also demonstrates that the irreversible capacity loss mainly
15 generates in the first charge-discharge process, which is highly in accordance with the
16 aforementioned CV observations.

17 Fig. 1c compares the rate performance of HC electrodes in electrolytes containing
18 different VC concentrations. It is obvious that VC free displays superior rate
19 capability at varied current densities from 80 mA g⁻¹ (335 mAh g⁻¹) to 2000 mA g⁻¹
20 (171 mAh g⁻¹). VC containing samples exhibit deteriorated rate performance with VC
21 contents increasing, among which VC-5 displays the lowest rate capacity. This
22 behavior can be attributed to an impedance rise in the cells as the amount of VC
23 increases [39]. It will also be confirmed in the electrochemical impedance
24 characterization below (Fig. 2). Notably, VC-1 shows approximate capacity when the
25 current density rises up to 800 to 2000 mA g⁻¹.

26 The stability of the VC free and VC containing samples were evaluated by
27 long-term charge-discharge cycling at the current density of 400 mA g⁻¹ (Fig. 1d). All
28 the cells were discharged and charged for 3 cycles at 20 mA g⁻¹ prior to cycling tests.
29 It can be seen that after 500 cycles, VC-1, VC-3 and VC-5 still remain 161, 143 and
30 136 mAh g⁻¹, keeping capacity retention over 78%, 81% and 85%, respectively, which

is much higher than capacity retention of VC free (about 72%). Moreover, VC-1 exhibits the highest capacity after 100 cycles, though VC-3 and VC-5 deliver lower capacities than VC free at 400 mA g⁻¹. Therefore, it is expected that those cells with the higher VC concentrations show better cycling stability. When the VC concentration retains 1 % by volume, the HC electrode shows superior capacity performance.

Fig. 2a and Fig. 2b show the Nyquist plots of coin-cells with varying VC concentrations after the first 3 cycles and 100 cycles, respectively. Open symbols are original plots and lines are the fitting curves using equivalent circuit in Fig. 2c. Generally, according to the equivalent circuit, the coin-cells consist the following components of resistance: i) bulk resistance of the cell (R_b), which reflects electric conductivity of the electrolyte, separator, and electrodes; ii) resistance (R_{SEI}) and capacitance (C_{SEI}) of the solid electrolyte interphase layer formed on the surface of the electrodes, which corresponds to the semicircle at high frequencies; iii) charge transfer resistance (R_{ct}) and constant phase element (Q), which corresponds to the semicircle at medium frequencies; iv) the Warburg impedance (W) related to a combination of the diffusional effects of lithium ions on the interface between the active material particles and electrolyte, which is generally indicated by a straight sloping line at low frequency end [40-44].

The AC impedance measurement was conducted after 3 cycles to make sure that the formation of an SEI films were completed. In Fig. 2a, Nyquist plot are made up of two semicircles and a slash, and are fitted well via the equivalent circuit, as shown in solid lines. The relative values of the R_b , R_{SEI} and R_{ct} evaluated from this model are summarized in Table 1. It is easily found that R_{SEI} and R_{ct} increase significantly with the VC concentrations increasing, while R_b remains almost constant. It demonstrates that the components derived from decomposing of VC lead to declining lithium ion transport in SEI films and decreasing charge transfer rate at HC/electrolyte interface. Furthermore, these results reaffirm the poor rate capability of HC electrodes with high VC concentrations (Fig. 1c). The AC impedance measurements were also conducted after 100 cycles to investigate the effects of VC on HC electrodes. As shown in Fig.

2b, unlike the Nyquist plots in Fig. 2a, semicircles at high frequencies and medium frequencies merge into an irregular depressed semicircle while the slashes keep invariant. It seems that, after 100 cycles, the R_{SEI} and R_{ct} of VC free and VC containing samples tend to get lower than before, which is attributed to the suppression of VC on the growth rate of SEI [45] under repeated cycles.

Based on the above analyses of results, the effects of VC concentrations on electrochemical performance of HC electrodes at 25 °C are summarized as following: i) an increase of VC concentrations in electrolyte leads to elevated resistances of SEI and charge transfer, which results in declined reversible capacity and poor rate capability of HC anodes. ii) VC additive in electrolyte improves the cycling stability of HC electrodes. Besides, since a large part of the capacity is released below 0.1 V, the capacity of HC electrodes are extremely susceptible to the over-potential or electrochemical polarization in the discharge-charge processes at room temperature. This has been verified by our previous observations [5, 46]. Consequently, VC, which will increase the resistance of the cells thus leading to electrochemical polarization, is an unsatisfactory additive for HC electrodes operated at room temperature.

Given the facts above, it sounds like that VC hardly has any positive effects when applied to HC anode based cells. However, the resistance of cells no longer plays a crucial role in the electrochemical performance of HC electrode under high temperature, because of fast ions migration and electrons transport at elevated temperatures. Hence, the stability of the electrolyte and SEI films becomes more critical than resistance to HC electrode performance. Below the temperatures electrolyte beginning to get unstable, some electrochemical characterizations of HC electrodes operated at 50 °C were conducted to investigate the impacts of VC additive on the high temperature performance.

Figure 2 Nyquist plots of coin-cells with varying VC concentrations (a) after the first 3 cycles and (b) after 100 cycles at the potential of 0.1 V vs. Li/Li⁺. Open symbols are original plots and lines are the equivalent circuit fitting curves of coin-cells. (c) Equivalent circuit used for fitting the Nyquist plots.

Table 1 Impedance data of coin-cells with varying VC concentrations after 3 cycles

Sample	R_b (Ω)	R_{SEI} (Ω)	R_{ct} (Ω)
VC free	4.7	20.6	7.1
VC-1	3.1	33.5	12.4
VC-3	4.5	43.6	14.1
VC-5	8	50.5	19.7

3.2 Effect of VC on the electrochemical performance at 50 °C

Fig. 3a shows the charge-discharge curves of HC electrodes with varied VC concentrations at a current density of 80 mA g⁻¹ at 50 °C. VC free, VC-1, VC-3 and VC-5 deliver a reversible capacity of 423, 486, 455 and 393 mAh g⁻¹, respectively, which is much larger than the capacity obtained at 25 °C (see Fig. 1c). As mentioned above, due to accelerated ions migration and electrons transport at elevated temperature, which results in decreasing electrochemical polarization, HC electrodes attract and release more lithium ions. It demonstrates that HC electrodes show great potential at high temperatures (not higher than the disabled point of electrolyte). It

should be noted that the reversible capacity tends to decrease with the VC concentrations increasing from 1 % to 5 % by volume, though VC-1 and VC-3 still exhibit higher capacity than VC free. Fig. S5 shows three cycles of HC electrodes with varied VC concentrations at 50 °C. As one can see, the reversible capacity at 50 °C decays at a slightly higher rate than at 25 °C. Furthermore, 100 cycles at a current density of 400 mA g⁻¹ were conducted at 50 °C, as shown in Fig. 3b. Interestingly, all the VC containing samples display comparable capacities which are larger than those released by VC free. The capacity retention of VC-1, VC-3 and VC-5 is 64.6%, 63.5% and 63.2%, respectively, which is also higher than that of VC free (56.7%).

Figure 3 (a) Galvanostatic charge-discharge curves of VC free, VC-1, VC-3 and VC-5 at a current density of 80 mA g⁻¹ at 50 °C. (b) Cycling stability at 400 mA g⁻¹ in the 0-2 V range for VC free, VC-1, VC-3 and VC-5 at 50 °C. All the cells tested at 50 °C were previously cycled 3 times at 25 °C.

After 100 cycles at 50 °C, the cells were discharged to 0.1 V at a current density of 20 mA g⁻¹, and then the EIS measurements were performed at 25 °C. Fig. S4 shows Nyquist plots of the cells with varied VC concentrations. It clearly shows that VC free presents the highest resistances and VC-1 gives the lowest resistances among the samples. What is more, the resistances displayed at 50 °C become approximately dozens of times higher than those obtained at 25 °C. Based on these results, we can conclude: i) the resistances of cell increase sharply after cycling at 50 °C. ii) Compared to the blank electrolyte, the electrolyte containing VC additive

considerably diminishes the resistances of cells cycled at 50 °C. In summary, VC additive is beneficial for electrochemical performance of HC electrodes operating at 50 °C. Thus, VC can be considered as a desirable additive for the HC anodes operated at elevated temperatures.

3.3 Effect of VC on the surface chemistry of HC electrodes

To better understand the function of VC additive on components of SEI, surface characterization is essential for cycled HC electrodes. In general, FTIR and XPS, which are not only highly surface sensitive but are also complementary to each other, are the most widely used two techniques for the SEI analysis. In this article, FTIR spectra were firstly measured to obtain information on the chemistry of the SEI layers formed in blank electrolyte and VC containing electrolyte. Fig. 4a shows the FTIR spectra of SEI layers formed in VC containing and VC free electrolytes at 25 °C. The pronounced peaks at 1635 cm^{-1} ($\nu_{\text{C=O}}$, as), 1402 cm^{-1} (δ_{CH_2}), 1086 cm^{-1} ($\nu_{\text{C-O}}$) and 851 cm^{-1} (δ_{OCO_2}) are attributed to ROCO_2Li or $(\text{CH}_2\text{OCO}_2\text{Li})_2$ species, which are the major reduction products of alkyl carbonate solutions [24, 47]. Peaks around 1516 cm^{-1} and 851 cm^{-1} that can be assigned to Li_2CO_3 [47, 48]. It should be noted that spectra of SEI films formed in VC containing electrolyte, especially in VC-5, include not only the typical above mentioned peaks of ROCO_2Li and Li_2CO_3 , but also an additional peak around 1171 cm^{-1} which is absent in spectra of SEI films formed in VC free electrolyte. The spectral differences of the SEI layers described above are attributed to the possible polymerization of VC and/or the VC reduction products via their double bond. The double bond in VC, which adds more strain to this molecule compared to EC, makes it more reactive on the surface of electrode at slightly higher reduction potential than EC, which is also validated in CV results above. The reduction mechanisms of VC were proposed by Aurbach et al [24] and Ota et al [49].

Fig. 4b shows FTIR spectra of HC electrodes cycled in the VC free and VC-1 electrolyte at 50 °C. These two spectra display similar peaks. The peaks around 1635 cm^{-1} ($\nu_{\text{C=O}}$, as), 1402 cm^{-1} (δ_{CH_2}), 1059 cm^{-1} ($\nu_{\text{C-O}}$) and 851 cm^{-1} (δ_{OCO_2}) are typical of ROCO_2Li or $(\text{CH}_2\text{OCO}_2\text{Li})_2$ [24, 47]. Peaks around 1516 cm^{-1} and 851 cm^{-1} that can be assigned to Li_2CO_3 [47, 48]. In addition, a weak peak around 1153 cm^{-1}

appears in the spectrum of VC-1 while it is absent in VC free, due to the possible polymerization of VC and/or the VC reduction products as mentioned above. Hence, on the one hand, some similarities are shown in the spectra of the HC electrodes treated in the electrolyte with and without VC additive. All of the spectra reflect the formation of lithium alkyl carbonate species and Li_2CO_3 . On the other hand, there are also pronounced differences in the FTIR spectra and we attribute the pronounced peaks ($1153\text{--}1171\text{ cm}^{-1}$) to polymerization of VC and/or the VC reduction products. It is clear that VC has influences on the surface chemistry of the electrodes, though the spectral studies described above cannot provide the exact identification of the VC reduction products. Finally, the FTIR spectra of SEI films formed at $50\text{ }^\circ\text{C}$, in both of that electrolyte, show the same features as those obtained at $25\text{ }^\circ\text{C}$, which indicates that no extra organic functional groups generate.

Figure 4 FTIR spectra collected from cyclicd HC electrodes in VC containing and VC free electrolytes at (a) $25\text{ }^\circ\text{C}$ and (b) $50\text{ }^\circ\text{C}$, respectively.

The surface chemistry of cyclicd HC electrodes was also characterized as a function of VC concentrations using XPS technology. Fig. 5 shows the surface atomic concentrations obtained from cyclicd HC electrodes in electrolyte with varied VC concentrations at $25\text{ }^\circ\text{C}$ and $50\text{ }^\circ\text{C}$. The corresponding concentration values are given in Table S1 (Supplementary). After cycling 100 times at $25\text{ }^\circ\text{C}$, the C content in VC containing samples remains almost steady (around 30 at%) and is slightly lower than that in VC free (31.9 at%). The amount of O on the surface gently increases from 36.3 at% (VC free) to 38.7-40 at% in VC containing samples. The concentration of F

suffers a drastic decrease from 6.8 at% (VC free) to 2.4 at% (VC-1) and then remains stable. As for Li concentrations, it experiences a steady increase from 24.9 at% (VC free) to 29.6 at% (VC-5) with the VC concentrations increasing. The results above mainly reveal that VC additive can prevent the deposition of F-containing species on the HC electrodes as well as inhibit the decomposition of LiPF_6 salt because the F on the surface of electrodes primarily originates from the electrolyte. As LiF is a typical product of the anion (PF_6^-) decomposition on the active surfaces, it further shows suppression of LiF formation on the electrode's surface when VC is present (see Fig. 6). The increases of O and Li atom concentrations are attributed to the more amount of Li_2CO_3 or semicarbonates. Fig. 5b compares the surface atomic concentrations of HC electrodes cycled in VC free and VC-1 solutions at 50 °C. The content of O, F and Li in VC-1 is lower than those in VC free except C content. The O content and Li content at 50 °C are higher than at 25 °C in VC free, and the C content and F content decrease at 50 °C. As for VC-1, C content increases from 29.4 at% (25 °C) to 33 at% (50 °C) and O content decreases from 40 at% (25 °C) to 37.4 at% (50 °C). F content and Li content remain almost constant. All these results indicate that the surface chemistry of HC electrodes changes at 50 °C and VC additive seems to impose an opposite influence on the trends of surface atomic concentrations from 25 °C to 50 °C.

Figure 5 Surface atomic concentrations obtained from HC electrodes in electrolyte with varied VC concentrations at (a) 25 °C and (b) 50 °C. The values are obtained from XPS survey scans, see Table S1 (Supplementary).

The C 1s, F 1s, O 1s, and Li 1s spectra of HC electrodes cycled in electrolytes with varied VC concentrations at 25 °C are presented in Fig. 6. Intensity of all the spectra is normalized to contrast with each other. The C 1s spectra of all samples display four peaks at binding energies of around 284.8, 286.5, 288.5 and 289.8 eV, indicating presence of at least four different carbon bonding environments. The binding energy positions of the deconvolved peaks obtained from the HC electrodes are presented in Table 2, where the peaks are assigned to the compounds associated with FTIR observations and using references [24, 47, 50-56]. It has been demonstrated that Li_2CO_3 and $(\text{CH}_2\text{OCO}_2\text{Li})_2/\text{ROCO}_2\text{Li}$ (lithium alkyl carbonate) are among the suggested products of the carbonate-based compounds [47, 51, 53]. A strong C 1s peak at 289.8 eV is clearly observed which can be assigned to the lithium carbonate, which is also evidenced by O-C=O (~531.7 eV) signals in the O 1s spectra as well as peaks at ~55.3 eV in the Li 1s spectra. The C=O bond in $(\text{CH}_2\text{OCO}_2\text{Li})_2$ or ROCO_2Li (lithium alkyl carbonate) typically gives a peak at 288-289 eV. The carbonate peak originates from either: i) solvents remaining on the surface, and/or ii) solvent molecules that have been decomposed forming $(\text{CH}_2\text{OCO}_2\text{Li})_2$ and/or ROCO_2Li species. The shoulder appearing in the vicinity of 286.5 eV is more likely to be from C-F bond (PVDF) and/or C-O (ether bond), and that the later may be associated with oxygen-containing polymeric species formed on solvent decomposition. Also, C-F bond is affirmed in F 1s spectra (Fig. 6). The peak at the lowest binding energy, at 284.8 eV in the C 1s spectra is related to species containing the C-C/C-H bonds.

The F 1s spectra of all samples consist of 3 peaks at binding energies of around 688, 687 and 684.8 eV, representing CH_2CF_2 (PVDF), P-F bond and LiF, respectively [24, 50, 55]. A weak shoulder appears at 688 eV is assigned to CH_2CF_2 (PVDF), which has already been confirmed in C 1s spectra, since the binder PVDF should be covered by SEI layers and the penetration depth of non-destructive XPS only reach around 10 nm. The rest two peaks are related to LiF and P-F species that originate from the products of LiPF_6 salt decomposition. Furthermore, presence of LiF is also verified in Li 1s signal.

The peaks related to C=O and C-O in C 1s spectra decrease gradually in intensity

and appears to broaden upon VC concentrations increasing, resulting in an increase of relative contribution of CO_3^{2-} to the C 1s peaks. Given that the VC prone to polymerization and/or being reduced prior to EC/PC, as discussed previously, increasing content of VC sample displays decreasing amounts of lithium alkyl carbonates and ethers on the surface of the HC electrodes. Hence, the relative content of Li_2CO_3 in surface of HC electrodes increases when the VC concentrations in electrolyte grow. Moreover, the intensity of peaks representing P-F bond and LiF in F 1s spectra decreases dramatically after adding VC additive into electrolytes. It should be noted that the intensity of F 1s signal retain stable from VC-1 to VC-5. Based on these findings associated with surface atomic concentrations (Fig. 5a), we can confidently rule out that VC additive independent of the amount can effectively suppress the accumulation of species containing F atoms predominantly decomposed from LiPF_6 salt, as generally evidenced on graphite [24] and Si anodes [57] in VC containing electrolyte.

Table 2 Summary of Binding Energy positions and the assigned compounds obtained by the deconvolution of the XPS spectra of HC electrodes cycled in varied VC concentrations at 25 °C presented in Fig. 6 using refs [24, 47, 50-56]

XPS signal	Binding Energy (eV)				Assignment
	VC free	VC-1	VC-3	VC-5	
C 1s	289.8	289.8	289.9	289.9	CO_3^{2-} (Li_2CO_3)
	288.4	288.5	288.5	288.4	C=O (ROCO_2Li or $(\text{CH}_2\text{OCO}_2\text{Li})_2$)
	286.6	286.4	286.4	286.5	CH_2CF_2 (PVDF), C-O (ether bond)
	284.8	284.8	284.8	284.8	C-C/C-H (hydrocarbon)
F 1s	688	687.8	687.9	688	CH_2CF_2 (PVDF)
	687	687	687	687	P-F
	684.8	684.5	684.8	684.6	LiF

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O 1s	533	533.1	533.4	533.3	C-O (ether bond)
	531.6	531.7	531.8	531.7	O-C=O
					(carboxylates/ carbonates)
Li 1s	56	56.1	56	56.5	LiF
	55.1	55.3	55.5	55.3	Li ₂ CO ₃

Figure 6 C 1s, F 1s, O 1s, and Li 1s spectra of HC electrodes cycled in electrolytes with varied VC concentrations at 25 °C, respectively.

The further investigation of effects of VC additive on the surface chemistry of HC electrodes was performed. C 1s, F 1s, O 1s, and Li 1s spectra of HC electrodes cycled

100 times in VC free and VC-1 electrolytes at 50 °C are presented in Fig. 7. Similarity of the surface chemistry stands out in the two kinds of electrolytes. As mentioned above, the C 1s spectra consist of 4 peaks at binding energies of around 284.8, 286.5, 288.5 and 289.8 eV, respectively, representing hydrocarbon, ethers, carboxylates and carbonates from the lowest to the highest binding energies, respectively. It should be noted that the contribution of CO_3^{2-} to C 1s spectrum of VC free at 50 °C is larger than that at 25 °C. On the contrary, the relative content of CO_3^{2-} of VC-1 seems to decrease from 25 °C to 50 °C. In addition, the relative amount of C-C/C-H bonds on the SEI films of VC-1 increases from 25 °C to 50 °C and vice-versa is for VC free. These results are consistent with the trends of C and O atom concentrations on surfaces with temperatures rising (see Fig.8 or Table S1). The F 1s signal is composed of three peaks that are assigned to CH_2CF_2 (PVDF), P-F bond and LiF, respectively. Compared to the relative peak intensity of F 1s spectrum in Fig. 6, the relative amount of P-F and LiF in VC free changes dramatically in the opposite direction with the temperature rising from 25 °C to 50 °C, indicating the thermal instability P-F in SEI films [20]. LiF makes the largest contributions to F 1s signal of VC free at 50 °C. However, VC-1 shows a relative lower proportion of LiF than the proportion of P-F bond that is similar as the situation at 25 °C. The spectra of O 1s include C-O bond and CO_3^{2-} indicating carboxylates and/or carbonates. Li 1s spectrum in VC free reveals two distinguished peaks at 56.1 and 55.4 eV, which are characteristic of LiF and Li_2CO_3 figuration respectively. However, the peak at around 56 eV representing LiF vanishes in VC-1. This may be ascribed to the traces of LiF concentration in SEI films formed in VC-1, which is also confirmed in F 1s spectra in Fig. 7. Furthermore, the surface F atom concentration displayed in Fig.8 and Table S1 also supports this speculation.

Based on the observation from XPS surveys (see Fig. 5 - Fig. 7), several obvious changes on surface chemistry of HC electrodes are summarized as following: i) The presence of VC additive diminishes the amount of F atom concentrations and F-containing species, especially LiF, on SEI films of HC electrode at both 25 °C and 50 °C. In other words, VC additive considerably restrains the decomposition of LiPF_6

salt under cycling. ii) The Li_2CO_3 content on the surfaces of HC electrodes cycled at 25 °C is inclined to increase with the VC concentrations increasing. iii) When HC electrodes are charged-discharged in VC free electrolyte at 50 °C, the proportion of Li_2CO_3 in SEI layers increases dramatically and the relative amount of P-F species decreases. For one thing, it demonstrates that at elevated temperatures, the components like lithium alkyl carbonates and semicarbonates tend to convert to the stable components like Li_2CO_3 . For another, the surface composition of HC electrodes cycled in VC-1 at 50 °C remains almost invariant indicating that VC additive exhibits its impressive function on stabilization of SEI films at elevated temperatures.

Table 3 Summary of Binding Energy positions and the assigned compounds obtained by the deconvolution of the XPS spectra of HC electrodes cycled in VC free and VC-1 electrolyte at 50 °C presented in Fig. 7.

XPS signal	Binding Energy (eV)		Assignment
	VC free	VC-1	
C 1s	289.8	289.8	CO_3^{2-} (Li_2CO_3)
	288.5	288.7	C=O (ROCO ₂ Li or (CH ₂ OCO ₂ Li) ₂)
	286.5	286.4	CH ₂ CF ₂ (PVDF), C-O (ether bond)
	284.8	284.8	C-C/C-H(hydrocarbon)
F 1s	687.8	688	CH ₂ CF ₂ (PVDF)
	687	687	P-F
	685	685	LiF
O 1s	533.2	533.1	C-O(ether bond)
	531.7	531.7	O-C=O (carboxylates/ carbonates)
Li 1s	56.1		LiF
	55.4	55.3	Li_2CO_3

Surface morphology was characterized by the Scanning Electron Microscope (SEM)

1 to study the influences of VC additive on HC electrodes. Fig. 8 shows SEM
2 micrographs of HC electrodes cycled in electrolytes with different VC concentrations
3 at 25 °C and 50 °C. It is obvious that the electrode surface is mainly composed of
4 irregular shaped large particles (HC) and micro- or nano- particles adhering to HC
5 particle surfaces, which is distinctly different from the presentation of uncycled HC
6 electrodes (Fig. S5a – b). The HC particles cycled at 25 °C in VC free are covered by
7 thick continuous layers and tiny grains (Fig. 8a and Fig. S5c). When HC electrodes
8 cycles in VC containing electrolytes at 25 °C, the surface morphology displays
9 increasing numbers of tiny grains on HC particles as well as thickness of SEI films
10 with VC concentrations rising, especially distinct in VC-5 (Fig. 8b –d). However, no
11 apparent thick layers, like those in VC free, are observed in these samples. Comparing
12 the surface morphology of HC electrode cycled at 25 °C and at 50 °C in VC free (Fig.
13 8a, e and Fig. S5c, e), visible changes are observed in VC free. The surface layers in
14 VC free tend to become rougher due to more grains deposited on them, whereas the
15 surface morphology in VC-1 at 50 °C remains almost the same as at 25 °C (Fig. 8b, f
16 and Fig. S5d, f).

17 From these SEM observations combined with above XPS results, it is proposed that
18 the abundant grains on electrode surfaces cycled in VC containing electrolytes are
19 attributed to the increasing amount of Li_2CO_3 components in surface layers. Also,
20 increased Li_2CO_3 components in surface layers of VC free at 50 °C is responsible for
21 the roughness of surface morphology.

Figure 7 C 1s, F 1s, O 1s, and Li 1s spectra of HC electrodes cycled in VC free and VC-1 electrolytes at 50 °C, respectively.

Figure 8 SEM micrographs of HC electrodes cycled in electrolytes of (a) VC free, (b) VC-1, (c) VC-3 and (d) VC-5 at 25 °C, respectively. HC electrodes cycled in (e) VC free and (f) VC-1 at 50 °C.

Considering all the results of surface chemistry characterization combined with those electrochemical performance, we can accurately describe the effects of VC additive on HC electrodes. First of all, VC additive is reduced and/or polymerized prior to EC/PC consuming more lithium ions to form SEI films in the initial charge-discharge process at 25 °C, resulting in an increase of irreversible capacity loss as well as a declining initial Coulombic efficiency. Secondly, SEI films formed on in VC containing electrolytes show more amount of Li_2CO_3 and less F species, like LiF etc., than VC free, which contributes to increases of R_{ct} and R_{SEI} . As a result, the

reversible capacity of HC electrodes at 25 °C declines linearly when the VC concentrations in electrolyte increase, on account of HC anodes' susceptibilities to elevated impedances and expanded electrochemical polarizations. However, the cycling stability is improved when the VC concentrations increase beyond 1% by volume. Therefore there is a trade-off between long cycle life and low cell impedance. Thirdly, HC electrodes in VC containing electrolytes (concentration lower than 3% by volume) at 50 °C deliver much more reversible capacities than in VC free. It is assumed that lithium ion transport and migration rates as well as reactivity should be enhanced at elevated temperatures, though the impedances increase by 2 times (VC-1) and even by 10 times (VC free) due to increased amount of Li_2CO_3 . Reasonable Li_2CO_3 content in the SEI films can improve the battery performances, which is evidenced by Aurbach's group [58]. Last but not the least, the surface chemistry of SEI films on HC electrode changes significantly at elevated temperatures resulting in drastic enlargement of cell impedance, besides optimal VC concentration (~ 1%) not only maintains the surface components stable but also improves the electrochemical performance of HC.

4. CONCLUSIONS

In this article, the pros and cons of VC additive on electrochemical performance of HC electrodes are primitively described. At 25 °C, an increase of VC concentrations in electrolyte leads to elevated resistances of SEI and charge transfer, which results in declined reversible capacity and poor rate capability of HC anodes, though VC additive slightly improves the cycling stability of HC electrodes. When the operation temperature of HC electrodes climbs to 50 °C, the brilliant advantages of VC appear, such as enhanced reversible capacity, improved cycling stability and decreased total resistances of cell. Also, surface chemistry analyses of HC electrodes using FTIR, XPS and SEM indicate that VC additive is reduced and/or polymerized prior to EC/PC to form a stable SEI film upon cycling, which contains increased Li_2CO_3 and decreased F species. Components and morphology of electrode surface change considerably without VC from 25 °C to 50 °C. It demonstrates that SEI formed in the presence of VC helps suppress salt anion (PF_6^-) decomposition as well as SEI

transformation occurred at 50 °C. Finally, the VC concentration is critical for the performance of HC electrode and the optimal VC concentration in this article is 1% by volume. In conclusion, VC additive is desirable for HC anode, especially at elevated temperatures, in LIBs or maybe in sodium ion batteries.

ASSOCIATED CONTENT

Supporting Information Available: Brief statement in non-sentence format listing the contents of the material supplied as Supporting Information.

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