



Ab initio study of the operating mechanisms of tris(trimethylsilyl) phosphite as a multifunctional additive for Li-ion batteries



Dong Young Kim^{*}, Hosang Park, Woon Ih Choi, Basab Roy, Jinah Seo, Insun Park, Jin Hae Kim, Jong Hwan Park, Yoon-Sok Kang, Meiten Koh^{**}

Samsung Advanced Institute of Technology, Samsung Electronics, 130 Samsung-ro, Suwon, Gyeonggi-do 16678, Republic of Korea

HIGHLIGHTS

- The additive $P(\text{OSi}(\text{CH}_3)_3)_3$ scavenges HF and forms solid electrolyte interphases.
- Ab initio calculations were used to examine the operating mechanism of this additive.
- O–Si bond cleavage is the main pathway for HF scavenging.
- PO_3 -based products maintain HF scavenging ability during the oxidization process.
- O–P bond cleavage is stabilized by electron-withdrawing groups on Si.

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ABSTRACT

Tris(trimethylsilyl) phosphite ($P(\text{OSi}(\text{CH}_3)_3)_3$) is a multifunctional electrolyte additive for scavenging HF and forming a cathode electrolyte interphase (CEI). Systematic analysis of the HF reaction pathways and redox potentials of $P(\text{OSi}(\text{CH}_3)_3)_3$, $\text{OP}(\text{OSi}(\text{CH}_3)_3)_3$, $P(\text{OSiF}_3)_3$, and $\text{OP}(\text{OSiF}_3)_3$, and their reaction products, using ab initio calculations allowed us to elucidate the operating mechanism of $P(\text{OSi}(\text{CH}_3)_3)_3$ and verify the rules that determine its HF reaction pathways and electrochemical stability. While O–Si cleavage is the predominant HF scavenging pathway for $P(\text{OSi}(\text{CH}_3)_3)_3$, O–P cleavage is stabilized by replacing CH_3 with an electron-withdrawing group. Thus, $P(\text{OSiF}_3)_3$ scavenges HF mainly through O–P cleavage to produce PF_3 , which has high oxidation stability. However, the O–Si cleavage pathway produces $P(\text{OSi}(\text{CH}_3)_2\text{OH}$, $P(\text{OSi}(\text{CH}_3)_2(\text{OH})_2$, and $P(\text{OH})_3$ sequentially, along with $\text{Si}(\text{CH}_3)_3\text{F}$. These PO_3 systems, which are oxidized earlier than carbonate solutions and form tightly bonded units following oxidation, act as seed units for compact CEI growth. Moreover, the HF scavenging ability of PO_3 systems is maintained during oxidation until all O–Si bonds are broken. As a strategy for developing additives with enhanced functionality, modifying $P(\text{OSi}(\text{CH}_3)_3)_3$ by replacing CH_3 with an electron-donating group to exclusively utilize the O–Si cleavage pathway for HF scavenging is recommended.

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1. Introduction

Li-ion batteries are widely used for portable electronic devices [1]. However, for large-scale applications, such as electronic vehicles, the energy density of Li-ion batteries needs to be improved and their safety enhanced [2,3]. Therefore, major scientific interest has focused on developing and optimizing high-voltage cathode

materials that enable battery operation above 4.5 V [4–10]. However, commonly used carbonate-based electrolytes limit the operation of Li-ion batteries above 4.5 V owing to their electrochemical windows [11,12]. One strategy to resolve this problem is the development of completely new electrolytes with higher electrochemical windows [13–17]. Another is the development of functional additives that enable the formation of a protective film, known as a cathode electrolyte interphase (CEI) [18]. A CEI allows Li-ion transfer but prevents electron transfer, thereby preventing oxidative degradation of electrolytes in the vicinity of the cathode surface [19–22]. Recently, tris(trimethylsilyl) phosphite (TMSPi, $P(\text{OSi}g_3)_3$, $g = \text{CH}_3$) has drawn increasing attention as a

^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: dy777.kim@samsung.com (D.Y. Kim), mc.koh@samsung.com (M. Koh).

multifunctional additive for high-voltage electrodes, as it shows outstanding performance compared with other additives, especially for LiMO_2 ($M = \text{Ni, Co, and Mn}$) electrodes [23–30]. $\text{P}(\text{OSig}_3)_3$ is not only known to form low-resistance CEI layers on the cathode surface, but also to eliminate detrimental HF. HF is known to be generated during hydrolysis of LiPF_6 , and its further reactions with the CEI increase resistance and promote metal dissolution from electrode materials [31]. In addition, $\text{P}(\text{OSig}_3)_3$ is known to scavenge O_2 , forming $\text{OP}(\text{OSig}_3)_3$. O_2 gas generation can be attributed to poor interfacial stability of LiMO_2 electrodes at high operating voltages, and O_2 gas in the cell degrades the electrolyte components. Owing to the excellent performance of $\text{P}(\text{OSig}_3)_3$, various studies have examined the operating mechanisms of $\text{P}(\text{OSig}_3)_3$ as an electrolyte additive [25–27,32]. Choi and co-workers defined the multifunctional roles of this additive and proposed possible HF reaction pathways by investigating the characteristics of the protective layer on cathode surfaces using *post-mortem* analysis with X-ray photoelectron spectroscopy (XPS) [25,26]. Han et al. proved that this additive reacts with F^- through a pathway in which the O–Si bond is broken, affording phosphite and silyl ether components in the protective layer on the electrode surface. In addition, it has been proposed that this additive remarkably reduces internal pressure by effectively scavenging O_2 gas in the cell [32].

The goals of this study are to provide a more profound understanding of $\text{P}(\text{OSig}_3)_3$ –HF reactions and the associated electrochemical aspects, and to obtain insight into tuning and controlling the chemical and electrochemical characteristics of P–O–Si structures towards designing new additives. Four different systems were selected for systematic study: $\text{P}(\text{OSig}_3)_3$, $\text{OP}(\text{OSig}_3)_3$, $\text{P}(\text{OSiF}_3)_3$, and $\text{OP}(\text{OSiF}_3)_3$, as shown in Fig. 1, and we identified the HF reactions of

these systems. We also compared and analyzed the redox stabilities along their HF reaction pathways. It should be noted that $\text{P}(\text{OSig}_3)_3$ can be converted to $\text{OP}(\text{OSig}_3)_3$ by self-oxidation with O_2 , and $\text{P}(\text{OSig}_3)_3/\text{OP}(\text{OSig}_3)_3$ can be converted to $\text{P}(\text{OSiF}_3)_3/\text{OP}(\text{OSiF}_3)_3$ by reaction with HF through Si–C bond breakage. Using the analysis of the HF scavenging reaction pathways and the redox potentials of these four molecules and their reaction products, we propose design rules for the discovery of new functional additives.

2. Calculation methods

Ab initio calculations were performed based on density functional theory using the Gaussian 09 package [33]. The geometries of the stationary points were optimized with the M062X functional [34] and the 6-311 + G** basis set, and all calculations were performed at the same level of theory. All molecular structures reported here are the lowest-energy structures for each given conformation and have zero imaginary frequencies. To identify the transition state structures with a single imaginary frequency, intrinsic reaction coordinate (IRC) calculations were performed. The Gibbs free energy was calculated at 298 K with zero point energy (ZPE) correction. The condensed-phase energies were determined from single-point energy calculations performed based on the self-consistent reaction field (SCRF) theory, using the isodensity surface polarized model (IPCM). The dielectric constant of acetone (20.5) was used for the SCRF/IPCM calculations [35]. Atomic charges were calculated from the atomic polar tensors (APTs). The oxidation potential versus Li/Li^+ was calculated using $V_{\text{ox,Li}} = (IE_1 - 1.4)/F$ and the reduction potential was calculated using $V_{\text{red,Li}} = (EA - 1.4)/F$, where IE_1 is the first ionization energy,

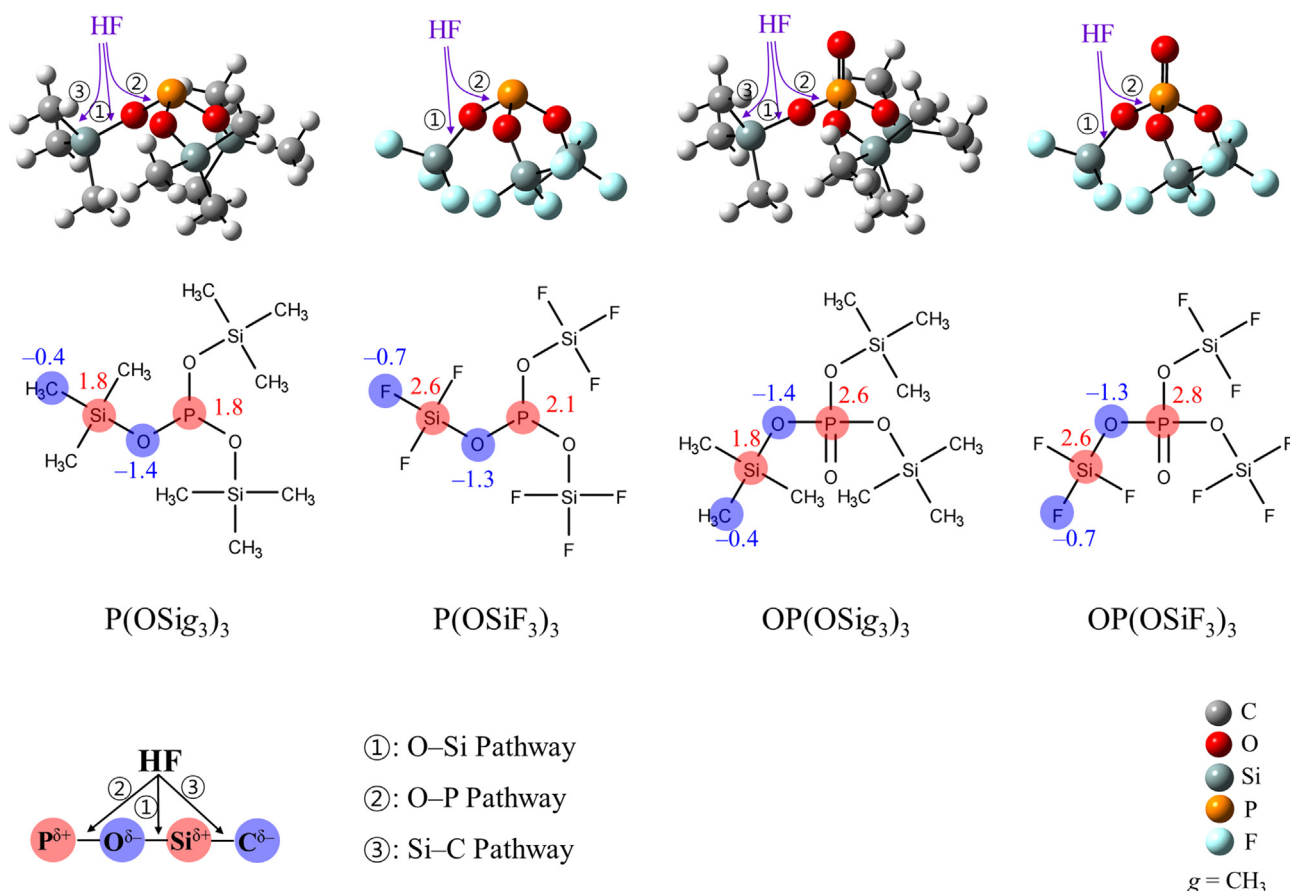


Fig. 1. Ball and stick models of the four selected molecules showing available bond cleavage reaction pathways with HF. Given the alternating signs of atomic polar tensor (APT) charges along the P–O–Si–C or P–O–Si–F branches, three different kinds of bonds can break for reaction with HF, which are named as the O–Si, O–P, and Si–C pathways.

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