



Characterization of low-flammability electrolytes for lithium-ion batteries[☆]

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ABSTRACT

In an effort to develop low-flammability electrolytes for a new generation of Li-ion batteries, we have evaluated physical and electrochemical properties of electrolytes with two novel phosphazene additives. We have studied performance quantities including conductivity, viscosity, flash point, and electrochemical window of electrolytes as well as formation of solid electrolyte interphase (SEI) films. In the course of study, the necessity for a simple method of SEI characterization was realized. Therefore, a new method and new criteria were developed and validated on 10 variations of electrolyte/electrode substrates. Based on the summation of determined physical and electrochemical properties of phosphazene-based electrolytes, one structure of phosphazene compound was found better than the other. This capability helps to direct our further synthetic work in phosphazene chemistry.

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1. Introduction

The electrolyte is a major cost factor and limitation for the next generation of Li-ion batteries foreseen for a variety of electric vehicle and grid applications. Currently, the most common industrial electrolyte formulations for Li-ion batteries are a LiPF_6 salt dissolved in a mixture of organic carbonate solvents. These electrolyte formulations are highly flammable with flash points around 30 °C.

In recent years, more stringent safety and energy density requirements for large lithium-ion cells require development of electrolytes of lower flammability and with wider electrochemical window to make the batteries safer, with higher operating voltage and, therefore, higher energy. Several classes of additives and/or co-solvents have been proposed in literature to retard flammability, mainly: phosphates, phospholanes, phosphazenes, borates, siloxanes, silanes, fluorinated carbonates and fluorinated ethers, and mixtures thereof [1–6]. Among organophosphorus compounds, compared to other additives, phosphazene compounds cause markedly less degradation in battery char-

acteristics [7]. Therefore, in our work we decided to focus on low molecular weight phosphazene compounds as additives to conventional electrolytes. The novelty of the work comes from the synthetic accessibility to a wide variety of derivatives of these compounds. Synthesis of closely related series of compounds affords the opportunity to understand the effect of the additive in blends with conventional electrolytes. By discovering optimal additive molecular structure(s), combination with conventional electrolytes may demonstrate desirable unique properties pertaining to transport properties and formation of passivation films.

The primary emphasis of this work was initial characterization of modified electrolytes in terms of conductivity, viscosity, flash point, electrochemical window and influence on formation of solid electrolyte interphase (SEI) films. In order to compare properties of SEI in different electrolytes, a new electrochemical voltammetry method and new criteria related to battery performance were developed.

2. Experimental

2.1. Chemicals and materials

1.2M LiPF_6 EC-MEC (2:8) electrolytes (battery grade) was obtained from Sumitomo Seika Chemicals Co., Ltd. It was used as received for baseline measurements and for making the blends with phosphazene compounds.

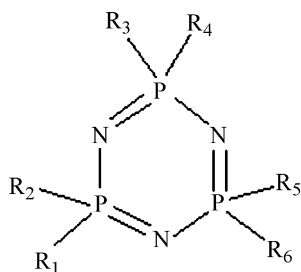
Two novel phosphazene compounds, coded as SM4 and SM5 were synthesized in-house through new synthetic pathways. The

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basic molecular structure is that of a cyclic trimer with the generalized formula as shown:



For SM-4, the R groups are methoxyethoxide and ethoxide. For SM-5, the groups are isopropoxide and ethoxide. Each substitution pattern is random as the synthetic route involves macromolecular nucleophilic replacement of halogen atoms on the phosphazene core [8,9]. Before making the blends with base-line electrolyte, the phosphazenes were saturated with LiPF_6 salt. Saturated molar concentrations were 0.84 M for SM4 and 0.66 M for SM5. Proportions of saturated with LiPF_6 phosphazenes in electrolyte blends were chosen as 3, 10, 30, 50% by weight.

Aluminum, nickel and copper foils, received from Aldrich, were used for making working electrode for electrochemical studies. Aluminum foil was 0.25 mm thick; 99.999% metal basis. Nickel foil was 0.125 mm thick; 99.9% metal basis. Copper foil was 0.25 mm thick; 99.98% metal basis. Carbon-coated aluminum foil, from Showa Denko Packaging Co., was used as received for making working electrodes. Lithium ribbon from Aldrich, 0.38 mm thick, 99.9%, was used to make counter and reference electrodes. Nickel wire, 0.25 mm diam., 99.9+%, was used as the terminals for lithium counter and reference electrodes. In order to separate electrodes in three-electrode electrochemical cell, Celgard 2500 microporous membrane was used.

2.2. Equipment, test instruments and procedures

Water content in the electrolytes was measured using a Mettler Toledo DL39 KF coulometer. The water contents were found to be in the range of 3–7 ppm. Preparation of electrolyte blends and assembly of electrochemical test cells were carried out in an argon-filled glove box made by Vacuum Atmospheres. Water and oxygen contents in the dry box were less than 0.1 ppm.

A TOA CM-30R conductivity meter was used to measure conductivity of the electrolytes. The average obtained from ten independent measurements was used to make the plots herein. The data were not corrected for temperature. All samples were at room temperature ($\sim 27^\circ\text{C}$). Samples were placed in a small vial, the probe inserted, and the vial sealed with Teflon tape to prevent evaporation of the volatile components during the measurements.

The viscosity data was the average of 9 independent measurements taken with a Cambridge Instruments falling cylinder viscometer. The data were not corrected for temperature. All samples were at room temperature ($\sim 27^\circ\text{C}$). Samples were placed in the viscometer chamber, the cylinder inserted, and the chamber sealed with paraffin film to prevent evaporation of the volatile components during the measurements.

The flash point data was the average of 3 independent measurements taken with a Setaflash Series 8 closed cup flash point analyzer using a ramp method. The flash point was validated and corrected for barometric pressure, all values corrected to 760 Torr. 2.0 mL electrolyte samples were passed out of the glove box in tightly sealed bottles. The instrument was interfaced into an open freezer at $\sim 0^\circ\text{C}$ to record sub-ambient flash points. After the instrument had reached the target starting ramp temperature, the sample was

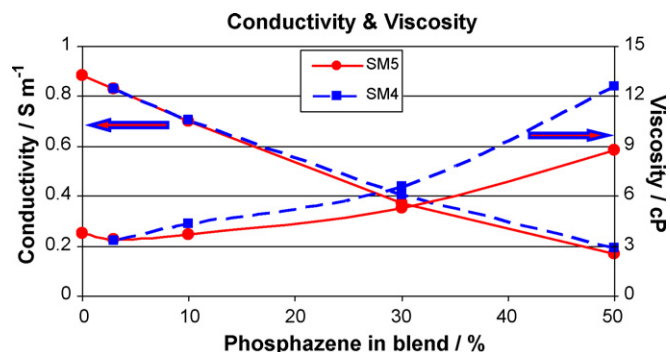


Fig. 1. Conductivity and viscosity of electrolyte blends of 1.2 M LiPF_6 EC:MEC (2:8) with SM4 or SM5 phosphazene compound.

introduced into the closed cup. Three sequential runs were made without opening the cup and the data were averaged.

For electrochemical voltammetry studies, a Solatron SI 1287 Electrochemical Interface was used. For potentiodynamic (PD) steps, a 5 mV s^{-1} sweep rate was used, while a $5 \mu\text{A}$ current was chosen as a cut off current at potentiostatic (PS) steps. Nickel and later copper electrodes were used for polarization in negative direction and aluminum electrode for polarization in positive direction from open circuit potential (OCV). Because each material has limitations, electrodes from more than one material were required to cover a wide potential range. For example, Ni oxidizes at potentials higher than 3.2 V without passivation and Al electrochemically alloys with Li at potentials below 1 V. In this paper, all potentials were measured and referenced against lithium reference electrode.

2.3. Electrochemical test cells

Small three-electrode electrochemical cells made in-house were used with an electrolyte volume of 0.8–1.0 mL. The working electrode was in the shape of flag and was cut from the foil from different materials with 1 cm^2 working area and with a 5 cm long and 1 mm wide terminal. The counter electrode was 1.44 cm^2 Li foil with an impressed (cold-welded) terminal from Ni wire. The reference electrode was narrow Li chip with an impressed Ni wire terminal. The electrodes were stacked and tightly placed in the slot of a plastic rod, which was tightly tailored into a capped glass vial. The electrodes were stacked such that the working and reference electrode were on the same line divided with separator and facing a larger sized counter electrode which was also divided with separator. Use of a plastic rod insert allowed us to minimize electrolyte volume and fix the electrode stack. All electrode terminals were fed through the holes in the vial's cap and were reliably connected to testing equipment wires. After cell assembly, the holes were plugged with plastic plugs to minimize electrolyte evaporation. In calculating current densities, it was assumed that only one side of working electrode, which faced counter electrode, was involved in electrochemical reactions.

3. Results and discussion

3.1. Physical properties of the electrolytes

For the physical properties of the electrolytes with phosphazene additives, only conductivity, viscosity, and flash points will be discussed in this paper.

Results for conductivity and viscosity are presented in Fig. 1 and results for flash point analysis are presented in Fig. 2.

Measured conductivity and viscosity show opposite trends, which is usual for organic electrolytes. Conductivity decreases with

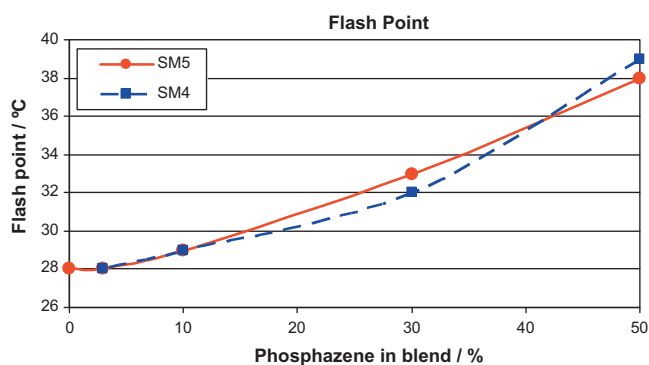


Fig. 2. Flash point of electrolyte blends of 1.2 M LiPF₆ EC:MEC (2:8) with SM4 or SM5 phosphazene compound.

increasing in viscosity. It is interesting to note that at low phosphazene concentrations, the percentage decrease in conductivity as we increase the amount of additive does not correspond to the increase in viscosity, as might be projected from a Stoke's Law analysis. This indicates there is some other mechanism of internal interactions that is affecting conductivity, particularly in the case of SM5. One plausible mechanism is that these phosphazenes have a propensity to aggressively bind with the free lithium ions through electron doublet transfer at the nitrogen members of the phosphazene rings. Such an interaction can be chelative in nature, producing in effect a relatively strong quasi-irreversible bond between nitrogen and lithium, which will decrease the population of charge carriers and thus, decrease electrolyte conductivity. This associative behavior between cations and nitrogen-containing solvents, which are non-hydrogen bond donors (some amines, amides, phosphazenes, etc.), is mirrored by relatively high donor numbers [10].

The tested phosphazene formulations do increase the flash point of electrolyte blends. This increase is modest in comparison with required tasks for safe electrolytes in battery applications. However, these two phosphazene formulations are a first series of synthesized compounds, which are used for validation of experimental methods and approaches. Trends in performance revealed for these initial compounds will be used for direction in further synthesis.

Overall, based on the previous discussion SM5 phosphazene mixtures have moderately better physical properties in regards to battery applications than SM4 mixtures.

3.2. Electrochemical window of electrolytes

Fig. 3 depicts PD curves obtained for three electrolytes: the baseline (control) system, and the baseline blended to contain 30% SM4 or SM5. Range of potentials in both directions from OCV, where currents are extremely low (less than $1\text{--}2\ \mu\text{A cm}^{-2}$) and do not exhibit significant reduction or oxidation processes, was considered as the electrochemical window. We do not claim high accuracy in measurements of the electrochemical window in this paper. There are a number of methods and definitions, described in the open literature, as to how to characterize and measure the electrochemical window. All of these methods are relative and based on key assumptions. Our measurements are sufficiently accurate to see meaningful differences in the three electrolytes.

Fig. 3 shows that our phosphazenes do increase the electrochemical window. This fact also indicates that there are some beneficial interactions between control electrolyte components and the phosphazenes additives. These interactions produce other specie(s), which have different red/ox potentials. The position of cathodic waves (reduction processes) in the range of potentials between 0.8 and 2.7 V differs in different electrolytes which indi-

cates a reduction activity of phosphazenes species or new species formed because of interactions. Regarding oxidation processes of electrolyte species on Al substrates, they exhibit similar potentials for the onset of oxidation reactions in all electrolytes. The only noticeable difference is the slope of the waves, which indicates a difference in the resistance of the interfacial area. Based on the shape of the anodic curves, it is difficult to make definite conclusions on the oxidation activity of phosphazenes species.

Fig. 3 shows that the electrochemical windows in all three electrolytes are less than the operating voltage for Li-ion batteries. Li-ion batteries can operate as they do because surface passivation occurs at potentials beyond the electrochemical window. These passivating layers are called the solid electrolyte interphase (SEI) at negative electrodes of Li-ion batteries. Regarding passivating layers on positive electrodes, there is not unanimous agreement on how to name them [11]. Most scientists agree that they are functionally similar to SEI and therefore they can be named as SEI, and we adopt that convention herein. Stability of passivating layers and therefore electrolytes at potentials beyond electrochemical windows is a crucial question for Li-ion battery performance. There are numerous literature reports on SEI properties and SEI characterization by different means. In this short paper, we will not discuss all of these methods. As a general note, an extensive current knowledge on electrochemistry in Li⁺-ion containing organic aprotic media [11,12] suggests that SEI properties primarily are a function of electrolyte composition and polarization potential. Additionally, in the same aprotic media SEI composition at similar ranges of potentials is similar on anode active materials, as well as inert substrates (Ni, Cu) and lithium. Therefore, using Ni and Cu electrodes instead of anode active materials for SEI studies at anode potential ranges is a legitimate approach. The same is true for passivation phenomena studies on Al substrate at cathode potentials where Al is stable. Moreover, using inert substrates instead of active materials for general SEI studies has several advantages because such SEI are more simple and uniform in their structure which provides for the easiest comparison and interpretation of results. Usually, such SEI films are not affected by catalytic reactions as found in the case of some carbonaceous anode materials, for example. By starting with the metal substrates in our study, we will be able to ascertain the effect of the heterogeneous porous electrode laminates on SEI characteristics when we later progress from the ideal metal electrodes to full cell materials. For more details regarding SEI and related topics, interested researchers can refer to a relatively recent compilation of SEI literature [11].

In this work, we pursued an effort to develop a simple method and criteria to characterize electrolytes and SEI at potentials beyond the electrochemical window and relate these criteria to critical parameters of battery performance. Taking into account the recent high interest in the development of high-voltage and high energy cells, points of our interest were at 5.2 V and 20 mV against a lithium reference electrode.

3.3. New method of electrochemical characterization of electrolytes and SEI

3.3.1. Introduction of the method

The method is based on PD and PS coulometry. In other words, this is a "bulk electrolysis" process until formation of surface layers under polarization is accomplished. We used Ni, Cu and Al substrates for polarization. We also used carbon coated Al substrate in a limited run. In the case of Ni and Cu substrates, PD polarization started from OCV and went in the negative direction towards Li electrode potential. At 20 mV vs. Li/Li⁺ PD polarization was switched to PS polarization until the cathodic current dropped below $5\ \mu\text{A cm}^{-2}$. We used slightly positive end potential against Li/Li⁺ in order to only form SEI but avoid dendritic lithium

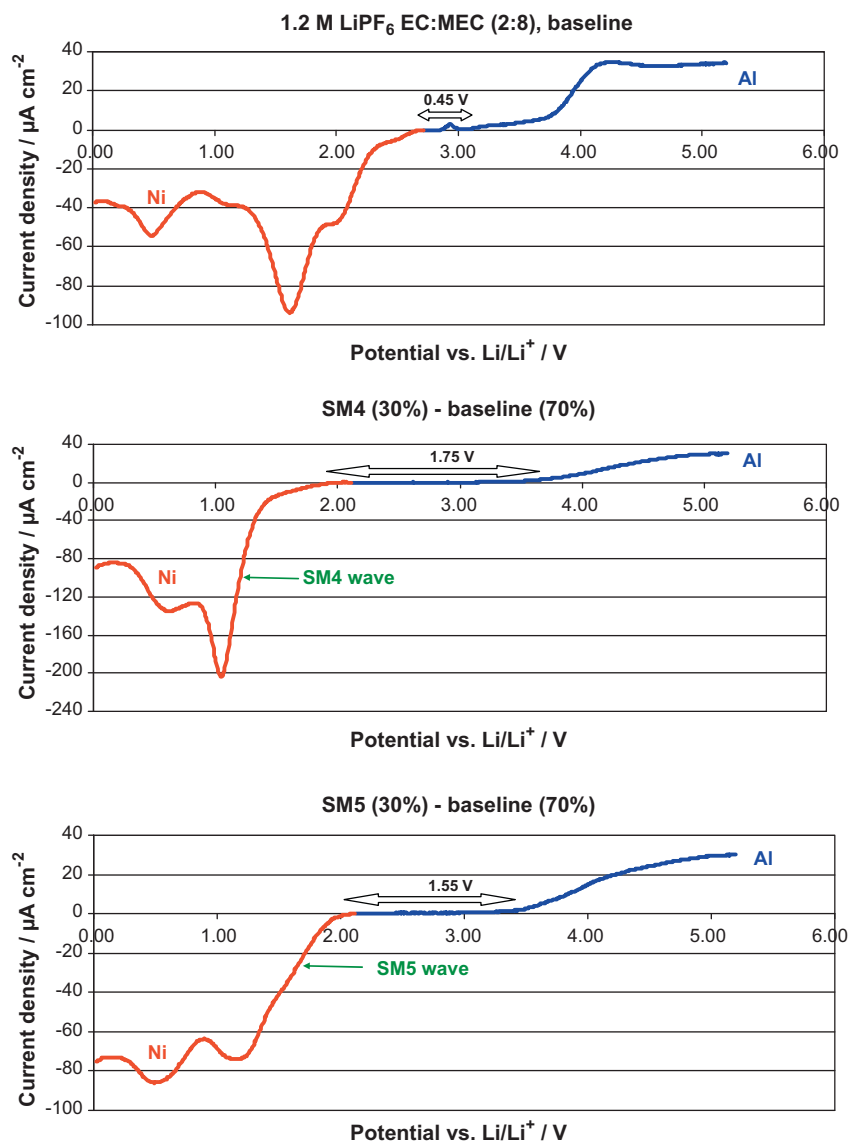


Fig. 3. Potentiodynamic curves in three electrolytes: 1.2 M LiPF₆ EC:MEC (2:8), baseline; SM4 (30%)–baseline (70%); and SM5 (30%)–baseline (70%).

deposition. This procedure mimics formation process of negative electrode in Li-ion battery.

In the case of Al substrates, PD polarization also started from OCV except this time it was pointed in the positive direction. At 5.2 V vs. Li/Li⁺ PD polarization was switched to PS polarization until the anodic current dropped below 5 µA cm⁻². The 5.2 V vs. Li/Li⁺ is a high potential. It is higher than the expected potential under charge conditions for conventional Li-ion batteries. However, we chose this high potential intentionally for two reasons. First, we wanted to clearly see all of the participant oxidation reactions. Second, high voltage electrolytes and high voltage cathodes are recent targets under development for high-energy batteries. Any other sufficiently positive potential can be chosen for similar studies. The described procedure on Al substrate mimics formation process for positive electrode in Li-ion battery.

Capacity from both PD and PS steps on the first run was measured. We named this capacity as the SEI formation capacity. With regard to Li-ion battery performance, it contributes to an irreversible capacity loss at cell formation. Fig. 4 is graphical representation of the method. On this graph, the first point at zero time (intercept) is SEI formation capacity.

In order to get more information on SEI properties, we used following procedure.

After the first run, which is for the determination of SEI formation capacity, we let the system come to rest. After the rest, we ran the PD and PS sequences again with a follow up rest. We did that several times as shown in Table 1.

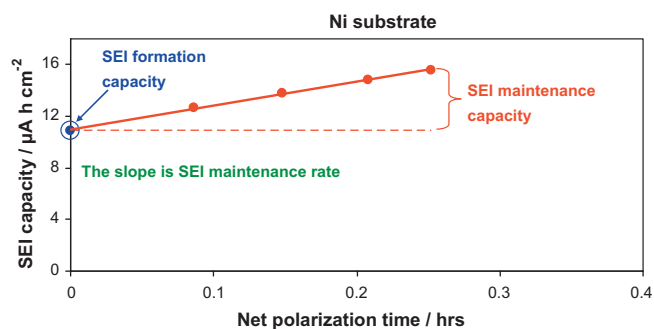


Fig. 4. Graphical representation of a new method and new parameters of electrochemical characterization of electrolyte and SEI.

Table 1
Test protocol.

Step	Procedure	Extracted data
0	Initial rest, 2.5 h	
1	1st PD + PS run	Time, SEI formation capacity
2	1-h rest	
3	2nd PD + PS run	Time, SEI maintenance capacity
4	1-h rest	
5	3rd PD + PS run	Time, SEI maintenance capacity
6	1-h rest	
7	4th PD + PS run	Time, SEI maintenance capacity
8	1-h rest	
9	5th PD + PS run	Time, SEI maintenance capacity
10	6-h rest	
11	6th PD + PS run	Time, SEI maintenance capacity

It is well known that the SEI in any Li-ion cell is not perfect. It has pores and defects, and may even be partially soluble. All of these artifacts can cause irreversible self-discharge. During the rest step, the SEI might partially dissolve and restructure, revealing some defects. The extent to which this process differs between ideal metal substrates and actual heterogeneous porous Li-ion electrodes is a question for our future research.

It is difficult to find a way how to precisely measure such degradation phenomena because rates of all constituents of the degradation process change over the time. We found a way to address this part of SEI performance. Instead of measuring the rate of degradation, we measure the rate of maintenance of the degraded structure. In order to accomplish this, the protocol in Table 1 was designed. Each subsequent polarization step after each rest step maintains the SEI, fixing the defects. Some additional capacity and time is required for this maintenance process. This additional each time capacity has been termed the SEI maintenance capacity. In Fig. 4, these additional capacities, added to the initial SEI formation capacity, form a linear response when the X-axis is net polarization time which is a sum of the PD and PS times. The rest time is not included in net polarization time. The slope of this line is the SEI maintenance rate, Fig. 4. The rate of SEI maintenance depends on the SEI protective properties, and for full Li-ion cells relates to irreversible self-discharge and subsequent fade in power. Thus, this quantity will be a key metric in future studies as we progress from ideal metal substrates to actual active electrode materials.

It is interesting that even after a 6-h rest time, the last point on the graph fits in line every time. It is understandable, because we are considering a constant maintenance rate, and not a degradation rate that is changeable over time. It emphasizes the robustness and simplicity of the method.

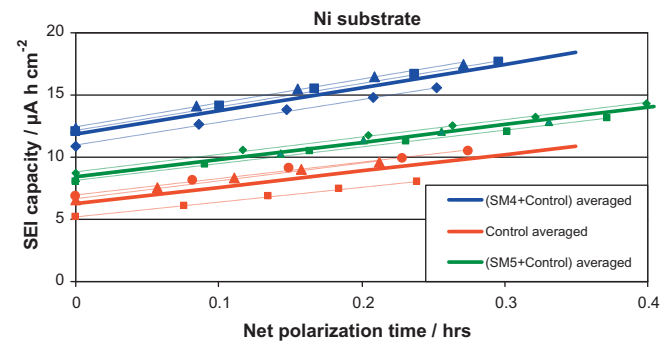
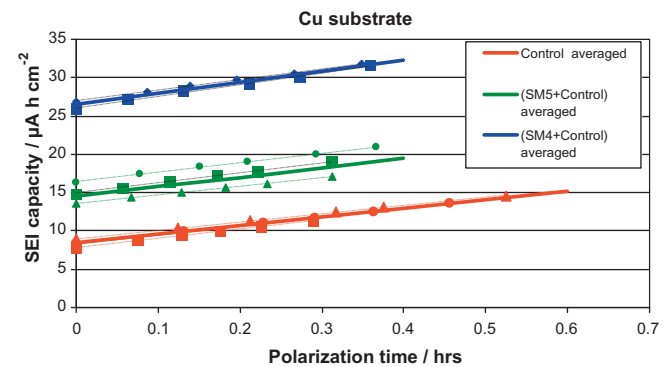
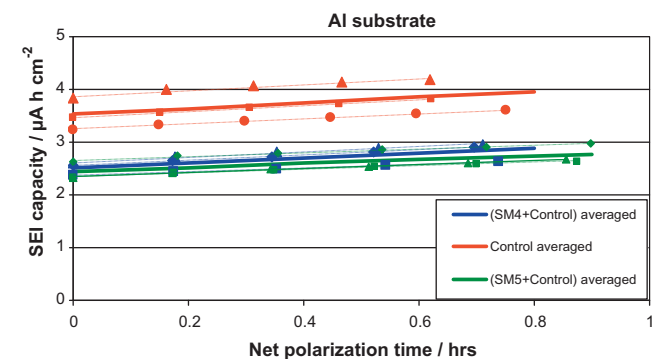
3.3.2. Validation of the method and discussion

Validation of the method was done on ten combinations of substrate plus electrolyte, Figs. 5–8. In all cases, clear linear dependences were received. Tables 2 and 3 contain values of SEI formation capacity and SEI maintenance rate, respectively, which were calculated from averaged linear dependences. Averaging was done for three closest measurements for each variation.

Ideal SEI morphology and the absence of solubility should result in zero slopes. Also, lesser quantities of these SEI parameters indi-

Table 2
SEI formation capacity ($\mu\text{A h cm}^{-2}$).

Electrolyte	Substrate			
	Ni	Cu	Al	C-coated Al
Baseline	6.30 ± 0.97	8.40 ± 0.59	3.53 ± 0.31	12.77 ± 0.31
SM 5 (30%)–baseline (70%)	8.45 ± 0.37	14.51 ± 0.77	2.45 ± 0.17	Not tested
SM 4 (30%)–baseline (70%)	11.85 ± 0.75	26.53 ± 0.58	2.52 ± 0.13	Not tested

**Fig. 5.** Experimental data for Ni substrate polarization in three electrolytes: 1.2 M LiPF₆ EC:MEC (2:8), baseline; SM4 (30%)–baseline (70%); and SM5 (30%)–baseline (70%).**Fig. 6.** Experimental data for Cu substrate polarization in three electrolytes: 1.2 M LiPF₆ EC:MEC (2:8), baseline; SM4 (30%)–baseline (70%); and SM5 (30%)–baseline (70%).**Fig. 7.** Experimental data for Al substrate polarization in three electrolytes: 1.2 M LiPF₆ EC:MEC (2:8), baseline; SM4 (30%)–baseline (70%); and SM5 (30%)–baseline (70%).

cate better properties of the electrolyte and SEI with regard to electrochemical efficiency and stability. The ultimate goal in finding a preferred electrolyte/electrode combinations is to minimize both the formation and maintenance capacities.

Table 3
SEI maintenance rate ($\mu\text{A cm}^{-2}$).

Electrolyte	Substrate			
	Ni	Cu	Al	C-coated Al
Baseline	13.05 \pm 0.97	11.43 \pm 0.78	0.52 \pm 0.10	0.59 \pm 0.04
SM 5 (30%)–baseline (70%)	13.83 \pm 0.34	12.44 \pm 1.24	0.36 \pm 0.03	Not tested
SM 4 (30%)–baseline (70%)	18.81 \pm 0.43	14.42 \pm 0.81	0.45 \pm 0.09	Not tested

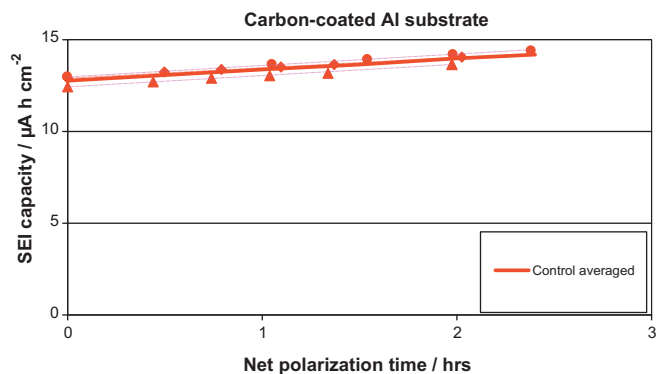


Fig. 8. Experimental data for carbon-coated Al substrate polarization in three electrolytes: 1.2 M LiPF₆ EC:MEC (2:8), baseline; SM4 (30%)–baseline (70%); and SM5 (30%)–baseline (70%).

Analysis of values in Tables 2 and 3 allows us to draw several conclusions. Formation capacity of SEI on Al is 1.8–4.7 times less than on Ni. SEI maintenance rate on Al is 25–42 times less than on Ni. This means that the SEI on Al is more stable and more uniform (has fewer defects). SEI formation capacity on Cu is approximately from 1.3 to 2.2 times higher than on Ni in all three electrolytes. This may be explained by the fact that copper has more oxides on the surface than Ni and this requires more capacity to reduce them to copper metal. On the other hand, rate of SEI maintenance on Cu is approximately from 10 to 30% less than on Ni which reveals a more defect free SEI. Defectiveness of SEI on carbon-coated Al is similar to bare Al which indicates a similarity of SEI structure and chemical formulation. SEI formation capacity on carbon-coated Al is 3.6 times higher than on bare Al which is in agreement with higher actual surface area of carbon-coated substrate. SM4 and SM5 co-solvents worsen SEI properties of baseline electrolyte on Ni and Cu because of increase in SEI capacity and SEI maintenance rate. In contrast, the phosphazenes slightly improve SEI properties on Al. This indicates better stability of phosphazene-based electrolytes at anodic polarization at least on an aluminum current collector. Thus, in terms of SEI issues we conclude SM5 is a better co-solvent than SM4. The SM5 compound only slightly degrades the properties of the electrolyte on Ni and Cu substrates.

4. Conclusions

Two phosphazene-based electrolytes have been characterized in terms of conductivity, viscosity, flash point, electrochemical

window, and properties of passivating layers at potentials above electrochemical window.

A new simple method and criteria to determine stability of new electrolytes beyond electrochemical window were proposed. These new criteria also are powerful for the characterization of passivating films (SEI). They are relevant to battery irreversible capacity, battery power, and shelf life. The method has been successfully validated on 10 combinations of substrate plus electrolyte. The method is flexible and can be used for any range of potentials, as well as a wide variety of types of organic electrolyte and substrates.

Based on summation of studied physical and electrochemical properties, the SM5 phosphazene co-solvent is better suited to current battery applications than SM4. The SM5 additive/co-solvent has little or no negative impact on SEI formation while increases flash point, an added safety benefit. This observation was taken into account in aligning the future direction of our synthetic work on new phosphazene structures.

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