

Electrochemical Behavior of Tripodand-Type Silanes as Electrolyte Solvents for Electrochemical Capacitors

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Five tripodand-type silane compounds with different functionalities have been examined as potential electrolyte solvents for electrochemical double layer capacitors (EDLCs) with lithium salt as ion source. For the assembly of model capacitors commercial chemically activated carbon material NORIT® SX 2 (BET surface area after activation 2312 m²g⁻¹) was used. The capacitances have been determined by means of galvanostatic cycling, cyclic voltammetry and electrochemical impedance spectroscopy techniques. It was found that Si-tripodands are effective as conductive medium for Li⁺ cations in EDLCs and the measured capacitances strongly depend on the type of functionality.

Keywords: electrochemical double layer capacitor; silicon podand; activated carbon

1. INTRODUCTION

Electrolyte composition is one of crucial factors (beside surface properties of carbon electrodes) that determine the EDLC's electrical characteristics [1-3]. The electrolyte must be a liquid medium electrically conducting by mean of ions. Ionic liquids are examples of ionically conducting media which at the same time are liquid [4]. Another option is a salt dissolved in a molecular solvent. Lithium salt solutions in organic solvents attract growing interest as supercapacitor electrolytes along with the emergence of the concept of hybrid supercapacitor (HSC), in which one of the electrodes is a lithium intercalation electrode known from Li-ion batteries [5-6]. Therefore it is justified to continue

research on solvents with precisely tailored properties in order to optimize the electrolyte contribution to the output of lithium-based EDLCs.

If the salt contains lithium cation, the solvent must be selected in such a way that excellent dissociation is ensured. In the present work a family of new solvents for lithium salts, referred to as silicon podands (in this particular case – tripodands), are thoroughly evaluated as potential electrolytes for supercapacitors. Silicon tripodands are polyether-functionalized silanes in which three polyoxaethylene chains are attached to a central silicon atom. The fourth valency of silicon can be used for attaching virtually any desired functionality [7-17]. Molecular structures of this type can be potentially interesting as electrolyte solvents or co-solvents for electrochemical capacitors for several reasons. Firstly, free electron pairs at ether oxygen atoms provide excellent solubility towards salts, in particular alkali metal salts. Moreover, cations solvated by tripodands are known to be trapped within the “cage” formed by the three polyoxaethylene chains, thus preventing ion-pairing [18-19]. Going further, some silicon podands exhibit self-assembling in the presence of cation [18]. Last but not least, silicon podands are easy and inexpensive in synthesis and are known to decompose to environmentally benign products like silica and glycols, thus can be considered as “green” chemical agents. Silicon podands have also important disadvantages, like instability in water and relatively high viscosity. These problems may be to a large extent avoided by adopting high purity, water-free processes.

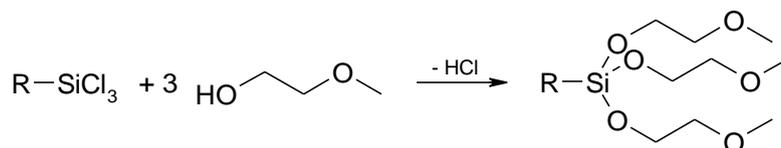
The motivation of this study was a preliminary assessment of five representatives of well defined class of compounds - silicon tripodands - as potential electrolyte solvents for EDLCs. To our knowledge, any silanes have never been reported as potential solvents for supercapacitors.

2. EXPERIMENTAL

Table 1. Symbols, systematic names and semi-structural formulas of Si-tripodand solvents

Symbol	Systematic name	Semi-structural formula
MeSi23	methyl tris(-2-methoxyethoxy)-silane	$\text{CH}_3\text{-Si}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$
EtSi23	ethyl tris(-2-methoxyethoxy)-silane	$\text{CH}_3\text{CH}_2\text{-Si}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$
ViSi23	vinyl tris(-2-methoxyethoxy)-silane	$\text{CH}_2=\text{CH-Si}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$
PhSi23	phenyl tris(-2-methoxyethoxy)-silane	$\text{C}_6\text{H}_5\text{-Si}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$
MtSi23	3-(methacryloxy)propyl tris(-2-methoxyethoxy)-silane	$\text{CH}_3\text{C}(=\text{CH}_2)\text{COO}(\text{CH}_2)_3\text{-Si}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$

Methyl tris(-2-methoxyethoxy)-silane (MeSi23) and vinyl(-tris-2-methoxyethoxy)-silane (ViSi23) were purchased (ABCR, Germany) and used for the experiments as received. Ethyl tris(-2-methoxyethoxy)-silane (EtSi23), phenyl tris(-2-methoxyethoxy)-silane (PhSi23) and 3-(methacryloxy)propyl tris(-2-methoxyethoxy)-silane (MtSi23) were synthesized in our laboratories according to the following general reaction scheme:



where R = Me, Et, etc. Symbols, systematic names and semi-structural formulas of the reported Si-tripodand-type silanes are collected in Table 1. Electrolytes for EDLCs have been prepared in argon filled glove box (H_2O and O_2 content in the atmosphere below 1 ppm) as 1M solutions of LiPF_6 (Aldrich, 99.99 %) in the examined solvents.

Conductivities were determined with the application of two-electrode Swagelok-type cells with internal teflon rings and with stainless steel electrodes (St | gel | St) at several temperatures (0 – 70 °C) on the basis of impedance spectra obtained by means of PARSTAT 2263 (Princeton Applied Research) impedance analyzer in the frequency range 100 kHz – 1 Hz. Typically each measurement was repeated several times to ensure good reproducibility of results. The cells were thermostated during measurements in a climatic chamber (Vötsch).

Commercial carbon NORIT[®], activated in KOH (1:4) was used as model electrode material. The material after activation is designated as AN2300 and exhibits the surface area of 2312 $\text{m}^2 \text{g}^{-1}$ (as determined by nitrogen adsorption with the application of ASAP porous structure analyzer, Micromeritics). Electrodes of the test capacitors consisted of 85% of AN2300, 10% of polymeric binder (KynarFlex 2801, Atofina) and 5% of acetylene black. The electrodes were prepared in the form of pressed pellets (8.5–12.4 mg) with the geometric surface area of 0.8 cm^2 . Electrochemical investigations were performed in the Swagelok-type cells using golden current collectors. Specific capacitances expressed per the mass of one electrode were determined by galvanostatic charging/discharging (100 – 2000 mA g^{-1}), cyclic voltammetry (1 – 50 mVs^{-1}) and electrochemical impedance spectroscopy (100 kHz–1 mHz) using VMP3 potentiostat (Biologic).

3. RESULTS AND DISCUSSION

Fig. 1 exhibits specific conductivities measured for the examined electrolytes at 25 °C. Fig. 2 shows how specific conductivities vary depending on temperature, presented in the Arrhenius coordinates, that is as logarithms of specific conductivities versus reciprocal temperature. In spite of close similarity of molecular structures, there are significant differences in the measured conductivities among the solvents. Three of them, namely MeSi23, EtSi23 and ViSi23 exhibit more than $10^{-3} \text{ S cm}^{-1}$ at 25 °C, whereas the two others (PhSi23 and MtSi23) lag behind. As can be seen on Arrhenius plots, at lower temperatures these differences are even more pronounced. $10^{-3} \text{ S cm}^{-1}$ is often regarded as arbitrary limit for viable electrolytes for energy storage devices. From conductivity data it can be concluded that EtSi23 and ViSi23 should be the most promising in terms of electrochemical behavior (1.57×10^{-3} and $1.71 \times 10^{-3} \text{ S cm}^{-1}$ respectively).

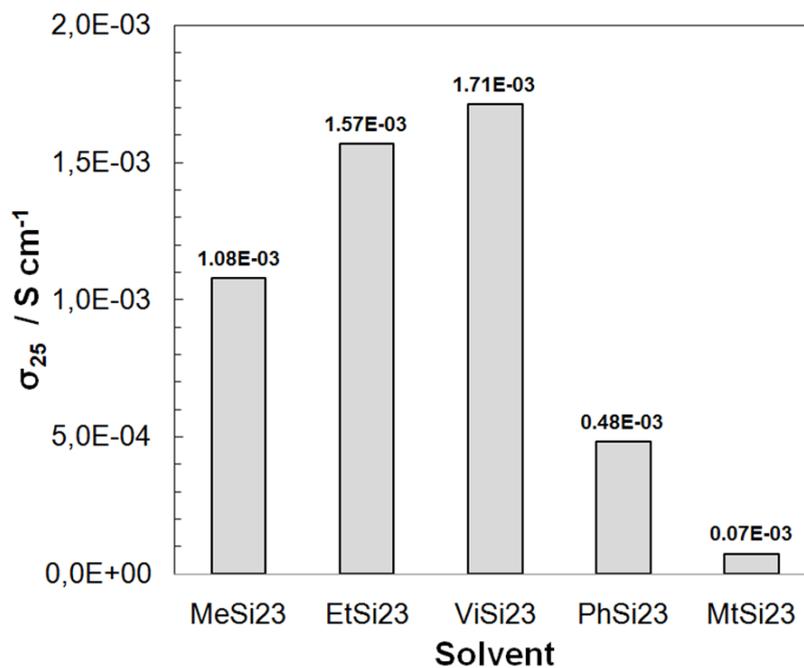


Figure 1. Conductivities at 25 °C for 1M LiPF₆ solutions in studied solvents

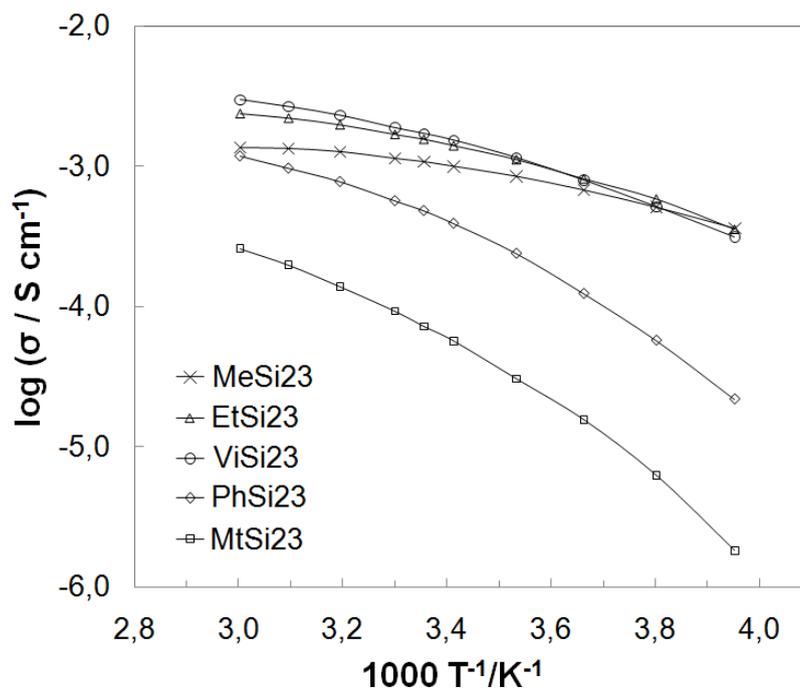


Figure 2. Temperature dependencies of ionic conductivities determined for 1M LiPF₆ solutions in the studied solvents

Table 2 displays capacitance data collected from cyclic voltammetry measurements at three different scan rates. Electrolyte with EtSi23 solvent proves to perform best at all scan rates, with model

carbon capacitance as high 139 Fg^{-1} at 1 mVs^{-1} . As scan rate increases, the measured capacitances diminish as a result of ionic diffusion constraints. The results confirm that MeSi23, EtSi23 and ViSi23 provide the best conditions for ionic transport phenomena in electrochemical capacitors. In the cyclic voltammetry experiment EtSi23 performs best, which is reflected very clearly in cyclic voltammetry curves at 5 mVs^{-1} showed in the Fig. 3. Shape of the EtSi23 voltammogram is characteristic for EDLC cells with high capacitance and favorable transport conditions (voltammetric curve somehow approaching the idealized rectangular shape), which is particularly well visible in comparison with markedly worse MeSi23 and ViSi23 characteristics, and with very poor PhSi23 and MtSi23 behavior.

Table 2. Capacities of capacitors with silane-based electrolytes determined on the basis of cyclic voltammetry measurements at three scan rates

Solvent	Capacitance / F		
	1 mVs^{-1}	5 mVs^{-1}	10 mVs^{-1}
MeSi23	78	58	38
EtSi23	139	108	95
ViSi23	75	53	27
PhSi23	49	39	26
MtSi23	52	43	32

Table 3. Capacities of capacitors with silane-based electrolytes determined on the basis of galvanostatic measurements at three current densities

Solvent	Capacitance / F		
	100 mAg^{-1}	200 mAg^{-1}	500 mAg^{-1}
MeSi23	79	64	38
EtSi23	120	105	96
ViSi23	71	55	25
PhSi23	48	36	21
MtSi23	48	39	29

Table 3 compares capacitance data obtained on the basis of galvanostatic measurements at three different current densities. Fig. 3 shows galvanostatic characteristics at 200 mAg^{-1} for three best podand solvents. The results entirely confirm the conclusions from cyclic voltammetry in that EtSi23 performs best, followed by MeSi23 and ViSi23. As previously, the model carbon exhibits the lowest capacitances with PhSi23 and MtSi23 solvents. Obviously the capacitances consistently rise together with increasing current rate. EtSi23 shows also the most favorable shape of galvanostatic curve (see Fig 4). Especially striking is the lowest ohmic drop observed for EtSi23, in comparison with other solvents.

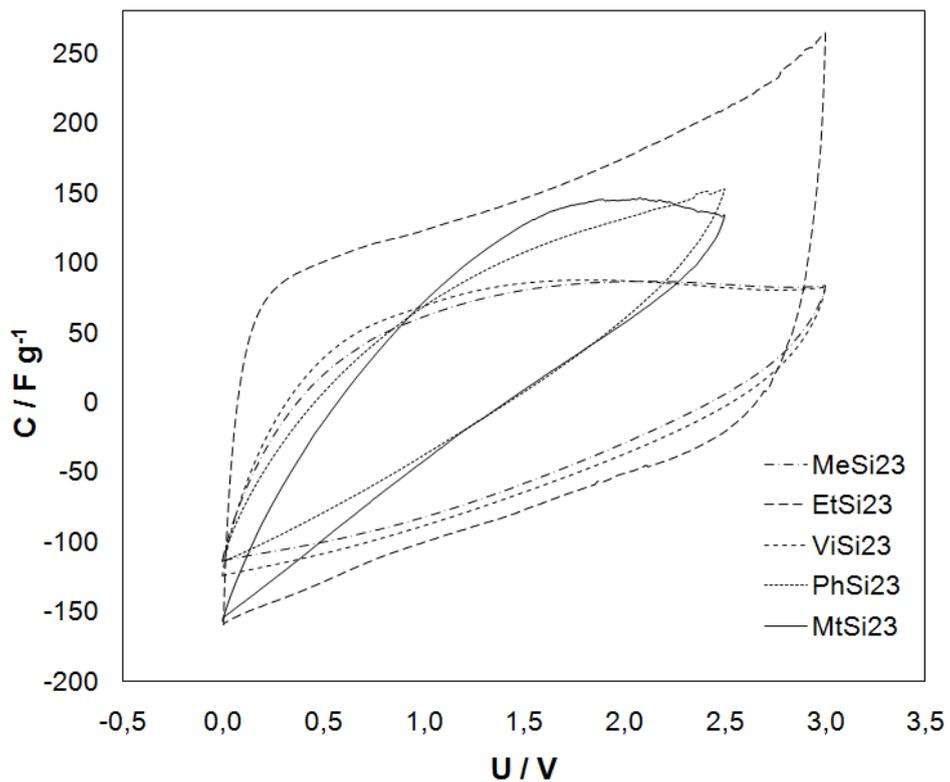


Figure 3. Cyclic voltammetry characteristics of EDLCs with the examined silane solvents; scan rate – 5 mVs⁻¹

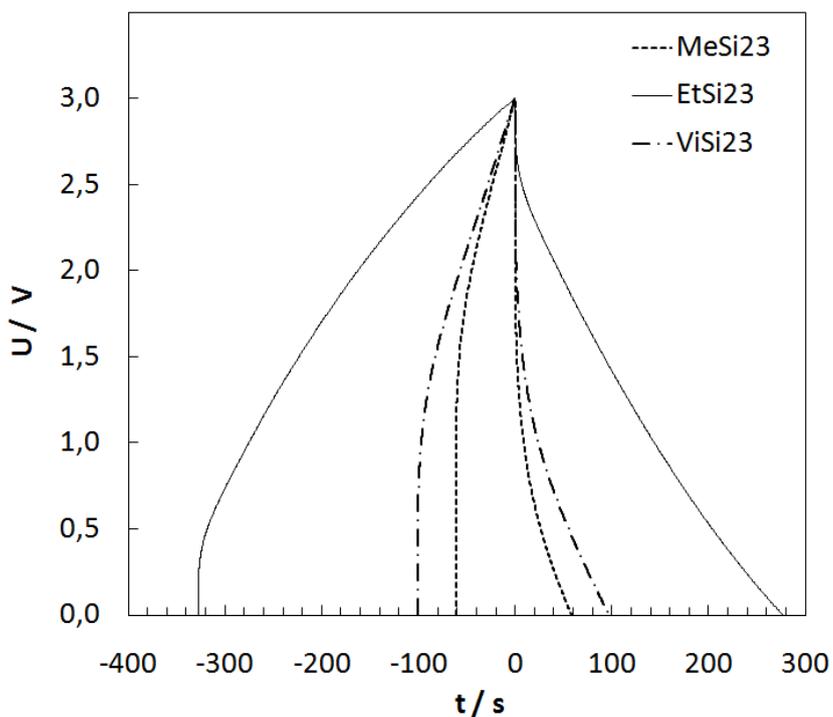


Figure 4. Galvanostatic characteristics of supercapacitors with different tripodand solvents

The last technique applied for the evaluation of tripodand solvents is impedance spectroscopy. Fig. 5 presents the specific capacitances as a function of frequency of sinusoidal perturbation of the cell voltage (as logarithms). Capacitances can be read and compared from the vertical axis of this plot at a given frequency. For instance, at $\log f = -3$ (which corresponds to the frequency of 1000 s) capacitances of EtSi23, ViSi23 and MeSi23 are ca.: $C = 100 \text{ Fg}^{-1}$, 74 Fg^{-1} and 68 Fg^{-1} , respectively. PhSi23 and MtSi23 both exhibit about 45 Fg^{-1} . Again, the results are in general agreement with the data from other techniques in terms of the order of capacitances.

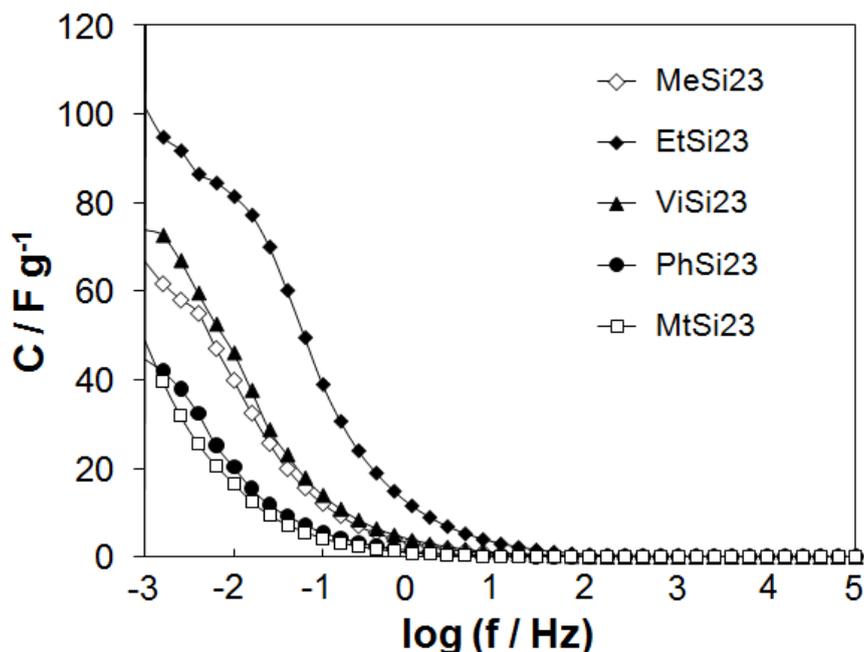


Figure 5. Impedance spectroscopy determination of cell capacitances in function of electrolyte solvent

Silanes have never been considered so far as organic solvents for lithium-based electrochemical capacitors. In a somewhat comparable work Khomenko *et al.* [5] studied both symmetric and hybrid systems with Norit Super 50 activated carbon electrodes and “conventional” organic Li-based electrolytes. For acetonitrile as solvent they obtained capacitance as high as 76 F g^{-1} in EIS experiment at low frequency regime, which is a moderate value as compared to our silane solvents (EtSi23 exhibits about 100 F g^{-1} , see Fig. 5). For more rigorous comparison, however, the examined electrolytes must be tested in hybrid capacitor setups with one intercalation electrode, which is not within the scope of the present work. In fact, the most direct reference for lithium-based electrolytes, including those described here, are typical electrolytes for Li-ion batteries. This is also evident from the works of Khomenko *et al.* [5] and Decaux *et al.* [6], who consistently rely on ethylene carbonate/dimethyl carbonate as solvent mixtures for their hybrid systems. This is fully reasonable since these systems are in half based on lithium insertion phenomena. Hybrid systems are also the ultimate target for the tripodand-type electrolytes so this approach will also be subject of our future investigations.

It is well known that two main factors have particular influence on the performance of an electrolyte in EDLCs. One of them is ionic conductivity, which affects the accessible rate of charge and discharge of the device by governing the ohmic drop across the cell. The other factor is more complex and relates to the steric hindrance encountered by a solvated ion approaching the surface of porous carbon electrode. More specifically, dimensions of the solvation cloud dragged by an ion decide whether this ion has access to the surfaces of all micro and nanopores in the carbon. Only when all internal surfaces are accessible for the charge carriers, the whole electrode can contribute to the measured capacitance. It is worth noticing that the capacitance data determined for various electrolytes must be analyzed in connection to the type of carbon used in test supercapacitors. In the present work we use common carbon for all the electrolytes, so the results can be compared, however the absolute magnitudes of capacitances must be treated with caution and may be different for other type of carbon. Also the electrolyte salt may be chosen differently. This analysis is intended to preliminarily assess the viability of silicon tripodands as possible electrolyte solvents for supercapacitors.

Given all that, it is visible that capacitances (whatever method of determination is taken) do not follow exactly the order of specific conductivities measured at room temperature. One can nevertheless easily notice that podands with bulky functional groups (phenyl and methacryloxy) perform significantly worse than those with “small” groups (methyl, vinyl and ethyl). See Fig. 5 for a sequence of increasing volumes of respective functional groups.

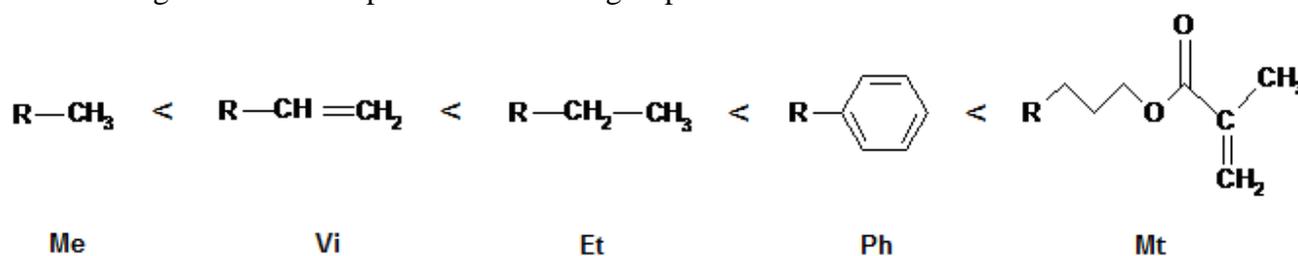


Figure 6. Order of increasing volumes of functional groups

EtSi23 performs best in all capacitance measurements. Somewhat striking is relatively poor performance of MeSi23 and ViSi23, in spite of good conductivities. Low capacitances of ViSi23 may result from polymerization via vinyl groups. Leading to the creation of larger assemblies, incapable of penetrating low-diameter pores of carbon electrodes. Low capacitances observed for MeSi23 are difficult to explain, especially in comparison with EtSi23. Unexpectedly good behavior of the later must be result of a particularly favorable combination of fast ionic transport, steric predisposition and other factors that need closer inspection.

4. CONCLUSIONS

Tripodand-type silanes have been examined as possible low cost, low toxicity electrolyte solvents for electrochemical double layer capacitors. The electrolytes proved to be generally viable in terms of the achieved capacitances, however with significant differences resulting from different

functionalization. Solvents with bulky phenyl and methacryloxypropyl groups behave the worst which can be clearly attributed to lower specific conductivities. However, least bulky compounds with methyl, ethyl and vinyl groups do not follow exactly the order of conductivities, giving rise to the assumption that steric phenomena, understood as the spatial compatibility of solvent molecules with the carbon pores, contribute to the overall electrochemical output. In this respect particularly surprising are the highest capacitances observed for the compound with ethyl group, which deserves further investigation.

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