Enabling an intrinsically safe and high-energy-density 4.5 V-class Li-ion battery with nonflammable electrolyte

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Abstract
Developing nonflammable electrolyte with a wide electrochemical window has become an urgent demand for high-energy-density and high-safe lithium-ion batteries (LIBs). Herein, a fluorinated nonflammable phosphate electrolyte is developed to construct a safe 4.5 V-class LIB (Si-SiC-C/0.35Li2MnO3·0.65LiNi0.5Mn0.5O2). The proposed fluorinated phosphate electrolyte, 0.8 M LiPF6/tris(2,2,2-trifluoroethyl)phosphate (TFEP) + 5 vol% fluoroethylene carbonate (FEC) + 5 vol% vinylene carbonate (VC), is not only completely nonflammable but also exhibits excellent oxidative/reductive stability on 0.35Li2MnO3·0.65LiNi0.5Mn0.5O2 cathode and Si-SiC-C anode. The in situ differential electrochemical mass spectrometry and X-ray photoelectron spectroscopy proved that TFEP-based electrolyte does not decompose into gases but forms a high-quality electrode-electrolyte interface on cathode surface at high working potential. The 4.5 V-class LIBs using 0.8 M LiPF6 TFEP-based nonflammable electrolyte shed some light on potential application for high-safe and low-cost larger-scale energy storage.

KEYWORDS
high energy density, lithium-ion battery, nonflammable electrolyte, safety

1 | INTRODUCTION
Lithium-ion batteries (LIBs) are the most competitive candidates in current portable electronics market and potentially dominate the electric vehicles due to their high energy density, long-term lifespan and environmental benignity. These applications in turn draw higher demands in energy densities of LIBs, which are required to develop novel cathode materials with higher specific capacity and operating voltage. Layered lithium-rich manganese oxide (LRMO) with large capacity (>250 mAh g\textsuperscript{-1}) is considered as a promising cathode material for high-energy-density LIBs.\textsuperscript{1,2} Combining LRMO cathode with Si anode to construct a 5 V-class battery could realize ~500 Wh kg\textsuperscript{-1} in full-cell energy density (only based on cathode and anode active materials).\textsuperscript{1,2} However, the LRMO cathode possesses...
a high operating potential of >4.5 V, which needs a high oxidation-stable electrolyte system. Conventional carbonate-based electrolytes are anodically unstable so as to decompose readily into gas when the charging potential is over 4.4 V vs Li/Li+. On the other hand, the highly flammable carbonate electrolytes can be readily ignited, causing serious battery safety issues. Therefore, high oxidative stability and nonflammable electrolyte have become urgently necessary for the development of LIBs with considerable energy density and safety.

Recently, highly concentrated electrolytes (HCEs) have been proved as an attractive electrolyte with wide electrochemical window and enhanced thermal stability and reduced flammability. For example, Wang and coworkers reported a carbonate-based HCE (10 M LiFSI in EC/DMC) and demonstrated their enhanced oxidation stability by constructing a Li/LiNi0.6Mn0.2Co0.2O2 half-cell. In addition, Xu’s group expanded the narrow electrochemical stability window (1.23 V) of aqueous electrolytes to ~3.0 V by constructing a “water-in-salt” HCE. Some high-concentrated (or high-molar-ratio) nonflammable phosphate electrolytes were also used to enhance the stability and safety of the electrolytes. However, the poor ionic conductivity and high viscosity of HCEs have hindered their practical applications.

Fluorine-substituted solvents, owing to the high electronegativity and low polarizability of the fluorine atom, have high oxidation stability, low melting point, and high flash point. Wang’s group reported a fluorinated electrolyte with fluoroethylene carbonate/3,3,3-fluoroethylmethyl carbonate/1,1,2,2-tetrafluoroethyl-2’,2’-trifluoroethyl ether (FEC/FEMC:HFE, 2:6:2 by weight) and demonstrated its superior oxidation stability by constructing high oxidation potential 5 V LIB full cells. Some carbonate electrolytes with fluorinated phosphate esters as additive show not only flame-retardant properties but also good electrochemical compatibility with high-voltage cathodes. Furthermore, the flame-retardant-modified PE separator also shows nonflammable property. However, these methods still suffer from potential safety hazard due to the majority flammable component. Therefore, it is vital to explore the high-oxidation-stable and nonflammable electrolyte for development of high-energy-density and safe LIBs.

Although some low molecular weight phosphates have been studied as promising nonflammable electrolytes for LIB to exhibit high safety property, these phosphate solvents are more reactive at high oxidation potential due to their relatively high highest occupied molecular orbital (HOMO). Herein, we report a 5 V-class Si-SiC-C (SSC)/0.35Li2MnO3·0.65LiNi0.5Mn0.5O2 (LRMO) full cell based on fluorinated nonflammable electrolyte (0.8 M LiPF6/tris(2,2,2-trifluoroethyl) phosphate (TFEP) + 5 vol% fluoroethylene carbonate (FEC) and 5 vol% vinylene carbonate (VC)). This TFEP-based electrolyte is not only completely nonflammable but also exhibits a remarkably high thermal and oxidation stability toward LRMO cathode, as well as electrochemical compatibility with Si anode. The SSC/LRMO full cell with the TFEP-based electrolyte using conventional concentration LiPF6 exhibits ultrahigh energy density (~500 Wh kg−1) and low electrolyte cost. This study opens a new avenue for the design of low-cost, high-energy-density, and high-safety LIBs.

2 RESULTS AND DISCUSSION

The flammability of the electrolytes can be visualized in Figure 1A and Videos S1 and S2. As expected, the TFEP-based electrolyte cannot be ignited while the conventional carbonate electrolyte (1.0 M LiPF6/EC:DEC = 1:1 by vol) shows obvious burning once ignited (Figure 1A and Videos S1 and S2). Thermal stability test is carried out to compare the exothermic properties of the TFEP-based carbonate electrolyte with charged LRMO cathode. The differential scanning calorimetry (DSC) curves of the electrolytes with charged LRMO are shown in Figure 1B. One major exothermic response (218°C) is observed for the electrolyte based on 1.0 M LiPF6/EC: DEC = 1:1 by vol, while the TFEP-based electrolyte exhibits only a weak exothermic peak. The overall exothermic heat generated by the reaction between the charged LRMO and the TFEP is only 5.5 J g−1, which represents less than 1% of the exothermic heat (632 J g−1) in carbonate electrolyte. On the other hand, the TFEP-based electrolyte shows a higher onset temperature (211°C) than the carbonate electrolyte (202°C) (Figure 1B). These results suggest that the charged LRMO material is less reactive toward the nonflammable electrolyte, exhibiting an improved thermal stability. The temperature dependences of conductivity for the TFEP-based electrolyte are shown in Figure S1A. Owing to the high electronegativity and low polarizability of fluorine atom, LiPF6 salt shows low solubility and ionization degree in the pure TFEP electrolyte (only dissolving 0.5 M LiPF6). Thus, in order to improve the solubility and ionization degree of salt in TFEP solvent, a bifunctional additive—FEC is applied to form the 0.8 M LiPF6/TFEP + 10 vol% FEC(0.8 M LiPF6/TFEP + FEC) electrolyte, which not only increases the dissociativity of Li salt but also helps to build a protective layer on both Si anode (solid electrolyte interface, SEI) and LRMO cathode (cathode electrolyte interface, CEI). The TFEP-based electrolyte exhibits a conductivity of approximately 1.1 mS cm−1 at 25°C, which can meet the requirement of LIB’s applications to some extent. Based on the Arrhenius equation, the activation energy of the TFEP-based electrolyte is calculated to be
16.02 kJ mol\(^{-1}\) lower than that of the organic carbonate electrolyte (24 kJ mol\(^{-1}\)), implying the lower temperature dependence of ionic conductivity.

Oxidation stability is an important criterion in designing high voltage electrolyte. The cyclic voltammetry (CV) using Pt microelectrodes (0.5 mm) over a voltage window of 0 to 5 V (vs Li/Li\(^+\)) is performed on the TFEP-based electrolyte at a scan rate of 50 mV s\(^{-1}\) to evaluate its oxidation stability (Figure S1B). No obvious redox peak is observed in TFEP-based electrolyte even at 5 V, indicating high stability against oxidation. In addition, there is a pair of reversible Li plating/stripping peaks confirming its high electrochemical compatibility on Li metal electrode. Overall, the TFEP-based electrolyte shows considerable stability toward both the low (the potential of Li-metal anode) and high (5 V against Pt electrode) potential values.

CV of the LRMO cathode in the TFEP-based electrolyte is carried out at a scan rate of 0.1 mV s\(^{-1}\) with voltage window from 3.0 to 4.8 V, as shown in Figure S2. In the initial anodic scan, two major oxidation peaks appear at 4.25 and 4.6 V, which are associated with the Ni\(^{2+}\)/Ni\(^{4+}\) couple and irreversible electrochemical activation of LRMO. The cathodic peaks at 3.8 and 3.3 V result from the reduction of Ni\(^{4+}\) and Mn\(^{4+}\), respectively.\(^3\) In pure TFEP electrolyte, LRMO cathode only shows weak oxidation/reduction peaks, while these peaks get stronger and more reversible in the electrolyte with additives, indicating that the additives help to form SEI film on LRMO cathode (Figure S2). Figure 1C and Figure S3A show the initial charge/discharge profiles of LRMO cathode in different phosphate electrolytes and carbonate electrolyte. Although the LRMO delivers an initial reversible capacity of approximately 225 mAh g\(^{-1}\) in all studied electrolytes, it is manifested that the initial coulombic efficiency (ICE, 77%) in the TFEP-based electrolyte with 10% FEC is higher than those in the carbonate electrolyte (75%) and nonfluorinated phosphate electrolytes (71% for trimethyl phosphate-based and 70% for triethyl phosphate-based) (Figure S4). Additionally, the average CE of TFEP-based electrolytes with 10% FEC reach 99.4% over 50 cycles) (Figure 1D), which is higher than that (98.5%) of over 50 cycles in carbonate electrolyte (Figure S3B). This phenomenon illustrates that the fluorinated electrolyte possesses higher oxidation stability than carbonate and nonfluorinated phosphate electrolytes, which could be ascribed to the high electronegativity and low polarizability of the fluorine atom. Besides, when another additive,
VC, is added to further assist the CEI formation, the LRMO electrode can achieve a higher ICE (78%, Figure 1C), a better capacity retention (72% after 100 cycles, Figure 1D), and a super-high average CE (99.7%). It suggests that the construction of the stable CEI film is very necessary to improve the electrochemical performance of the LRMO electrode in the high-potential region.

The mechanism of performance improvement by using the FEC and VC coadditive is investigated by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) (Figure 2A-D and Figure S5). The SEM images of the LRMO electrodes cycled in the TFEP electrolyte with and without VC exhibited their original morphology, suggesting that the CEI film on the electrode is extremely thin (Figure 2A and Figure S5A). The surface compositions of the cycled LRMO electrodes are further investigated by XPS (Figure 2B-D and Figure S5B-D). The XPS spectra exhibit slight differences between the cycled cathode in the electrolytes with and without VC. The C1s and F1s spectra show that polyvinylidene fluoride (PVDF) binder (290.7 eV, 286.2 eV for C1s and 688.5 eV for F1s) and carbon black (284.8 eV) are presented in the cycled cathodes, confirming that the films on the cathode is very thin. In the O1s spectra, the signal of M-O (531.2 eV) corresponds to the bonds between transition metal and oxygen arose, indicating that the CEI in VC-containing electrolyte is much thinner. From the C1s and O1s spectra, the formation of compounds containing oxygenated organic species (534.2 eV for O1s) and Li2CO3 (532.2 eV for O1s and 288.35 eV for C1s) was clearly observed at the surface of the discharged electrode after cycling. The signal of inorganic decomposition product Li2CO3, a by-product of FEC or VC electrochemical reaction, which suffers from continuous reversible change accompanied with Li+ intercalation/deintercalation in LRMO, is weaker in the O1s spectrum of cathode cycled in electrolyte with VC. The results indicate that the formed SEI film is stabilized in the electrolyte with VC. All of the evidences indicate that the FEC and VC coadditive is capable of having a synergistic effect upon forming a dense and stable CEI film so as to enormously suppress the decomposition of the electrolyte.

It is reported that conventional carbonate-based electrolytes are anodically unstable when charging potential is over 4.4 V vs Li/Li+, resulting in CO2 generation due to the decomposition of the carbonate solvent. To evaluate the oxidation stability of the LRMO in carbonate and TFEP-based electrolytes, in situ differential electrochemical mass spectrometry (DEMS) experiment is conducted to detect gas evolution through CV measurement at a scan rate of 0.5 mV s−1. Figure 2E,F compares the potential and gas evolution profiles recorded during the first two cycles for the cells using carbonate electrolyte (Figure 2E) and TFEP-based electrolyte (Figure 3F). In carbonate electrolyte (Figure 2E), CO2 evolves from 4.4 V in the initial positive scan, indicating the constant oxidative decomposition of electrolyte on the surface of the LRMO electrode. In the initial negative scan, CO2 generation remains until discharge to 3.75 V, which can also be attributed to the continuously oxidative decomposition of the electrolyte. Subsequently, CO2 evolution decreases to nearly zero at ~2.0 V. In the second cycle, no CO2 signal is observed, indicating that a CEI surface film on the LRMO electrode has been formed during the first cycle, which suppresses further decomposition reaction of carbonate electrolyte. In contrast, there is no CO2 gas evolution in TFEP-based electrolyte all through the charging/discharging process (Figure 2F), suggesting the higher oxidation stability of TFEP-based electrolyte.

To investigate the reductive stability of TFEP-based electrolyte on high-capacity Si-based anode, the TFEP-based electrolytes are tested in Li/SSC half cells (Figure 3 and Figure S6). Figure S6 reveals that without additives, SSC anode only shows a strong peak at 1.1 V, assigning to the electrolyte decomposition and no reversible redox peaks of the insertion of lithium ions into Si. With FEC, a pair of weak peaks corresponding to the Li alloying/dealloying reactions appears, while these peaks get stronger and more reversible in the electrolyte with VC, indicating that the FEC-VC coadditive also exhibits a synergistic effect on the anodic SEI film formation. Figure 3A and Figure S7A show the initial charge/discharge profiles of the SSC anodes in different electrolytes. Compared to the ICE (80%) of SSC anode in carbonate electrolyte (Figure S7A), lower ICEs are observed in the cells using TFEP-based electrolyte without VC (73%) and with VC (74%) (Figure 3A). These results indicate that the irreversible decomposition reaction of TFEP is stronger than that in carbonate electrolyte. In both TFEP-based electrolytes, the SSC anode can deliver a reversible capacity of ~800 mAh g−1 (Figure 3A). However, the SSC anode cycled in the TFEP-based electrolyte with VC shows a capacity retention of 93% and average CE (98.1%) after 100 cycles, which is higher than those in the TFEP-based electrolyte without VC (62% and 97.8%) (Figure 3B) and in the carbonate electrolyte (84% and 97.8%) (Figure S7). The results imply that the FEC-VC coadditives can form a more stable SEI film to realize high performance of Si-based anode in TFEP electrolytes.

In order to explore the mechanism of performance improvement for the Si-based anode by using the FEC-VC coadditives, SEM and XPS of cycled electrodes in different electrolytes are examined (Figure 3C-F and Figure S8). The surface of the cycled SSC in the electrolyte with VC additive is covered by a smooth film (Figure 3C), while some rough deposits are observed on the surface of the
electrode cycled in the electrolyte without VC (Figure S8A), indicating that the introduction of VC additive can form a denser film. The surface chemistry of the cycled SSC electrodes is further examined by XPS (Figure 3D-F and Figure S8B-D). In the electrolyte with only FEC, the presence of \((-\text{CHFCH}_2\text{)}_n\), LiF, and Li$_2$CO$_3$ is evidenced by the C1s, F1s and O1s peaks (Figure S8B-D).\(^{34}\) It is found that in the electrolyte with the coaddition of FEC and VC, an extra produce, organic polyvinylidene carbonate, is detected due to the reduction of VC (Figure 3D).\(^{27,35}\) In addition, the content of LiF decreases significantly, corresponding to the suppression of TFEP decomposition reaction (Figure 3E and Figure S8C). The organic SEI film (polyvinylidene carbonate and \((-\text{CHFCH}_2\text{)}_n\)) derived from VC and FEC can effectively coat on the surface of materials to make SEI film more cohesive and flexible, while the inorganic component (LiF) can hinder the permeation of the solvent. Therefore, the inorganic-organic composite film can efficiently prevent TFEP from contacting with the SSC electrode, leading to a higher cycling CE and capacity retention (Figure 3).

The excellent results inspire us to further investigate the electrochemical performance of full cells with SSC anodes and LRMO cathodes. The full cell is a cathode-excess design to balance the irreversible initial capacity of the SSC anode. The full cell using 0.8 M LiPF$_6$/TFEP + FEC + VC electrolyte delivers a reversible specific capacity of 815 mAh g$^{-1}$ (in terms of the anodic mass) and an ICE of 66% (Figure 4a). An average output voltage of 3.26 V leads to an energy density above 500 Wh kg$^{-1}$ based on the total active mass of anode and cathode. The cycling test shows that the full cell has an insufficient capacity retention of 50% after

**FIGURE 2** Decomposition performance of TFEP-based electrolyte on the LRMO cathode. A, SEM image and (B-D) XPS spectra of the LRMO electrodes cycled in 0.8 M LiPF$_6$/TFEP + FEC + VC electrolyte for 10 cycles. B, C1s; C, F1s; D, O1s. DEMS data for LRMO electrode in (E) 1.0 M LiPF$_6$/EC:DEC (1:1 by vol) electrolyte (E) and TFEP-based electrolyte (F), respectively, at a scan rate of 0.5 mV s$^{-1}$. Blue line: scanning potential. Yellow line: evolution rate of CO$_2$.
50 cycles (Figure 4B), which might be due to the imperfect match between the cycling CE of the anode and cathode during cycling and no pre-activation of the SSC anode in order to provide a more realistic reference for practical applications. The cycling stability could be improved by perfect balance in capacity and CE of anode and cathode, and
effective film-formed additives in the future studies. In our previous work, we have reported a series of non-flammable electrolyte contain TMP (Sb/LiFePO4), TEP (graphite/LiCoO2), TFEP (hard carbon/Na3V2[PO4]3), and so on.17,18,24,25 Compared with them, the highly stable fluorinated solvent (TFEP) avoids the use of high-concentrated salt, is close to practical application in the case of the cost, and shows high stability toward both the low (the potential of Li-metal anode) and high (against RLMO) potential. Nevertheless, the SSC/LRMO full cell with TFEP nonflammable electrolyte preliminarily exhibits super-high energy density, cyclability, and safety to meet the urgent requirement of large-scale LIBs.

3 | CONCLUSION

In summary, a nonflammable fluorinated TFEP-based electrolyte is introduced to investigate its electrochemical compatibility in a wide potential range. The fluorinated electrolyte meets all the basic requirements for the high-energy-density and safe LIBs, including nonflammability, high thermal stability, and acceptable ionic conductivity. Moreover, the LRMO cathode in the TFEP-based electrolyte with FEC and VC coadditives can deliver a high reversible capacity of 225 mAh g\(^{-1}\) with an ICE of 78% in the potential of 2–4.8 V, an excellent capacity retention (72% at 100th cycle), and an average CE of 99.7%, exhibiting high oxidation stability. A 5 V-class SSC/LRMO full cell in the TFEP-based electrolyte shows not only high energy density (500 Wh kg\(^{-1}\)) and considerable cycling performance but also high safety due to use of nonflammable electrolyte. The highly stable fluorinated solvent avoids the use of high-concentrated salt and is close to practical application in the case of the cost. Therefore, it is demonstrated that rational design of multifunction phosphate solvent could provide an approach to solve the high-energy-density and safety issues encountered by the present LIBs.

4 | EXPERIMENTAL SECTION

4.1 | Materials

The Si-SiC-C (SSC) composite was prepared by a two-step ball-milling process. First, a 1:2 mass ratio of the commercial Si (<100 nm, Sigma-Aldrich) and nano-SiC (99.5% purity, 40–60 nm) were mixed and ball milled in a SPEX-8000 high-energy mechanical mill for 8 hours. Then, the reactant product was further ball milled with graphite powder (99% purity, <5 mm) in a planetary mill (QM-1SP04, Nanjing, China) at a rotation speed of 200 rpm for 6 hours. The weight ratio of graphite to the total amount of Si-SiC was designed as 1:9, so that the final composite is composed of 30 wt% Si, 60 wt% SiC, and 10 wt% graphite. The composition of the anode was 70 wt% SSC, 20 wt% Super P (TIMCAL, Graphite & Carbon Inc.), and 10 wt% polyacrylic acid (PAA). The composition of the cathode was 80 wt% 0.35Li2MnO3·0.65LiNi0.5Mn0.5O2 (LRMO), 10 wt% polyvinylidene fluoride (PVDF), 5 wt% Super P, and 5 wt% acetylene black. The LRMO electrode used in DEMS analysis consisted of the 80 wt% LRMO, 10 wt% Super P, and 10 wt% polytetrafuoroethylene (PTFE) binder. The TFEP used in this work was synthesized by reacting trifluoroethanol with phosphorus oxychloride.36 TFEP was purified with a redistillation step under vacuum after dehydration with CaH2 under an atmosphere of inert gas for 12 hours. Battery-grade LiPF6, fluoroethylene carbonate (FEC), vinylene carbonate (VC), and carbonate electrolyte (1 M LiPF6 EC: DEC = 1:1 by vol) were purchased from Shanshan Co. Ltd., Dongguan, China. All the electrolytes were prepared in a glovebox (MIKROUNA) under high-purity Ar gas.

4.2 | Electrolyte characterization

Thermal analysis of the electrolytes against electrodes was carried out on a DSC (Q200 TA) at a heating rate of 10°C min\(^{-1}\) from 60°C to 400°C. The ionic conductivities of the selected electrolytes were measured on DDS-307 (INESA Scientific Instrument Co. Ltd., Shanghai, China) at a temperature range of −40 to 60°C.

4.3 | Electrochemical measurements

The cyclic voltammetry (CV) was performed on a CHI600C Electrochemical Analytical Instrument (Chenhua, Shanghai, China) in selected electrolytes to measure the electrochemical stability windows by using a microelectrode with a Pt disk of 0.5 mm diameter as working electrode and a Li foil as both reference and counter electrodes. The CV experiments for the electrode materials were tested in selected electrolytes using a two-electrode system with an SSC anode or an LRMO cathode as the working electrode, and Li plates as both the reference and counter electrodes. The performance of half-cell was tested on a battery test system (CT-4008, Neware, Shenzhen Neware Electronics Co., China) with CR2016 coin cells.

4.4 | DEMS measurement

The gases generated during charging/discharging were detected by in situ differential electrochemical mass spectrometry (DEMS). The cell was constructed by Li foil,
separator, and the LRMO electrode. The cell was purged continuously with Ar gas, which flowed from the cell into the mass spectrometer carrying the evolved gases for MS analysis. The cell potential was raised in 0.5 mV s⁻¹ from open circuit voltage to 4.8 V, and the ion current of CO₂ was monitored as a function of time.

4.5 | Electrode characterization

The morphological images of the SSC anodes and LRMO cathodes after cycling in different electrolytes were obtained using FESEM (Zeiss Merlin Compact VP, Germany). The chemical composition on the surface of the cycled electrodes in VC-free and VC-containing electrolytes was characterized by X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB 250Xi) with monochromatized Al Ka radiation. The cycled cells were disassembled in a glove box under argon atmosphere. The cycled SSC anodes or the LRMO cathodes were harvested and rinsed with anhydrous dimethyl carbonate (DMC) to remove residual LiPF₆ and TFEP, followed by vacuum drying at room temperature (25°C) for SEM and XPS characterization. To avoid contamination or side reactions with atmospheric moisture and oxygen, the electrodes were quickly transferred from the glove box to the SEM chamber by using sealed vessels filled with Ar gas. DSC measurement was carried out on a Q200 TA instruments under a nitrogen atmosphere. Samples were hermetically sealed in Al pans in the glove box. The measurements were conducted with the samples heated to 150°C at a rate of 10°C min⁻¹.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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SUPPORTING INFORMATION
Additional supporting information may be found online in the Supporting Information section at the end of this article.

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