# MACROMOLECULAR SILICON COMPOUNDS AS FILM-FORMING ELECTROLYTE COMPONENTS FOR LI-ION CELLS WITH GRAPHITE ANODES

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## Abstract

The aim of the presented work is to demonstrate a new family of additives for propylene carbonate-based electrolytes for lithium-ion batteries, as a means of overcoming the inherent incompatibility of propylene carbonate and graphite. The additives belong to the class of silicon podands, macromolecular compounds having two or three polyoxaethylene chains of variable length attached to the silicon atom and capable of coordinating alkali metal cations. It is proved that when only 10% by weight of certain silicon podands is added to propylene carbonate, the mixture thus formed can be successfully employed as electrolyte solvent in Li-ion cells with highly graphitic anodes. Several silicon podands are presented, differing in length of the polyoxaethylene chains as well as in the nature of the terminating functional group. Special attention is devoted to vinyl podands. Factors affecting the applicability of podands as electrolyte components as well as mechanisms of passivation are discussed on the basis of the collected electrochemical data.

## Introduction

Electrolyte composition is believed to be one of the crucial factors as far as performance of lithium-ion batteries is concerned. During the first charging of the Li-ion cell the electrolyte components are reduced on the carbon anode and the decomposition products form a passivating film, often called solid electrolyte interface (SEI). Structure of passivating film is a matter of decisive importance for the efficient work and good cycleability of the cell and depends greatly on the nature of chemical species forming the electrolyte solution. Early works have proved that propylene carbonate (excellent solvent for most lithium salts, successfully employed as co-solvent in primary lithium batteries) is not a suitable electrolyte component for Li-ion batteries with graphite anode. This is caused by the fact that upon first charging of the cell propylene carbonate (PC) molecules are co-intercalated together with lithium ions into the graphite interplanar spaces followed by its decomposition [1]. Gaseous propylene which is evolved in this process causes the graphite particles to exfoliate thus making the passive layer unstable.
Many attempts have been made in the past to overcome the inherent incompatibility of PC and graphite in the Li-ion system. An obvious approach is to replace PC by other organic compound having the property of forming a stable passive layer on the graphite surface. A typical example is ethylene carbonate which is widely applied in Li-ion technology. This is

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in spite of the fact that melting point of ethylene carbonate is relatively high, therefore it is always used in mixture with other low-viscosity solvent, typically diethyl carbonate or dimethyl carbonate. However even in such configuration EC-based electrolytes have limited applicability for low-temperature work.

Since the main problem in PC-based electrolytes is that its molecules tend to co-intercalate into the graphite lattice together with the lithium cations, another possible approach is to introduce to the system molecules that would compete with PC for co-ordination of lithium. Such effect is well known in the case of crown ethers [2]. Very recently compounds possessing vinyl functional groups have been proposed as additives for PC as a cure against its incompatibility with graphite anodes. The beneficial effect of vinyl additives was attributed to their ability to electropolymerise upon reduction on graphite [3,4].

In the present work a new family of film-forming additives for PC-based electrolytes is presented. The family comprises certain silicon podands, compounds having a general formula $RSi[(OCH_2CH_2)_nOR]_3$, where three polyoxaethylene chains form a cage capable of complexing alkali metal cations [5-7]. The presented compounds belong to a wider class referred to as supramolecular complexes of host-guest type and can be regarded as open-chain analogues of such macrocyclic compounds as crown ethers. On the other hand, some of them can also be regarded as a members of a large family of vinyl additives for the electrolytes.

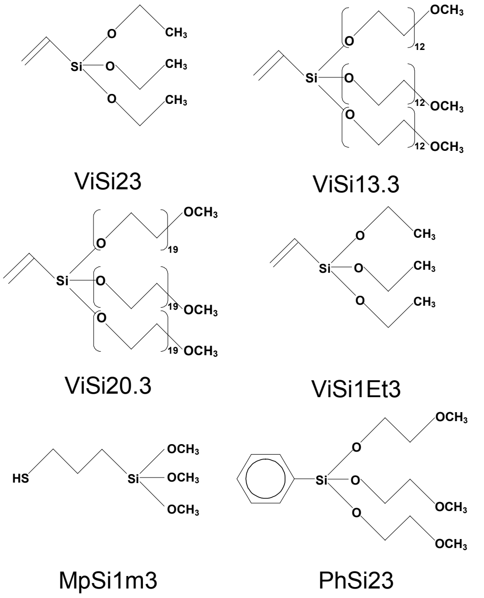
## Experimental

Silicon podands were synthesized according to the procedure described in [8]. If not stated otherwise, electrolytes were prepared by dissolving $LiPF_6$ (Aldrich, reagent grade) in a mixture of propylene carbonate (Merck, used without any additional treatment) and a silicon podand (10 % by weight). The electrolytes were prepared in a glove box filled with a dry argon (water content less then 20 ppm).

For examination of electrolytes' performance during cathodic reduction a highly crystalline UF2 (Kropfműhl) graphite was used. The electrodes were prepared by applying a slurry consisting of the graphite, acetylene black (10%) and PVdF binder (10%, Fluka) onto a copper foil current collector, followed by drying overnight in the vacuum at 120 °C. The graphite electrode and lithium foil counter electrode were sandwiched with a polypropylene separator (Celgard) and the whole stack was placed in a two-electrode Swagelok-type cell, followed by filling the cell by an excess of the investigated electrolyte composition. The cells were cycled galvanostatically at 10 mA per gram of active electrode mass in the voltage range 0 – 2 V vs $Li/Li^+$.

## Results and Discussion

Several compounds were chosen as representatives of the studied class. They were selected in a way enabling examination of the two principal characteristics of those compounds, namely length of the polyoxaethylene chains and chemical nature of the terminal functional group. Symbols of silicon podands and the respective structural formulas are presented in the Fig. 1.


ViSi23 ViSi13.3

ViSi20.3 ViSi1Et3

MpSi1m3 PhSi23

***Fig. 1*** *Structural formulas of the examined silicon podands*

The criterion for evaluation of podands were galvanostatic charge/discharge experiments. The electrochemical characteristics for all solvent compositions are presented in the Fig. 2 and the corresponding basic numerical data is collected in Table 1.

***Table 1*** *Basic electrochemical data for the graphite anode charged/discharged in various electrolyte solvent compositions.*

| Solvent composition | Charge capacity in the 1st cycle [mAh/g] | Discharge capacity in the 1st cycle [mAh/g] | Efficiency in the 1st cycle [%] |
|---|---|---|---|
| PC | | Electrode failure | |
| PC / ViSi23 | 502 | 352 | 70 |
| PC / ViSi13.3 | 245 | 85 | 35 |
| PC / ViSi20.3 | 1411 | 257 | 18 |
| PC / ViSi1Et3 | | Electrode failure | |
| PC / MpSi1m3 | | Electrode failure | |
| PC / PhSi23 | | Electrode failure | |
| PC / PhSi23 / $H_2O$ | 807 | 371 | 46 |

Fig. 2a shows a typical voltage profile for the case of graphite electrode reduced in electrolyte composed of lithium salt dissolved in propylene carbonate alone, and can be regarded as a reference characteristic for further considerations. As can be seen, after reaching approximately 800 mV vs. $Li/Li^+$ the potential of the graphite electrode reaches a plateau which lasts as long as new PC molecules are co-intercalated into the graphite lattice and get decomposed with the evolution of the gaseous propylene. The described behaviour has been confirmed by many researchers, being an important obstacle to commercialization of Li-ion batteries until the invention of film-forming properties of ethylene carbonate.

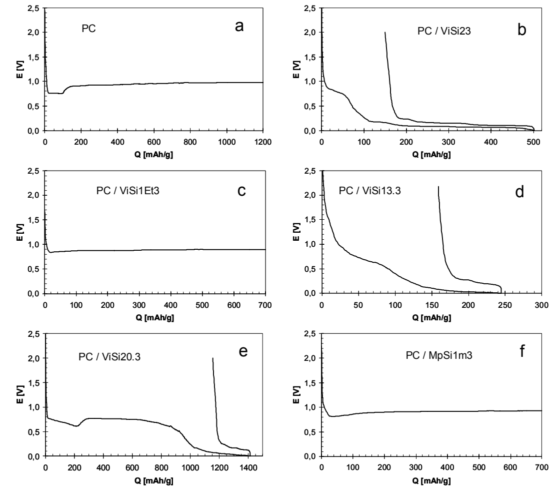


***Fig. 2*** *Galvanostatic charge/discharge characteristics for the examined solvent compositions.*

A glance at the Fig. 2 allows for the first conclusion that the observed impact on the electrochemical performance varies greatly according to the Si-podand added to PC. In case of ViSi1Et3 and MpSi1m3 there is no improvement in comparison to pure PC (see Fig. 2c and 2f respectively). A dramatic change is observed when 10% by weight of ViSi23 is used as co-solvent. The corresponding voltage profile (see Fig. 2b) indicates that a typical passive layer is formed on the graphite anode. The shape of part of the galvanostatic curve between 800 mV and 200 mV resembles very much that known for electrolytes containing ethylene carbonate. On the basis of this observation one can assume that the presence of ViSi23 effectively prevents PC from co-intercalation into graphite. After reaching ca 200 mV lithium ion intercalation starts. The intercalation proceeds via three stages and the corresponding three potential plateaux are clearly visible on the charge curve. The three plateaux are also present on the discharge part of the galvanostatic curve. These features unambiguously prove that solid electrolyte interface built on the graphite in the presence of ViSi23 allows for proper intercalation of lithium into the graphite lattice and thus reaching capacities that are satisfactory from practical point of view. The discharge capacity in the first cycle, which can be identified with the electrode's reversible capacity, attains a value of 352 mAh/g (see Table 1). A different behaviour is observed for ViSi13.3 compound. The charge capacity in the first cycle (245 mAh/g, see Table 1) is markedly lower that in the case of ViSi23 and the corresponding discharge capacity figures out at only 85 mAh/g. It is important to note here that although the capacities are lower than expected for graphite electrode in the Li-ion system, it is still a great progress in relation to the case of pure PC. In case of ViSi20.3 the exact weight percentage of podand in the solvent mixture is not known. Unlike the above described podands, ViSi20.3 is poorly soluble in PC. In order to prepare a solvent, ViSi20.3 was added to PC and left for several days to obtain a saturated solution. The unusual shape of the galvanostatic charge curve (see Fig. 2e) suggests yet another course of SEI development.

To sum up this part of the study, it can be said that most Si-podands with vinyl groups perform well as additives to PC. The most satisfactory result was obtained for ViSi23, which has the shortest polyoxaethylene chains. In addition to that, chains ending with $-OCH_3$ seem to be preferred, while ViSi1Et3 serves as an example that those ending with $-OCH_2CH_3$ are not. Good performance of vinyl compounds supports thesis set forth by

Möller and co-workers [3] that electropolymerisation of vinyl groups plays an important role in the SEI formation process. However, taking into account some exceptional properties of silicon podands it is justified to assume that other important mechanisms contribute to the overall process. It is a well known that in the presence of traces of water (which are inevitable even in water-free Li-ion cells) the polyoxaethylene chains are detached from the podand molecule to form a corresponding glycol. The product of this reaction will tend to condense with other podand molecules, leading eventually to the formation of a two-dimensional network. This hypothesis finds support in a striking behaviour of the PhSi23 podand (see Fig. 3).

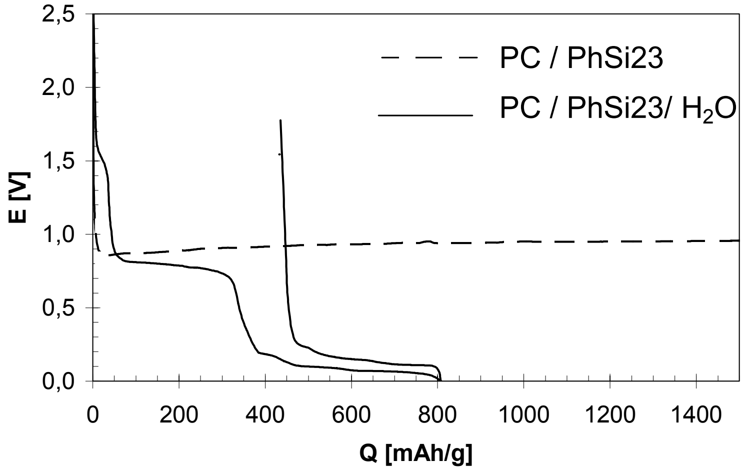


***Fig. 3*** *Galvanostatic charge/discharge characteristics for the examined solvent compositions.*

When a mixture of this compound and PC is used as an electrolyte solvent, the system performs in a manner similar to that known for PC alone. However, when some amount of water is intentionally added to the electrolyte, the galvanostatic characteristics start to reveal that stable passive layer is built, leading a satisfactory reversible capacity (371 mV, see Table 1).

The presented results of preliminary works on Si-podands prove that at least some representatives of this category of compounds can be considered as co-solvents for PC in the Li-ion cells with graphite anodes. The mechanisms involved in the SEI formation seem to be complex. In particular, it was shown that in certain conditions presence of vinyl group is not necessary for stable passivation of graphite. Further intensive research is in progress aiming at more in-depth study of the reactions of Si-podands on the electrode interface.

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