Electrochemistry Communications 61 (2015) 121–124

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

A combination of lithium difluorophosphate and vinylene carbonate as reducible additives to improve cycling performance of graphite electrodes at high rates

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ARTICLE INFO

Article history:
Received 16 October 2015
Accepted 25 October 2015
Available online 31 October 2015

Keywords:
Lithium–ion battery
Graphite
Anode
Electrolyte
Additive

ABSTRACT

Lithium difluorophosphate (LiDFP) as a reducible additive is employed to overcome the unsatisfactory rate capability and cycling instability of highly pressed graphite electrodes with high mass loading (8.1 mg/cm^2) with a vinylene carbonate (VC)-derived surface film that hampers the charge transport at the graphite–electrolyte interface at high rates. Our investigation reveals that LiDFP modifies the surface chemistry induced by VC and makes a more ionically conductive surface film on graphite, ensuring good rate capability.

1. Introduction

Recently, lithium–ion batteries (LIBs) have gained recognition as reliable power sources for transportation applications [1,2]. However, LIBs using graphite as an anode suffer from inferior rate capability, high cost, and safety issues [3–5]. To achieve good performance in terms of power, the electrodes should allow rapid charge transport at the electrode–electrolyte interface and good electronic conduction at the electrode–current collector interface [5]. Herstedt et al. demonstrated that one of the most important parameters that limit the performance of LIBs at high rates is the transport of lithium ions at the anode–electrolyte interface [6]. The continuous solid electrolyte interphase (SEI)-filming process that occurs via electrolyte decomposition on the anode consumes the limited Li$^+$ source, reduces the reversible capacity of the batteries, and leads to the formation of a thick surface film that impedes fast charge transport. The formation of protective films on the graphite electrode through the use of reducible additives such as vinylene carbonate (VC) and 1,3-propane sultone (PS) can lead to a noticeable improvement in the electrochemical properties of LIBs [7–11].

To develop high-rate-capable graphite electrodes via the formation of a more ionically conductive and robust surface film, we here present, for the first time, the electrolyte additives based on a combination of lithium difluorophosphate (LiDFP) and vinylene carbonate (VC).

2. Experimental

The reference (Ref) electrolyte was 1 M lithium hexafluorophosphate ($LiPF_6$) (Soulbrain Co., Ltd.) dissolved in a solvent mixture of ethylene carbonate (EC)/ethyl methyl carbonate (EMC)/dimethyl carbonate (DMC) with a 2:4:4 volume ratio. Solvents (Soulbrain Co., Ltd.) were used as received. 1 wt.% lithium difluorophosphate (LiDFP) (>99%, FOOSUNG Co., Ltd.) [12] and 1 wt.% vinylene carbonate (VC) (Soulbrain Co., Ltd.) were introduced into the Ref electrolyte as additives.

The graphite electrode was composed of 97.5 wt.% natural graphite and 2.5 wt.% binder (1 wt.% styrene–butadiene rubber (ZEON Co., Ltd.)/1.5 wt.% sodium carboxymethyl cellulose (Nippon Paper Group)). The specific capacity of the electrode and the loading of the active material were 2.92 mAh/cm^2 and 8.1 mg/cm^2, respectively.

A coin-type half cell (2016) with a graphite electrode and an Li metal electrode was assembled in an argon-filled glove box containing less than 1 ppm of oxygen and moisture. Microporous polyethylene film

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http://dx.doi.org/10.1016/j.elecom.2015.10.013
1388-2481/

(PE, SK Innovation Co., Ltd.) was used as a separator. The cells were galvanostatically precycled at a rate of C/10 (corresponding to a current density of 36 mA/g) between 0.01 and 1.5 V at 30 °C using a computer-controlled battery measurement system (WonATech WBCS 3000). Thereafter, charge and discharge cycling for the cells was performed at a rate of C/2 between 0.01 and 1.5 V at 30 °C. To investigate the charge (lithiation) rate capability of the graphite electrodes, the cells charged at various C rates were discharged at the constant C/5 rate. The discharge (delithiation) rate capability of the cells was also examined using the constant charge rate (C/5) and various discharge rates. dQ/dV plots were obtained by computing the differential capacity versus the potential of the half cells during precycling at 30 °C. After 100 cycles, the cells were opened in an Ar-filled glove box and the graphite electrodes were rinsed with dimethyl carbonate to remove the residual $LiPF_6$-based electrolyte and to investigate the surface chemistry of graphite. Ex-situ X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha system) measurement was conducted with Al Kα ($h\nu = 1486.6$ eV) radiation under ultrahigh vacuum. XPS spectra were obtained using a 0.10 eV step and 50 eV pass energy.

3. Results and discussion

Fig. 1a shows the voltage profiles of the highly pressed graphite electrode with high mass loading (8.1 mg/cm^2) and high electrode density (1.5 g/cm^3)/Li half-cells with and without functional additives (lithium difluorophosphate (LiDFP) and vinylene carbonate (VC)) for the precycle at a C/10 rate. The relatively low reversible capacity (~340 mAh/g) of graphite electrodes compared to the reported values (~350 mAh/g) is thought to be due to high mass loading and high electrode density of graphite electrodes. When the VC additive, which was identified as the most efficient SEI former for graphite electrodes [7,13], was introduced into the cell, a large IR drop was observed during the first charge (lithiation) process (Fig. 1a). Interestingly, the graphite electrodes with LiDFP- or VC + LiDFP-added electrolyte exhibited higher charge plateaus and lower discharge plateaus, indicating faster kinetics compared to those of the Ref and VC-containing electrolytes. This finding is most likely due to the effect of LiDFP, which modifies the resistive solid electrolyte interphase (SEI) structures formed by the VC additive or the Ref electrolyte; LiDFP thereby facilitates Li^+ ion transport into the graphite. As shown in the dQ/dV plots provided in Fig. 1b, a pronounced reduction potential (0.48 V), induced by EC decomposition, appeared for the graphite electrode with the Ref electrolyte. This relatively low onset potential for the EC decomposition compared to the reported values (~0.8 V) can be explained by the IR drop of highly pressed graphite electrode with high mass loading. Since the LiDFP-added electrolyte exhibited a reduction potential (0.59 V) higher than that of the Ref electrolyte, LiDFP is thought to act as a reducible additive on the graphite. Compared to the Ref electrolyte, the VC- and VC + LiDFP-added electrolytes show relatively high reduction potentials of 0.61 and 0.62 V, respectively. Thanks to the relatively lower lowest unoccupied molecular orbital (LUMO) energy of VC, the reduction of VC progresses before that of EC and thereby a VC-derived SEI layer is formed on the graphite surface [8]. The graphite electrodes with the VC-added electrolyte exhibited a slightly low initial coulombic efficiency (ICE) of 95.2% compared with that of the Ref electrolyte (95.5%) during precycling (Fig. 1c). This is presumably because VC decomposition results in capacity loss due to the consumption of Li ions, leading to SEI formation at the graphite–electrolyte interface. A reduction peak in the LiDFP-added electrolyte appeared at around 0.59 V, slightly lower than the peak potential of the VC-added electrolyte (0.61 V). Compared to the Ref electrolyte, which delivered a discharge capacity of 333 mAh/g and an ICE of 95.5%, the VC + LiDFP-containing electrolyte, which avoided large polarization during the first charge process (Fig. 1a), delivered a slightly improved discharge capacity of 338 mAh/g and an ICE of 95.8%. Despite the use of VC, the gradual capacity fading of graphite electrodes could not be restrained (Fig. 1d). This

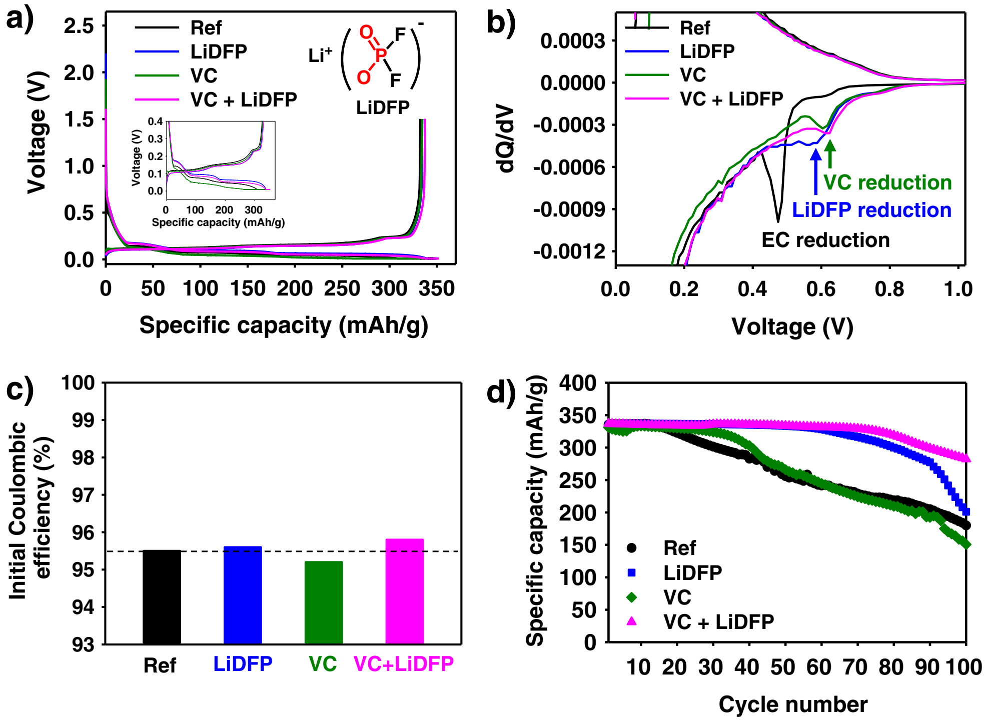

Fig. 1. Electrochemical performance of graphite/Li half cells: a) voltage profiles, b) dQ/dV plots during precycling (C/10) at 30 °C, c) initial coulombic efficiency, and d) discharge (delithiation) capacity (C/2) during 100 cycles at 30 °C. The inset of Fig. 1a represents the magnified voltage profiles.