

## Effect of FEC and VC Additives in Electrolyte on the Performance of Si Anode for Lithium Ion Cell

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### Abstract

The performance of a lithium-ion cell depends on the form of the solid–electrolyte interphase (SEI) layers which is composed on the electrode surface. Here, we present a components of the electrolyte solutions for LIBs, namely, fluoroethylene carbonate (FEC) and vinyl carbonate (VC). We discuss the effect of 2, 5 and 10% FEC and VC-based electrolyte solutions in LiPF<sub>6</sub> in EC:DEC to understand the SEI layer formed on Si anode.

**Keywords:** Li-ion battery, Electrolyte, SEI

### FEC ve VC Katkılı Elektrolitin Lityum İyon Hücrelerde Si Anot Üzerine Etkisi

### Öz

Lityum iyon hücrelerin performansı, elektrot yüzeyinde oluşan Katı Elektrolit Arayüzey (KEY)'in yapısına bağlıdır. Bu çalışmada, elektrolit çözeltisinin bileşeni olarak FEC (floroetilen karbonat) ve VC (vinil karbonat)kullandık. %2, %5 ve %10 FEC ve VC katkılanmış EC:DEC içinde LiPF<sub>6</sub> elektrolitinin Si anot üzerinde oluşan KEY tabakasına etkileri tartışılmıştır.

**Anahtar Kelimeler:** Li-iyon batarya, Elektrolit, SEI

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
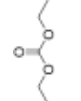
## 1. INTRODUCTION

The early development on rechargeable lithium battery began with lithium (Li) metal and Sony put into the market the first lithium ion batteries in 1991. Since that date the graphite has been used as commercial anode with the practicable capacity of 250 mAh/g and it has been yet reached the 290 mAh/g in 2015 [1]. In the development of high capacity anode materials for lithium ion batteries, silicon is apparently very promising as anode material due to its high theoretical capacity ~4200 mAh/g. However, the huge volume change (~300%) occurs during the cycling and it results breakdown of the conductive network of the composite electrode. This causes the electrical contact problem between conductive agent and the current collector, resulting low Coulombic efficiency and poor capacity retention for silicon-based lithium ion batteries (LIBs).

The electrolyte for LIBs is a mixture of a salt and organic solvent. In Lithium-ion batteries for electric cars and other electrical devices that are available today are mainly based on electrolytes using lithium hexafluorophosphate (LiPF<sub>6</sub>) salt [1] and organic solvent such as ethylene carbonate or propylene carbonate which are cyclic carbonate ester and dimethyl carbonate or diethyl carbonate which are linear carbonate ester. Electrolyte solution should be able for the transport of Li ions freely between the electrodes. Cyclic carbonate esters have high viscosity but high dielectric constant and linear carbonate esters have low viscosity but low dielectric constant [2]. So mixture of cyclic and linear carbonate esters becomes the suitable electrolyte. The major drawbacks of the LiPF<sub>6</sub> salts is thermal instability and its reactivity with moisture which results HF formation [3] that presents a safety issue. It is important to dry the electrode for eliminating this problem. In Table 1, it is shown that ethylene carbonate (EC) is the most important organic structure for LIB applications because of its high dielectric constant, low volatility, high thermal stability, and, in particular, its unique film formation ability [4].

Research on the electrolyte solutions for LIBs has focused on functional electrolyte additives, flame-resistant or non-flammable electrolyte solutions and new electrolyte salts.

**Table 1.** Physico- and electrochemical properties of state-of-the-art electrolyte solvents (EC and DEC) for LIBs [4]

Solvent properties	EC	DEC
Structure		
Dielectric constant	+	-
Viscosity	+	-
Melting temperature	+	-
Boiling temperature	+	-
Flash point	+	-
Volatility <sup>[a]</sup>	-	+
Contribution to SEI	+	-
Anodic stability	+	o
∑ safety	+	-

+ = high, o = medium, - = low. [a] According to NFPA30 (National Fire Protection Association), volatility refers to both flammable (e.g., linear carbonates) and combustible (e.g., cyclic carbonates) liquids.

For instance, Hoffman et. al. [5] aimed to evaluate the usability of novel mixtures composed of EC and DMSN as electrolyte solvents and LiPF<sub>6</sub>, LiBOB and LiDFOB as conducting salts for Li-ion based cells. They used graphite as anode and LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> (NMC) as cathode material. They had excellent discharge capacity performance which was obtained up to a discharge rate of 2C at room temperature and the electrolytes might be used down to ~5 °C where still >90% of discharge capacity can be used at 0.5C. Also Paillet et. al. [6] worked on the electrochemical stability of high-purity LiTDI. They evaluated in coin-cells (vs. lithium metal) with various standard carbon-coated cathode materials (LiFePO<sub>4</sub>, LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>, LiCoO<sub>2</sub> and LiMn<sub>2</sub>O<sub>4</sub>) to demonstrate the promising properties of this

organic Li-salt in electrolytes for Li-ion batteries. Their study demonstrated the superior thermal stability of LiTDI vs. LiPF<sub>6</sub> (285 °C vs. 164 °C), and LiTDI is safer in regards to thermal degradation; the TGA-MS studies showed that LiTDI does not produce HF. It also does not corrode aluminum and is able to form a passivation layer that protects the current collector and LiTDI can be used up to 4.5 V (vs Li<sup>+</sup>/Li) which is sufficient for use with standard cathode materials. Birrozzi et. al.[7] used poly acrylic acid binder and vinylene carbonate electrolyte additive. During the 75th cycle, the Li<sup>+</sup> insertion specific capacity was 135 mAh/g for PVDF electrodes, 390 mAh/g for PVDF/VC electrodes, 417 mAh/g for PAA/VC electrodes, corresponding to capacity retention values of 26%, 70% and 88%, respectively. One of the most studied compounds is fluorinated ethylene carbonate (FEC), which was first proposed by McMillan et al. [8] in 1999 as a lithium-ion electrolyte (co-)solvent. The addition of FEC to the organic carbonate based electrolyte resulted in a decreased first cycle irreversibility on the graphite anode. The fluorinated carbonates shows a reduced flammability compared with non-fluorinated carbonates [9, 10] and increased thermal stabilities [11] due to the presence of the strong carbon-fluorine bond [12,13]. The challenge of the fluorinated carbonates is increased viscosities, which lead to lower ionic conductivities [19]. The easily polymerizable electrolyte additives, such as VC (vinyl carbonate) [14-17], vinyl ethylene carbonate (VEC) [18], vinyl ethylene sulfite (VES) [19], FEC [14-16, 20] or TDI [14] are particularly effective for a stable and robust SEI layers on lithiated graphite. Moreover, these additives can provide reduced gas generation on SEI formation. For example, even 2% of VC additive into the electrolyte increase the electrochemical performance and safety of the lithium-ion cell due to the formation of polymeric surface layers. Because of these effects of VC and FEC additives on graphite surface we focused on the functional electrolyte additives into the LiPF<sub>6</sub> salt to improve the Si anode cyclability and specific capacity with using PFM binder. In this study we used EC:DEC

(1:1 w/w) with 2%, 5% and 10% VC and FEC additives.

## 2. EXPERIMENTAL STUDY

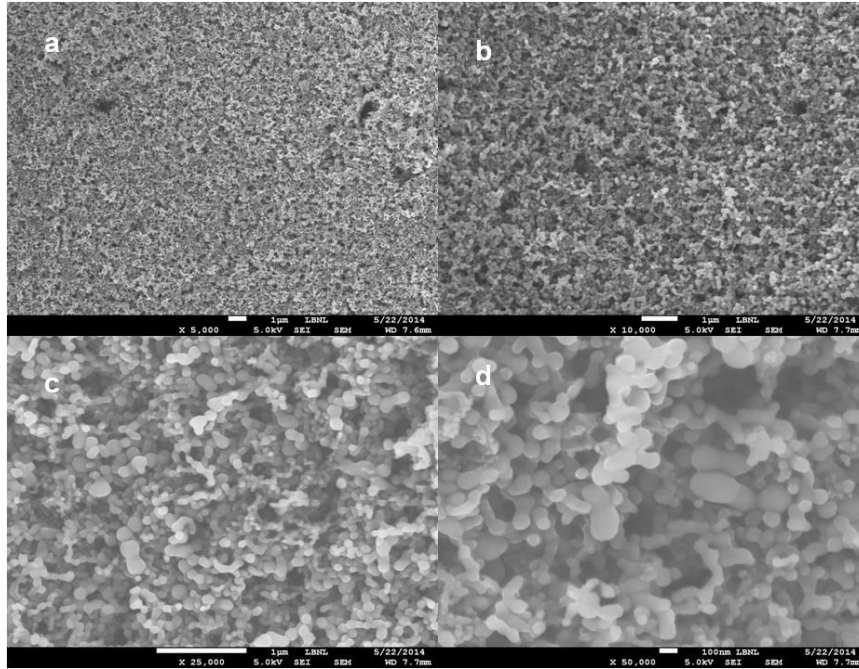
Si was obtained from Nanostructured & Amorphous Materials, Inc. and Celgard 2400 separator is obtained from Celgard. Lithium-ion electrolyte were purchased from BASF, including 1.2 M LiPF<sub>6</sub> in ethylene carbonate, diethyl carbonate (EC:DEC = 1:1 w/w). Carbonate additives were purchased from Sigma-Aldrich.

**Preparation of Electrodes and Assembly of Coin Cells:** All the electrodes and coin cells were prepared and assembled in the Ar-filled glovebox. The polymers were dissolved in chlorobenzene, and then silicon nanoparticles were added (weight ratio of Si nanoparticle/polymer =90/10). The mixture was mixed by using a homogenizer for 1 h, and the slurry was coated on the copper foil by using a doctor blade. The coated electrode was placed in the glovebox overnight and further dried in the vacuum oven at 90 °C for 12 h to completely remove the chlorobenzene solvents. The electrodes were used to assemble the coin cells. As a counter electrode, the Li metal was used. The performance of the assembled 2325 coin cells was evaluated with Maccor Series 4000 Battery Test system in a thermal chamber at 30 °C. The cut-off voltage of cell testing is between 1.0 V and 0.01V, assuming a theoretical value of 4200 mAh/g for Si.

**Characterization:** A JSM-7500F scanning electron microscopy (SEM) was used to characterize the morphology of the electrode surface. Cells were cycled at C/10 for 100 cycles.

## 3. RESULTS AND DISCUSSION

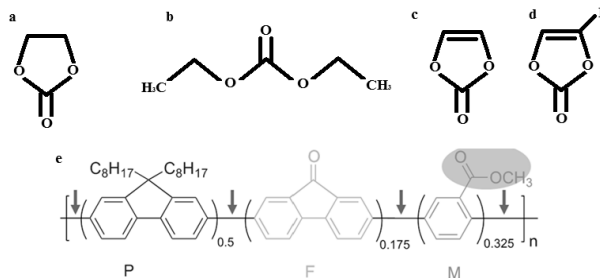
The microscopic morphologies of the Si/PFM electrodes under different magnification shown in Figure 1. SEM images show the uniform laminate structure and surface porosities. According to Figure 1, the particle size of silicon particles is around 50-100 nm. The polymer coating is uniformly coated on the surface of the silicon particles.



**Figure 1.** SEM images of Si/PFM electrode with a) 5000 b) 10000 c) 25000 d) 50000 magnification

To show effect of the electrolyte additives on electrochemical performance of lithium ion cells and SEI formation stability, 2%, 5% and 10% VC and FEC were added into the 1.2M LiPF<sub>6</sub> electrolyte which was dissolved in EC:DEC (1:1 w/w). In Figure 2 (a-d), the structure of EC, DEC, VC and FEC were given, respectively. EC is a cyclic carbonate and DEC is a linear carbonate

which are used to balance the viscosity and dielectric constant. In figure 2e, the functional conductive polymer binder, poly(9,9-dioctylfluorene-co-fluorenone-co-methyl benzoic ester) (PFM) was showed. It developed by combining adhesion and electrical conduction to provide molecular level electronic connections between the active material and the conductive polymer matrix [21].



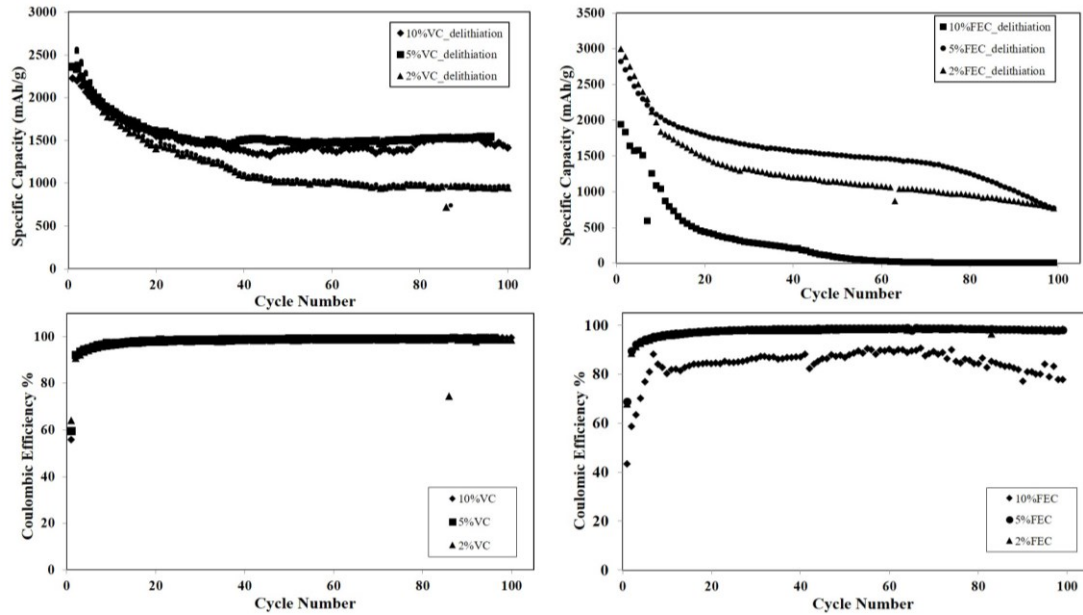
**Figure 2.** Schematic of a) ethylene carbonate b) diethylene carbonate c) vinyl carbonate d) fluoroethylene carbonate e) PFM binder

The cycling performance of half cells with a lithium electrode are shown in Figure 3. The

electrolyte was 1 M LiPF<sub>6</sub> in EC:DEC (1:1 w:w) with different addition ratio of VC and FEC. When

1, 5 and 10wt% FEC was used as the additive electrolyte solution, the silicon half cell reached 768 mAh/g after 100 cycles with 5% FEC addition at C/10. The half cells with 1, 5 and 10wt% VC additive into the electrolyte solution delivered the

best cycling solution for 5% VC addition with reaching the 1542 mAh/g specific capacity after 100 cycles at C/10 which are also summarized in Table 1.



**Figure 3.** Cycling data of cells with a) FEC additive into the electrolyte b) VC additive into the electrolyte and Coulombic efficiency of cells with a) FEC additive into the electrolyte b) VC additive into the electrolyte

**Table 1.** Electrochemical data of the cells with different VC additive ratio in the electrolyte solution

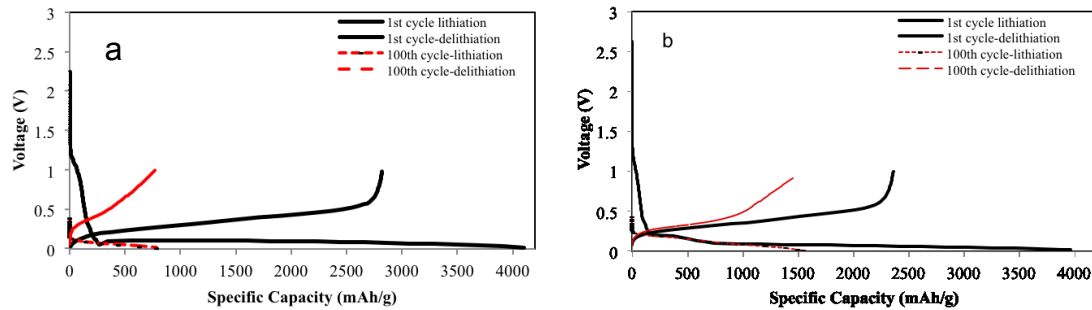
		2% VC	5% VC	10% VC
1 <sup>st</sup> cycle	$Q_c^a$ (mAh/g)	2355	2363	2227
	$\eta^b$ (%)	64.08	59.53	55.94
100 <sup>th</sup> cycle	$Q_c^a$ (mAh/g)	950	1542	1416
	$\eta^b$ (%)	98.56	99.43	99.48

In Figure 4, voltage profiles of half cells are given. In figure 4a, the 1st and 100th cycle voltage curves are shown for 5% FEC additive into the electrolyte. The first cycle lithiation capacity is 2819 mAh/g whereas it has 768 mAh/g after 100<sup>th</sup> cycle at C/10. When we compare the voltage profile of 5%VC additive into the electrolyte which is given in Figure 4b, it is seen that the capacities are 2363 and 1542 mAh/g after 1<sup>st</sup> and 100<sup>th</sup> cycle, respectively.

Although conventional carbonate-based electrolytes enable the flow of charge between the anode and cathode in lithium-ion batteries they are limited at higher voltages and temperatures. The another challenge of carbonate-based electrolytes is safety problem since they are flammable. These are the significant issues to overcome for commercial usage of LIBs safely.

**Table 2.** Electrochemical data of the cells with different FEC additive ratio in the electrolyte solution

		2% FEC	5% FEC	10% FEC
1 <sup>st</sup> cycle	$Q_c^a$ (mAh/g)	2998	2819	1942
	$\eta^b$ (%)	68.03	68.75	43.45
100 <sup>th</sup> cycle	$Q_c^a$ (mAh/g)	763	768	3,55
	$\eta^b$ (%)	98.48	98.08	76.47



**Figure 4.** Voltage profile of cells with a) 5% FEC additive into the electrolyte and b) 5% VC additive into the electrolyte

#### 4. CONCLUSION

In conclusion, this study showed the effect of different carbonate solution additive (VC and FEC) in the electrolyte on the half cell performance. 2, 5 and 10% additives were used to increase the cell performance. 1542 mAh/g specific capacity was achieved after 100 cycle at C/10 after 5%VC addition into the EC:DEC (1:1) based LiPF<sub>6</sub> electrolyte.

#### 5. REFERENCES

1. <http://www.emc2.cornell.edu/content/view/battery-anodes.html>, Alıntı Tarihi: 05.04.2018
2. Pistoia, G., 2014. Lithium-Ion Batteries Advances and Applications, Chapter 1, Elsevier.
3. Schmidt, G., Cayrefourcq, I., Paillet, S., Fréchetta, J., Barray, F., Clément, D., Hovington, P., Guerfi, A., Zaghbi, K., 2014. Evaluation of LiTdi Vs. LiPF<sub>6</sub> As Electrolytes in Contact with Several Cathodes and Anodes Materials, ECS Meeting Abstract, Session 11-Electrolyte, Materials, and Batteries Posters.
4. Kalhoff, J., Eshetu, G.G., Bresser, D., Passerini, S., 2015. Safer Electrolytes for Lithium-Ion Batteries: State of the Art and Perspectives, Chemsuschem Energy & Materials, Volume 8(13), 2154–2175.
5. Hofmann, A., Hanemann, T., 2015. Novel Electrolyte Mixtures Based on Dimethyl Sulfone, Ethylene Carbonate and LiPF<sub>6</sub> for Lithium-ion Batteries, Journal of Power Sources, 298(1), 322–330.
6. Pailleta, S., Schmidt, G., Ladouceur, S., Fréchetta, J., Barraya, F., Clément, D., Hovington, P., Guerfi, A., Vijha, A., Cayrefourcq, I., Zaghbi, K., 2015. Power Capability of LiTDI-based Electrolytes for Lithium-ion Batteries, Journal of Power Sources, 294, 507–515.
7. Birrozzi, A., Maroni, F., Raccichini, R., Tossici, R., Marassi, R., Nobili, F., 2015. Enhanced Stability of SnSb/graphene Anode Through Alternative Binder and Electrolyte Additive for Lithium Ion Batteries Application, Journal of Power Sources, 294, 248-253.
8. McMillan, R., Slegel, H., Shu, Z. X., Wang, W., 1999. Fluoroethylene Carbonate Electrolyte and its use in Lithium Ion Batteries with Graphite Anodes, J. Power Sources, 81, 20-26.
9. Tan, S., Ji, Y.J., Zhang, Z. R., Yang, Y., 2014. Recent Progress in Research on High-voltage Electrolytes for Lithium-ion Batteries. Chem Phys Chem 15(10), 1956-69.
10. Arai, J., Katayama, H., Akahoshi, H., 2002. Binary Mixed Solvent Electrolytes Containing Trifluoropropylene Carbonate for Lithium Secondary Batteries, J. Electrochem. Society, 149(2), A217-A226.
11. Benmayza, A., Lu, W., Ramani, V., Prakash, J., 2014. Electrochemical and Thermal Studies of LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> under Fluorinated Electrolytes, Electrochim. Acta, 123, 7-13.
12. Mcller, K.-C., Hodal, T., Appel, W. K., Winter, M., Besenhard, J.O., 2001. Fluorinated Organic Solvents in Electrolytes for Lithium Ion Cells J. Power Sources, 97–98, 595-597.

13. O'Hagan, D., 2008. Understanding Organofluorine Chemistry. An Introduction to the C-F Bond, *Chem. Soc. Rev.*, 37, 308-319.
14. Eshetu, G. G., Grugeon, S., Gachot, G., Mathiron, D., Armand, M., Laruelle, S., 2013. LiFSI vs. LiPF<sub>6</sub> Electrolytes in Contact with Lithiated Graphite: Comparing Thermal Stabilities and Identification of Specific SEI-Reinforcing Additives, *Electrochimica Acta*, 102, 133-141.
15. Zhang, S.S., 2006. A Review on Electrolyte Additives for Lithium-ion Batteries, *Journal of Power Sources*, 162 (2), 1379-1394.
16. Profatilova, I., Stock, C., Schmitz, A., Passerini, S., Winter, M., 2013. Enhanced Thermal Stability of a Lithiated Nano-silicon Electrode by Fluoroethylene Carbonate and Vinylene Carbonate. *J. Power Sources*, 222, 140-149.
17. Lee, H.H., Wang, Y.Y., Wan, C.C., Yang, M.-H., Wu, H.C., Shieh, D.T., 2005. The Function of Vinylene Carbonate as a Thermal Additive to Electrolyte in Lithium Batteries, *Journal of Applied Electrochemistry*, 35, 615-623.
18. Xu, S.D., Zhuang, Q.C., Wang, J., Xu, Y.Q., Zhu, Y.B., 2013. New Insight into Vinylene Carbonate as a Film Forming Additive to Ethylene Carbonate-Based Electrolytes for Lithium Ion Batteries, *International Journal of Electrochemical Science*, 8, 8058-8076.
19. Yao, W., Zhang, Z., Gao, J., Li, J., Xu, J., Wang, Z., Yang, Y., 2009. Vinyl Ethylene Sulfite as a New Additive in Propylene Carbonate-based Electrolyte for Lithium Ion Batteries, *Energy&Environmental Science*, 2, 1102-1108
20. Liu, B., Li, B., Guan, S., 2012. Effect of Fluoroethylene Carbonate Additive on Low Temperature Performance of Li-Ion Batteries, *Electrochemical and Solid-State Letters*, 15, A77-A79.
21. Liu, G., Xun, S., Vukmirovic, N., Song, X., Olalde-Velasco, P., Zheng, H., Battaglia, V.S., Wang, L., Yang, W. 2011. Polymers with Tailored Electronic Structure for High Capacity Lithium Battery Electrodes. *Adv. Mater.* 23, 4679-4683.

