A novel electrochemically compatible, high-voltage, and non-flammable electrolyte has been prepared based on a fluorinated ether with no flash point, that is, 1,1,1,3,3,3-hexafluoroisopropyl methyl ether (HFPM). Our experimental results demonstrate that this F-electrolyte is not only totally nonflammable in fire burning tests, but it also exhibits a remarkably high anodic stability of at least 5.5 V (vs. Li+/Li). In particular, this F-electrolyte has good compatibility with graphite anodes. Mesocarbon microbeads/LiNi$_{1/3}$Mn$_{1/3}$O$_2$ 18650 batteries made with this F-electrolyte display an excellent cycling stability with 82% capacity retention after 200 cycles at a high cutoff voltage of 4.9 V, confirming their potential as high-voltage lithium-ion batteries with enhanced safety and longevity.

1. Introduction

Recently, the demand for a high-voltage electrolyte has become a high priority for the integration of high-capacity lithium-ion batteries (LIBs) in transportation and grid-storage applications.$^{[1,2]}$ Owing to the high electronegativity and low polarizability of the fluorine atom, fluorinated solvents possess desirable properties, such as higher oxidation stability, lower melting point, and higher flash point. Therefore, fluorinated carbonate solvents appear to be a suitable electrolyte candidate for high-voltage electrolyte solvents.$^{[3-6]}$ In 2002, Ishikawa and co-workers$^{[7]}$ investigated, for the first time, the use fluoroethylene carbonate (FEC) as a co-solvent instead of the most commonly used ethylene carbonate (EC) in a high-voltage LiCoO$_2$ cathode, and the Li/LiCoO$_2$ cell containing the FEC-based electrolyte exhibited a higher and stable discharge capacity, even with a high upper cutoff of 4.5 V, compared with the cell containing the base electrolyte. In recent years, Hu et al.$^{[8]}$ reported that the FEC-based electrolyte improved the electrochemical performance of LiNi$_{1/3}$Mn$_{1/3}$O$_2$ at elevated temperatures. The high anodic stability of the electrolyte based on fluorinated carbonate solvents was supported by electrochemical evaluation results when using LiNi$_{1/3}$Mn$_{1/3}$O$_2$/Li and LiNi$_{1/3}$Mn$_{1/3}$O$_2$/Li$_x$Ti$_{2}$O$_5$ cells.$^{[8]}$ Markevich et al.$^{[9]}$ investigated the effect of the FEC-based electrolyte in LiCoPO$_4$/Li, LiCoPO$_4$/Si, and LiNi$_{1/3}$Mn$_{1/3}$O$_2$/Si cells, and reported better capacity retention, owing to the formation of protective surface films on these high-voltage cathodes. The FEC-based electrolyte has high anodic stability, and high-voltage LiNi$_{1/3}$Mn$_{1/3}$O$_2$ or LiCoPO$_4$ cathodes that use these electrolytes show significantly improved cycling stability. However, no firm conclusion can be drawn on the cycling stability of high-voltage graphite/LiNi$_{1/3}$Mn$_{1/3}$O$_2$ batteries when using these FEC-based electrolytes. The reason is that the compatibility of the FEC-based electrolyte with the graphite anode is poor, owing to FEC having a higher reduction potential compared to EC.$^{[10]}$ In a few papers, we find that several fluorinated ethers with the higher reduction potentials are investigated as film-forming additives for graphite.$^{[11,12]}$

For this reason, in the present study, we introduced a new fluorinated ether, 1,1,1,3,3,3-hexafluoroisopropyl methyl ether (HFPM; Figure 1a) as the main components of the FEC-based electrolyte solvent and prepared a novel electrochemically compatible, high-voltage, and nonflammable F-electrolyte solution $^{[1]}$ LiPF$_6$/FEC + dimethyl carbonate (DMC) + ethyl methyl (EMC) + HFPM (2:3:1:4, by volume); Figure 1b). This F-electrolyte is not only totally nonflammable in fire burning tests, but it also exhibits a remarkably high anodic stability of at least 5.5 V (vs. Li$^+$/Li) as well as compatibility with graphite anodes. Of particular importance, mesocarbon microbeads (MCMB)/LiNi$_{1/3}$Mn$_{1/3}$O$_2$ 18650 batteries made with this F-electrolyte show good performance in galvanostatic cycling, confirming their potential as high-voltage LIBs with enhanced safety and longevity.

2. Results and Discussion

Figures 1b–d show the physicochemical properties of these electrolytes. As displayed in Figure 1b, the conductivity of the F-electrolyte is 8.57 mS cm$^{-1}$, whereas it is 11.56 mS cm$^{-1}$ for the base electrolyte, which may be attributed to the high vis-
The conductivity of FEC and HFPM. The wetting behaviors of the electrolytes were assessed by adding a drop of the electrolytes to the surface of the separator, as seen in Figure 1c. Compared to the base electrolyte, the F-electrolyte indicates better wettability with the separator, which may stem from the low polarity and the weak intermolecular force of HFPM.[14,15] Additionally, the flammability of the F-electrolyte solution can be visualized in fire burning tests, together with the base electrolyte for comparison, as shown in Figure 1d. Clearly, the base electrolyte, 1 M LiPF$_6$/EC + DMC (3:7, by volume), is very flammable in fire, whereas the F-electrolyte cannot be ignited under the testing conditions. A lower combustibility of the electrolyte is expected to contribute to better safety of LIBs.[16–22] Arg[23] reported that the mixed solution obtained by mixing appropriate amounts of methyl nonafluorobutyl ether with co-solvents showed no flash point, resulting in improved safety of the batteries. Thus, these results clearly show that the F-electrolyte based on the fluorinated solvent has good wettability and is not flammable, which will be beneficial for improving the power performances and safety in cell operations.

To examine the electrochemical characteristics of the F-electrolyte solution, cyclic voltammetry (CV) measurements were performed. Figure 2 gives the CV curves of the base electrolyte 1 M LiPF$_6$/EC + DMC (3:7, by volume), 1 M LiPF$_6$/FEC, and the F-electrolyte 1 M LiPF$_6$/FEC + DMC + EMC + HFPM (2:3:1:4, by volume) at a scan rate of 5 mV s$^{-1}$. As lithium salts, such as LiPF$_6$ and LiTFSI, are insoluble in neat HFPM, we chose tetra-n-butylammonium hexafluorophosphate (nBu$_4$NPF$_6$) as a salt and prepared the electrolyte formulation of 0.1 M nBu$_4$NPF$_6$/HFPM in order to investigate the electrochemical window of HFPM. Thus, we also present the CV result of 0.1 M nBu$_4$NPF$_6$/HFPM in Figure 2c. As displayed in Figure 2c, we found that there is no apparent side reaction of the electrolyte 0.1 M nBu$_4$NPF$_6$/HFPM between 3.0 and 5.0 V, suggesting that HFPM is quite stable in this potential range. As shown in the inset of Figure 2, HFPM starts to be reduced around 1.2 V, which may be beneficial for forming the effective solid electrolyte interphase (SEI) on graphite. It can be seen in Figure 2 that the oxidation current of the electrolyte 1 M LiPF$_6$/FEC starts to increase from 6.5 V and becomes very large above 6.75 V, exhibiting high anodic stability. Comparing the CV curves of the base electrolyte and the F-electrolyte solution (Figures 2a and 2d, respectively), it can be found that the oxidation peak for the F-electrolyte arises from the onset potential of 5.5 V, whereas the anodic current of the base electrolyte appears at an onset potential of 4.3 V. These results indicate that the F-electrolyte solution demonstrates rather high anodic stability and can be suitably used for 5 V LIBs.

To confirm the electrochemical compatibility of the F-electrolyte with a high-voltage cathode and graphite anode, we measured the CV curves of the MCMB anode and LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode by using the F-electrolyte at a scan rate of 0.1 mV s$^{-1}$. As shown in Figure 3, the CV curves from the MCMB anode when using the F-electrolyte have two pairs of well-resolved redox peaks in the low potential region of 0.5–0.01 V, showing characteristics of reversible lithium insertion/extraction reactions with an active graphite anode.[24,25] As shown in the inset of Figure 3, the MCMB anode in the F-electrolyte displays two weak reduction peaks at 1.7 and 1.2 V versus Li$^+$/Li in the first negative scan, which relate to the SEI film-forming process, and then these two peaks disappear in the second scan. More specifically, FEC starts to be reduced around 1.7 V, and HFPM decomposes at about 1.2 V. As for the base electrolyte sample, EC is initially reduced at about 1.5 V. In addition, there is a cathodic peak positioned at about 0.7 V in the base electrolyte, which is ascribed to the reduction of DMC. In contrast, that peak disappears in the F-electrolyte, indicating that the SEI film originating from the decomposition of FEC and HFPM can prevent the reduction of DMC and EMC. These CV results demonstrate that the F-electrolyte is capable of forming an effective SEI on the MCMB anode surface. In the case of the high-voltage LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode, the CV curves of have...
quite symmetrical redox peaks, which is in good agreement with the well-documented CV data of LiNi$_{0.5}$Mn$_{1.5}$O$_4$-based electrodes.$^{[26, 27]}$ In addition, the redox peaks of the cathode and MCMB anode, when using the F-electrolyte, are overlapped for the subsequent two cycles, indicating excellent electrochemical stability. These CV features indicate that the F-electrolyte has excellent electrochemical compatibility and stability with the high-voltage cathode and graphite anode.

Figures 4a and 4b display comparisons of the galvanostatic charge–discharge profiles of the Li/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ coin cells cycled between 3.0 and 5.0 V at a constant current density of 40 mA g$^{-1}$, using two electrolyte solutions. As seen in the curve profile, we can observe two plateaus at 4.7 and 4.75 V (vs. Li$^+$/Li) associated with Ni$^{2+}$/Ni$^{3+}$ and Ni$^{3+}$/Ni$^{4+}$ oxidation potentials, respectively, and a short “plateau” at approximately 4 V associated with Mn$^{3+}$/Mn$^{4+}$, which is in accordance with the CV results (Figure 3). The Li/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ half-cells in the first cycle with the two electrolyte solutions display similar charge–discharge profiles, whereas the cell cycled with the F-electrolyte solution exhibits a significantly lower irreversible capacity of 6.5 mAh g$^{-1}$ compared to that of cells cycled with the base electrolyte (ca. 20 mAh g$^{-1}$), which could be ascribed to the high anodic stability of the F-electrolyte solution. As the cycle number is elevated from 1 to 130, the charge voltages of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cell in the base electrolyte slightly increase and the corresponding discharge voltages decrease, showing a gradually increased hysteresis, which is associated with base electrolyte decomposition at the high operating voltage to increase interfacial resistance. In contrast, with the F-electrolyte solution, the cell exhibits a highly reversible charge–discharge behavior with a discharge capacity of about 128.9 mAh g$^{-1}$ after 200 cycles, that is, 95.9% of its fifth capacity, showing a superior cycling stability of the high-voltage battery.

Figure 4c compares the cycling capacities and the coulombic efficiencies of high-voltage LiNi$_{0.5}$Mn$_{1.5}$O$_4$ electrodes in the base electrolyte and the F-electrolyte solution at a constant current density of 40 mA g$^{-1}$. It can clearly be seen that the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode cycled in the base electrolyte solution ex-
hbits a slightly higher reversible capacity of 125.7 mAh g\(^{-1}\) and a relatively low coulombic efficiency of 86.9% in the initial cycle: its capacity decreases to 118.1 mAh g\(^{-1}\) after 130 cycles, showing a low capacity retention of 91.4%. In contrast, the cathode cycled in the F-electrolyte solution demonstrates strong cyclability with a reversible capacity of 128.9 mAh g\(^{-1}\) at 200th cycle, corresponding to a superior capacity retention of 95.9% with respect to its highest capacity at the fifth cycle. At the same time, the F-electrolyte solution exhibits an obviously improved initial coulombic efficiency of 95.8% compared to the base electrolyte (86.9%). It is also notable that the coulombic efficiency of the F-electrolyte solution remains stable at 99.3% with prolonged cycling, whereas the coulombic efficiency of the base electrolyte shows a low coulombic efficiency of 98.7% during cycling. This comparison suggests that the F-electrolyte solution exhibits superior cyclic stability and increased coulombic efficiency of 5 V, high-voltage, spinel LiNi\(_{1/3}\)Mn\(_{1/3}\)O\(_4\) electrodes.

To evaluate the compatibility of the F-electrolyte solution with the graphite anode, the charge–discharge curves of Li/MCMB coin cells in the F-electrolyte were examined by galvanostatic testing, as shown in Figure 5. It can clearly be seen that the MCMB electrode in the F-electrolyte displays an initial discharge and charge (insertion and extraction) specific capacity of 420.9 and 354 mAh g\(^{-1}\), respectively, corresponding to an initial coulombic efficiency of 84.1%, which is slightly lower than that in the base electrolyte (85.3%). This may be attributed to the decomposition of FEC and HFPM. Moreover, as depicted in the inset of Figure 5a, owing to the decomposition of the electrolyte solvent, an irreversible discharge capacity of the F-electrolyte emerges in the slope potential range of 2.0–1.0 V in the first cycle. In contrast, an irreversible discharge capacity of the base electrolyte emerges in a potential range of 1.5–0.5 V. This different behavior can account for the higher reduction potential of the F-electrolyte compared to that of the base electrolyte, which is consistent with the CV data of Figure 3. The reversible capacity of the MCMB electrode at the 30th and 50th cycles can still reach 353.4 and 352.6 mAh g\(^{-1}\), corresponding to a capacity retention of 99.8 and 99.6%, respectively. In addition, Figure 5b compares the cycling performance of Li/MCMB half-cells in these two electrolytes. It can clearly be seen that the MCMB electrodes in both electrolytes exhibit almost the same cycling performance with a high capacity retention of >99% after 50 cycles. As shown in Figure 5b, in the initial few cycles, the reversible capacity of the MCMB electrode in the F-electrolyte is slightly higher compared to that observed from the base electrolyte, which may be attributed to the better wettability of the F-electrolyte. These data suggest that the F-electrolyte has no influence on the capacity and cycling stability of MCMB electrodes.

Figure 6 compares the charge–discharge curves and cycling stability of high-voltage MCMB/LiNi\(_{1/3}\)Mn\(_{1/3}\)O\(_4\) 18650 batteries with the F-electrolyte to those with the base electrolyte. As presented in Figure 6a, in the first cycle, the MCMB/LiNi\(_{1/3}\)Mn\(_{1/3}\)O\(_4\) batteries with F-electrolyte and base electrolyte display similar charge–discharge profiles, where the battery delivers a 0.049 Ah higher initial reversible capacity in the F-electrolyte than in the base electrolyte. As the cycle number is elevated from 1 to 200, the charge voltages of the 18650 battery in the base electrolyte increase and the corresponding discharge voltages decrease, showing a rapid potential drop, which is associated with electrolyte decomposition at the high operating voltage to increase interfacial resistance. In contrast, with the F-electrolyte, the battery exhibits highly reversible charge–discharge behavior with a discharge capacity of about 1.176 Ah after 200 cycles, that is, 82% of its initial capacity, showing a better cycling performance of the battery. According to the aforementioned results, we suggest that this phenomenon may be attributed to the excellent electrochemical compatibility and good wettability of the F-electrolyte with the electrode materials and the separator, respectively. Additionally, it can also be clearly seen from Figure 6b that the battery with the base electrolyte shows a high capacity of 1.385 Ah in the initial cycle, but the reversible capacity falls quickly to
This comparison shows that the F-electrolyte can further be obtained from (o Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. LiPF 18650 battery. Furthermore, the self-discharge a) Voltage profiles for the charge–discharge cycles and b) cycling battery within the voltage range of 3.3–4.9 V at the 0.5 C rate. 2015 in FEC/DMC/EMC/HFPM www.chemelectrochem.org powder, was dissolved in as solvent mixture FEC was purchased LiPF 8 10 days at 25 oC. The determination process includes charging open-circuit voltage (OCV) drop and capacity decay, as depicted in Figure S1. The wetting behaviors of the FC-electrolyte have no influence on the self-discharge of MCMB/LiNi0.5Mn1.5O4 18650 batteries. 3. Conclusions We propose a fluorinated ether with no flash point, HFPM, which has a higher polarity and higher intermolecular force, as the main component of the electrolyte solvent and prepare a high-voltage and nonflammable F-electrolyte. This F-electrolyte is not only totally nonflammable in fire burning tests, but also exhibits remarkably high anodic stability of at least 5.5 V (vs. Li+/Li). In particular, high-voltage MCMB/LiNi0.5Mn1.5O4 18650 batteries made with this F-electrolyte exhibit an excellent cycling stability, with 82% capacity retention over 200 cycles, confirming their potential as high-voltage LiBs with enhanced safety and longevity. Experimental Section High-voltage cathode materials, spinel LiNi0.5Mn1.5O4 powder, was prepared by using a solid-state reaction. FEC was purchased from BASF SE (purity 99.9%) without any additional in-house purification process. HFPM (purity 99.9%) was kindly supplied by the Zhejiang Research Institute of Chemical Industry, Ltd. (Hangzhou, China). Li-battery-grade DMC, EMC, and LiPF6 were obtained from Zhangjiagang Guotai Huangong New Chemical Materials Co. Ltd., China, and used without further purification. The F-electrolyte solution used in this work was 1 mol L-1 LiPF6 in FEC/DMC/EMC/HFPM 2:3:1:4 (by volume), and prepared in an argon-filled glove box with an oxygen level below 5 ppm. The conventional EC-based electrolyte, selected as the base electrolyte, was composed of commercially available 1.0 mol L-1 LiPF6 dissolved in a solvent mixture of EC and DMC in a 3:7 volume ratio, which was purchased from Zhangjiagang Guotai Huangong New Chemical Materials Co. Ltd. The conductivity of these electrolytes was measured on a DDS-307 instrument (INESA Scientific Instrument Co., Ltd, Shanghai, China) at a constant temperature of 30 °C. The wetting behaviors of the electrolytes were assessed by adding a drop of the electrolyte to the surface of the separator. The flammability tests of the base electrolyte and F-electrolyte solution was carried out by using fire burning measurements. The fiberglass sheets (ca. 4 cm in length, 2 cm in width) were soaked in the electrolytes for several minutes, absorbing approximately 5 g of the electrolytes, and were then ignited to evaluate the flammability of the electrolytes. CV experiments were carried out by using an Autolab Electrochemical Analytical Instrument (ECO CHEMIE, B. V. Utrecht, The Netherlands) in a three-electrode electrochemical cell with a Pt disk of 100 μm diameter as the working electrode and Li foil as both reference and counter electrodes. The Pt working electrode was cleaned before each sweep. The scan rate was 5 mV s-1. The negative electrode consisted of MCMB (90 wt%), Super P carbon black (5 wt%), and poly(vinylidene fluoride) (PVDF) (5 wt%), whereas the positive electrodes consisted of LiNi0.5Mn1.5O4 (85 wt%), Super P carbon black (7 wt%), and PVDF (8 wt%). The counter and reference electrodes were lithium sheets. The separator was a Celgard 2400 microporous membrane. The cells were assembled in an argon-filled glove box. After assembly, the charge and discharge measurements were performed by using a computer-controlled battery charger (CT2001A Land Battery Testing System, Wuhan, China).

Figure 6. a) Voltage profiles for the charge–discharge cycles and b) cycling performance according to the CC–CV protocol of the 18650 MCMB/LiNi0.5Mn1.5O4 battery within the voltage range of 3.3–4.9 V at the 0.5 C rate.
The 18650 batteries (18 mm in diameter and 65 mm in height) were built. The capacity of the batteries was designed to be 1500 mAh, corresponding to the specific capacity of the half-cell. The batteries used LiNi0.5Mn1.5O4 as the cathode, MCMB graphite as the anode, and polyethylene as the separator. For the LiNi0.5Mn1.5O4/MCMB batteries, we performed 200 cycles at voltages of 3.5–4.9 V at 750 mA (0.5C) by using the constant-current constant-voltage (CC–CV) protocol. The cycle performance tests of batteries with these two electrolytes (the base electrolyte and the F-electrolyte) were recorded by the software associated with LAND-CT2001B battery test systems.

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