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1 A new electrolyte formulation for securing high temperature cycling and storage  
2 performances of Na-ion batteries

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10 **Abstract**

11 The Na-ion battery is recognized as a possible alternative to Li-ion battery for applications where power  
12 and cost override energy density performances. However, the increasing instability of their electrolyte  
13 with temperature is still problematic. Thus, a central question remains how to design Na-based  
14 electrolytes. Here, we report discovery of a Na-based electrolyte formulation which enlists four additives  
15 (vinylene carbonate (VC), succinonitrile (SN), 1, 3-propane sultone (PS) and sodium  
16 difluoro(oxalate)borate (NaODFB) in proper quantities that synergistically combined their positive  
17 attributes to lead a stable solid electrolyte interphase (SEI) at both negative and positive electrodes  
18 surface at 55 °C. Moreover, we rationalized the role of each additive that consists in producing specific  
19 NaF coatings, thin elastomers, sulfate-based deposits and so on via combined impedance (EIS) and X-ray  
20 photoelectron spectroscopy (XPS). We demonstrated that empirical electrolyte design rules previously  
21 established for Li-ion technology together with theoretical guidance is a vital strategy in the quest for  
22 better Na-based electrolytes that can be extended to other chemistries. Overall, this finding, which we  
23 implement to practical 18650 cells, widens the route to the rapid development of the Na-ion technology  
24 based on the  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3/\text{C}$  chemistry.

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## 25 Introduction

26 Due to its success in the domain of power electronics, the lithium-ion battery is currently being  
27 considered as the most promising technology for electric vehicle propulsion and stands as a serious  
28 contender for grid applications.<sup>[1]</sup> However, the implementation of a lithium-based technology on a large  
29 scale faces an important challenge linked to the lithium availability and cost.<sup>[2]</sup> In anticipation of such a  
30 scenario, new sustainable chemistries have been studied, and the most appealing alternative is to use  
31 sodium instead of lithium. Sodium resources are in principle unlimited and sodium is very easy to  
32 recuperate. Mindful of these considerations, the sodium-ion battery has regained intensive interest over  
33 the last decade with the emergence of new materials for both positive and negative electrodes.<sup>[3]</sup>  
34 Practically speaking, efforts are presently parted between two technologies, both using carbon negative  
35 electrodes, but differing by the nature of positive electrode which can be either layered  
36  $(\text{Na}_{2/3}\text{Fe}_{1/2}\text{Mn}_{1/2}\text{O}_2)^{[4]}$  or polyanionic  $(\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3)^{[5]}$  compounds, denoted hereafter as NFM and NVPF,  
37 respectively. While the former shows inherently larger capacity in the half-cell configuration, it suffers  
38 from limited power rate and low energy density due to its low redox voltage as compared to the NVPF-  
39 based sodium-ion systems. That has sealed, our early decision to opt for the development of sodium-ion  
40 NVPF/C technology using 1 M  $\text{NaPF}_6$  in a 1: 1 (by volume) mixture of ethylene carbonate (EC) - dimethyl  
41 carbonate (DMC) as electrolyte. This approach has recently led to the assembly 18650 prototypes  
42 showing excellent long-term cycling performance (> 3000 cycles) and high-power rate capabilities at room  
43 temperature<sup>[6]</sup>.

44 Further probing this technology, we found that cycling together with self-discharge performances of  
45 the NVPF/C sodium-ion cells were rapidly degrading when increasing the temperature above 55 °C when  
46 linear carbonates (DMC, ethyl methyl carbonate (EMC), diethyl carbonate (DEC)) were part of the  
47 electrolyte composition. Such deterioration was shown through complementary *operando* ultraviolet (UV)  
48 spectroscopy and cyclic voltammetry (CV) analytical techniques to be nested in the existence of a shuttle  
49 mechanism. It enlists the formation of parasitic products at the negative electrode due to the reduction of  
50 linear carbonates that pass into solution and move to the positive electrode, hence accounting for the  
51 overall poor performance of the cell at high temperatures.<sup>[7]</sup> Such a finding came as a surprise, since

52 commercial lithium-ion cells are using linear carbonates based electrolytes without showing such  
53 limitations.

54 The problematic nature of electrolyte decomposition/instability is simply nested on the fact that  
55 Li(Na)-ion batteries operate beyond the thermodynamic stability voltage domain of the electrolytes,  
56 which is related to the positions of the highest occupied molecular orbitals (HOMO) and lowest  
57 unoccupied molecular orbitals (LUMO). In most cases, the redox potentials of the positive and negative  
58 electrodes fall outside this stability domain, hence triggering the formation of the solid electrolyte  
59 interphase (SEI) whose growth is kinetically governed. <sup>[8]</sup> Mastering/controlling parasitic reactions that  
60 lead to the formation of the SEI is then essential to enhance battery's cycle life, rate capability and  
61 durability. Ideally, the SEI should have a uniform morphology, a good adhesion to the electrode together  
62 with a high ionic conductivity for fast charge transfer while being mechanically strong, insoluble and  
63 stable upon cycling. Although the sodium-ion technology looks similar in its principle to lithium-ion  
64 batteries, the milder acidic character of Na<sup>+</sup> results in a different (comparatively higher) solubility of the  
65 formed SEI components (sodium-based organic/inorganic products) as compared to their lithium  
66 counterparts. <sup>[9]</sup> Both the parasitic reactions and solubility of SEI components are more pronounced at  
67 high temperatures (55 °C), hence necessitating the impetus to design a new electrolyte formulation for  
68 enhancing the performances of sodium-ion cells operating above 55 °C.

69 A common way to reach such an idealized situation is rooted in the use of film-forming electrolyte  
70 additives that are added in small amounts while not affecting the bulk electrolyte properties. Many years  
71 of experience have taught the need to have several additives that can operate in synergy to provide an  
72 optimal SEI, hence the countless amounts of papers and patents on film-forming additives. <sup>[10]</sup> This  
73 longstanding effort has yielded a colossal amount of data out of which one can extract several robust  
74 experimental trends/rules for selecting the proper additives that work in synergy. Among them is for  
75 instance the synergetic effect between triple-bonded and double-bonded moieties early demonstrated by  
76 Abe and recently used by J. Dahn to enable the proper functioning of Li-NMC/C lithium-ion cells up to 4.6  
77 V or the well-recognized beneficial effect of sulfur-containing electrolyte additives, which upon reduction  
78 to sulfites and sulfate species, lead to the robustness of the SEI film formed at the negative electrode. <sup>[11]</sup>

79 Utilizing such experiences and knowledge from Li-ion chemistry together with guidance from  
80 computational calculations, we report here a novel electrolyte formulation relying on the synergy  
81 between additives which enables high interfacial stability at 55 °C, hence setting a new milestone in the  
82 practical development of sodium-ion batteries based on the NVPF/C chemistry. Although well aware of  
83 the subtle differences between the lithium and sodium-ion chemistries in terms of electrolytes, we have  
84 used as starting point of inspiration the same trends pertaining to the lithium-ion technology for selecting  
85 additives to confection and optimize an electrolyte for sodium-ion batteries. This approach led us to the  
86 identification of an electrolyte formulation (1M NaPF<sub>6</sub> in EC-PC + a series of additives) that enables  
87 NVPF/C sodium-ion cells to operate at 55 °C with limited self-discharge and good cycling stability as none  
88 of the reported electrolytes could have done it. Such a finding was rationalized via complementary  
89 Electrochemical Impedance Spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS).

90 Finally, we have extended our studies with a combination of molecular dynamics (MD) and DFT  
91 calculations, to ascertain the validity of additive mixtures with the hope to demonstrate their synergy.<sup>[12]</sup>  
92 Such calculations can estimate the thermodynamic potential domain of electrolytes with and without  
93 additives, hence it is expected to provide guidance in identifying a proper electrolyte formulation. Our  
94 results show that these calculations are still limited to qualitative understanding only, and they cannot be  
95 used to probe a potential synergetic effect. Hence, despite the advances made, we still need to resort to  
96 trial and error approaches to identify the best electrolyte additives for new battery chemistries. For  
97 reasons of clarity we will first present the electrochemical performances of each additive prior to consider  
98 their synergetic effects.

## 99 **Results and discussion**

100 Mindful of our early results regarding the inadequacy of having linear carbonate such as DMC in the  
101 electrolyte,<sup>[7a]</sup> we opted for using a 1M NaPF<sub>6</sub> EC-PC (50:50 by volume) electrolyte solution as our  
102 "mother" electrolyte. Additives were selected based on both chemical considerations and DFT  
103 calculations aiming at determining their LUMO and HOMO. From the chemical survey, our choice boil-  
104 down to mainly four additives for reasons listed below. Lithium difluoro(oxalate)borate (LiODFB) was used  
105 in the lithium-ion technology because of its proven ability to enhance the SEI stability via the growth of an

106 SEI rich in LiF nanoparticles.<sup>[13]</sup> We thus decided to use the equivalent NaODFB salt hoping that it will  
107 behave alike in the Li-ion batteries. Getting further inspiration from the lithium-ion technology and the  
108 positive synergism between triple and double bonds we selected a combination of succinonitrile (SN) and  
109 vinylene carbonate (VC) additives with the former having the ( $-C\equiv N$ ) triple bond and the latter the ( $C=C$ )  
110 double bond. The choice for SN was additionally rooted in its strong nucleophilic character with the hope  
111 that it could, via surface interaction, stabilize the high oxidation state of  $V^{5+}$ , hence minimizing high  
112 voltage parasitic reactions associated to the electrolyte.<sup>[12a, 14]</sup> Lastly, bearing in mind the evidence of  
113 radical species formed during the formation of the SEI and its evolution upon cycling in NVPF/C Na-ion  
114 batteries as previously reported we decided to test the effect on the high-temperature performances of  
115 the 1,3-propane sultone (PS), since this molecule is known to trap radicals inside the electrolyte, thus  
116 forming reduced sulfite or sulfate inorganic compounds.<sup>[15]</sup>

117 To validate this choice, we determine the position of the LUMO-HOMO levels of each of these  
118 additives via DFT calculations bearing in mind that the best film-forming additives are the ones with  
119 HOMO- and LUMO falling within those of the electrolyte solvent molecules. As shown in supplementary  
120 figure 1, the most promising additives based on this criterion are the ODFB<sup>-</sup> anion and the VC. Albeit to a  
121 lesser extent, the two levels of the PS and the LUMO of the SN also stand between the ones of the EC and  
122 the PC, which suggests that these molecules may also react at the interfaces to form a SEI. Yet, while  
123 providing guidance regarding the selection of individual molecules, such calculations cannot be blindly  
124 used for reasons described elsewhere.<sup>[16]</sup> Moreover, such calculations fail to predict the synergism  
125 between additives, the reason why we have utilized systematic trial-and-error approach to identify the  
126 best electrolyte configuration.

127 All the aforementioned additives were obtained from Sigma-Aldrich and dried under molecular  
128 sieves prior to be used with the exception of NaODFB that is not commercialized. Thus NaODFB was  
129 homemade according to the following reaction via a process derived from the references<sup>[17]</sup>, which  
130 consists in  $BF_3$  reacting with  $Na_2C_2O_4$  in a 1,2-dimethoxyethane (DME) solution in 1:1 ratio, at 80°C under  
131 argon for 24 hours. NaODFB is then recovered by the removal of DME, dried under vacuum and stored in

132 an argon glove box prior to be identified as single phase by FTIR, XRD,  $^{19}\text{F}$  and  $^{23}\text{Na}$  NMR. (see  
133 supplementary figures 2-4)

134 For reasons of clarity, we will first present the effects of each additive (NaODFB, PS, VC and SN)  
135 separately (for amounts ranging from 1 to 5%) on the electrochemical performances of NVPF/C sodium-  
136 ion coin cells using 1M-NaPF<sub>6</sub> in EC-PC as mother electrolyte. Measurements were performed at 55°C, if  
137 not otherwise specified, according to an experimental protocol (Fig. 1b) that consists in cycling the cell 10  
138 times prior to performing a one week self-discharge at 100% state of charge (~4.3 V) and cycling again at  
139 C/10 rate (1C = 128 mA g<sup>-1</sup>). We solely report the data that has been duplicated twice. 55°C rather than  
140 room temperature testing was privileged to enhance the effect of additives onto the electrolyte stability  
141 since degradation is usually related to kinetically-driven parasitic reactions. We use four figures of merits  
142 to compare the electrolytes: i) the percentage of capacity retention before and after one week of self-  
143 discharge defined as  $Q_{11\text{th-dis}}/Q_{11\text{th-cha}}$  (discharge capacity divided by the charge capacity of the 11<sup>th</sup>  
144 cycle), ii) the percentage of recovered capacity determined as  $Q_{12\text{th-dis}}/Q_{11\text{th-cha}}$ , iii) the capacity  
145 retention and iv) the cell resistance evolution upon cycling.

146 Figure 1 compares the performances of each additive separately. From the first cycle voltage-  
147 capacity curves (Fig. 1a), it can be deduced that the irreversible capacity between the first charge and  
148 discharge is smaller for VC and NaODFB implying that such additives can partially mitigate the  
149 decomposition of the electrolyte at the carbon electrode by forming an effective SEI layer, as expected  
150 based on the DFT calculations. In contrast, the irreversibility is the largest for SN, suggesting its  
151 decomposition at the negative electrode consuming the sodium ions. Finally, PS has no effect on the  
152 irreversible capacity. The corresponding derivative curves, which we plotted from 2 to 2.8 V for better  
153 bring out anomalies (Fig. 1a, inset), reveal a sharp peak that is observed solely for electrolyte having  
154 NaODFB. This peak that appears at 2.1 V (in NVPF/ HC full cells) is due to the reduction of NaODFB at hard  
155 carbon electrode as confirmed by the cyclic voltammetry experiments (supplementary figures 5). In  
156 contrast, no distinct peaks are observed for VC, SN, or PS additives. The absence of a reduction peak for  
157 VC contrasts from its commonly observed behavior in lithium-based electrolytes,<sup>[18]</sup> suggesting a different  
158 reduction mechanism. Cycling-wise (Fig. 1c) NaODFB stands out among the other additives.

159 Fig. 1b shows the effect of various additives on the percentage of capacity retention in the self-  
160 discharge cycle ( $C_S$ ) and capacity recovered in the recovery cycle ( $C_R$ ) by holding the cells at 55°C for one  
161 week in self-discharge.  $C_S$  (inset left) and  $C_R$  (inset right) values range from 79 to 89.5 %, and 91.6 to 95.4  
162 % respectively. Such values bear interesting information if we keep in mind that the self-discharge is the  
163 result of cumulative side reactions taking place at the anode and cathode. The feasibility to recover a  
164 major fraction of the capacity implies that part of the parasitic reactions is reversible. Through our  
165 previous study we have demonstrated that the oxidation reaction taking place at the positive electrode  
166 and leading to the reduction of NVPF was nearly fully reversible, in contrast to the parasitic reaction  
167 taking place at the carbon electrode.<sup>[7b]</sup> Bearing this in mind, we can deduce that the best additives, self-  
168 discharge wise, are the ones showing both high  $C_S$  and  $C_R$  values, which is with minimum amounts of side  
169 reactions at the anode and cathode, respectively. On these metrics, both NaODFB and PS perform equally  
170 well while SN is the worst candidate, consistent with the fact that it leads to the highest initial irreversible  
171 capacity. Lastly, we compared the effect of these additives on the cell resistance and we observed a  
172 distinct increase in resistance with cycling for the NaODFB and VC (Fig. 1d), which does not come as a  
173 surprise since both of these additives are prone, as disclosed from the DFT calculation (see supplementary  
174 figure 1), to react at the interfaces to form a SEI.

175 Altogether, these results indicate that neither of the additives provides sufficient performances for  
176 practical applications, but NaODFB stands out as it displays the best figures of merit for three criteria,  
177 namely the initial reversible capacity, self-discharge performances and capacity retention. Besides  
178 identifying an additive it is also of paramount importance to determine its optimum concentration. From  
179 a survey of various electrolytes with increasing percentage content of NaODFB, we identified ~ 0.5 % as  
180 the optimum content. Greater contents were experimented to lead to unpractical oxidation of the ODFB  
181 anion at the NVPF electrode (see supplementary figure 6). Hence, from now on NaODFB in a content of  
182 0.5 % by weight will be used as additive in all new explored electrolytes formulations.

183 Our second experimental iteration aims to lower the cell resistance increase by using NaODFB (Fig.  
184 1d). To approach this issue we first surveyed the effects of PS and VC additives on the performances of  
185 1M EC-PC electrolyte solutions containing 0.5% of NaODFB. We found the addition of 3% PS gives lower



186 cell resistance (Fig. 2c), a good capacity retention (Fig. 2b) but a large self-discharge (27.9%), while the  
187 addition of 5% VC leads to poor capacity retention (Fig. 2b) in agreement with the progressive increase in  
188 the cell resistance (Fig. 2c). This does not come as a surprise since an increase in cell resistance was also  
189 observed when VC is used as a single additive (Fig. 1).

190 At this stage we extended this work to the exploration of the double-triple bond synergy between  
191 additives. A third additive SN ( $-C\equiv N$ ) was then added to the VC ( $C=C$ )-based electrolyte but without  
192 noticeable improvements. In contrast, low self-discharge and limited resistance increase were observed  
193 with the addition of 1% SN to the mixture of 3% PS and 0.5 % NaODFB (Fig. 2a and Fig. 2c). The negative  
194 results observed with VC were somewhat surprising owing the well admitted success of VC with the Li-ion  
195 technology. Indeed, by its nature VC enhances the stability of the SEI forming at negative electrode via an  
196 electrochemically-driven polymerization, provided that it is not used in excess. Otherwise, it can be  
197 detrimental to the cell performance due to its copious oxidative decomposition at the positive electrode  
198 that generates a cell impedance increase.<sup>40</sup> Thus, our last iteration has consisted of adding various  
199 content of VC to our best three components mixture so far isolated and exploring its electrochemical  
200 performance by varying its content from 0, 1, 2, 3 and 5 %. The results summarized in Fig. 3 indicate that  
201 the electrolyte consisting of 1M NaPF<sub>6</sub> in EC-PC + 3% PS + 0.5% NaDOFB + 1 % SN + 3% VC, and denoted  
202 hereafter as magic A, displays outstanding performances in terms of C<sub>R</sub> (99%) and C<sub>S</sub> (89.5%) with  
203 additionally the highest capacity retention (99%) after 60 cycles while having the lowest cell resistance of  
204 all the sodium-based electrolytes tried so far. It is worth mentioning that for VC contents exceeding 3%,  
205 alike for the Li-ion technology, a detrimental effect on the cell impedance is observed.<sup>[19]</sup>

206 Although this new electrolyte cocktail finding has been achieved through a trial and error approach,  
207 we must understand and rationalize the underlying science. Specifically, it is important to characterize the  
208 mechanisms by which this electrolyte leads to highly performing SEI. To provide insights into this issue we  
209 decided to conduct complementary EIS and XPS experiments since these two techniques allow probing  
210 interfacial phenomena.

211 For the EIS experiments, another set of NVPF/C sodium-ion coin cells were assembled with either 1M  
212 NaPF<sub>6</sub> in EC-PC or magic A as the electrolyte. As before, the tests were performed at 55°C with the cells

213 having been activated by carrying out 10 cycles prior to allowing each cell to self-discharge for one week  
214 and ultimately cycling it back afterwards. EIS spectra were collected at the end of discharge after 1<sup>st</sup>, 10<sup>th</sup>,  
215 11<sup>th</sup> and 61<sup>st</sup> cycle for both electrolytes and the Nyquist spectra are reported in Fig. 4a for EC-PC and Fig.  
216 4b for magic A. The data is also reported for the 62<sup>nd</sup> cycle when the cell was cooled down to 25°C; they  
217 all show a similar shape with a depressed semi-circle covering high frequency (interphase contacts,  
218 surface film) and high-medium frequency (charge transfer) phenomena with a low frequency Warburg tail  
219 restricted to solid phase Na<sup>+</sup> diffusion. The trends for variations of R<sub>sf</sub> (surface film resistance) and R<sub>ct</sub>  
220 (charge transfer resistance) vs. state of cycling for both electrolytes are deduced by fitting with the  
221 equivalent circuit model shown in Fig. 4d and reported in Fig. 4c and e, respectively. Whatever the  
222 electrolyte, R<sub>sf</sub> continuously increases upon cycling, but at a lower rate for magic A, indicative of the  
223 formation of a thinner SEI forming layer. Note that after the 61<sup>st</sup> cycle, R<sub>sf</sub> for EC-PC electrolyte is nearly  
224 twice larger than that for magic A when cooling down the cell from 55°C to 25°C. Interestingly, no change  
225 in R<sub>sf</sub> is observed when the cell based on magic A is cycled back to 25°C as opposed to a noticeable  
226 increase for EC-PC suggesting the presence of soluble species (alkyl-carbonates, alkyl-oxides) that might  
227 precipitate upon returning to room temperature. For the sake of completeness, similar measurements  
228 were done for an EC-DMC electrolyte for which we had previously demonstrated the presence of such  
229 species in solution and found an increase of nearly 45 % in the cell impedance (see supplementary figure  
230 7).

231 Turning to the charge transfer resistance (Fig. 4e), the same trend is observed with an even more  
232 pronounced effect of magic A since R<sub>ct</sub> is three times smaller after the 61<sup>st</sup> cycle for magic A as compared  
233 to the mother electrolyte. Moreover, the similar trend followed by both R<sub>sf</sub> and R<sub>ct</sub> is linked to the fact  
234 that a growth of the SEI (increase in R<sub>sf</sub>) will lead to poor ion transport that is reflected by an increase of  
235 the charge transfer, hence R<sub>ct</sub>. As previously noted, returning to room temperature does not produce any  
236 changes in R<sub>ct</sub> for magic A as opposed to a 30% increase for the EC-PC electrolyte, which simply translates  
237 by a prominent increase in the cell polarization between 55°C and 25°C. Altogether, these results nicely  
238 support the positive attributes of magic A over the EC-PC electrolyte that is rooted in a lower growing rate

239 of the SEI forming film, but did not bring any clues about its composition, hence limiting chances to know  
240 how it forms.

241 To grasp more insights into the composition of the SEI films formed at both negative and positive  
242 electrodes through our 55 °C testing protocol, we embarked into the study of electrodes recovered after  
243 the 1<sup>st</sup>, 10<sup>th</sup>, 11<sup>th</sup> and 61<sup>st</sup> by means of XPS. Once the targeted cycling was over, the cells were opened in  
244 an argon glove box, washed with DMC to remove the residual electrolyte, and dried prior to being packed  
245 into a hermetically sealed aluminum plastic bag for transportation. To prevent any sample exposure to  
246 moisture/air on the analysis site, the NVPF or carbon electrode samples were removed from the plastic  
247 bag within a glove box directly connected to the XPS spectrometer. The C<sub>1s</sub>, O<sub>1s</sub>, F<sub>1s</sub>, P<sub>2p</sub> and S<sub>2p</sub> spectra  
248 were collected for each NVPF and C samples recovered from the aforementioned NVPF/C cells. For  
249 reasons of conciseness, we solely report the data for the C<sub>1s</sub> (NVPF), O<sub>1s</sub> (NVPF), F<sub>1s</sub> (HC), and P<sub>2p</sub> (HC) core  
250 spectra that show the most prominent changes in Fig. 5 (other results are shown in supplementary figures  
251 8-10).

252 We first report the C<sub>1s</sub> and O<sub>1s</sub> spectra for NVPF in Fig. 5a and Fig. 5b respectively, for both mother  
253 electrolyte (EC-PC) and magic A electrolyte (left and right in each panel) with underneath the quantitative  
254 variation of each identified components as deduced from analysis of the core spectra. The C<sub>1s</sub> spectrum  
255 for EC-PC shows signals pertaining to conductive carbon black and PVdF binders. By integration of these  
256 signals we could plot their variation as a function of the cycling number and observe noticeable decrease  
257 (Fig. 5a bottom left), which implies they are masked by the growth of a cathode electrolyte interface (CEI).  
258 Such an effect still persists with our magic A electrolyte but in a lesser extent as witnessed (Fig. 5a bottom  
259 left), implying indirectly the formation of a thinner SEI layer with magic A electrolyte, hence confirming  
260 our EIS results. Besides the peaks associated to C black and PVDF, the C<sub>1s</sub> core spectra reveals upon  
261 cycling the appearance of 3 new peaks located at 285.9eV, 287.4eV and 289.2eV, which can be assigned  
262 to C-CO(=O) or C-CO<sub>3</sub>, C=O or O-C-O, and OC=O or CO<sub>3</sub>, respectively. We estimated the variation in  
263 amplitude of these signals as a function of cycling and the results are shown in Fig. 5a bottom. Their  
264 evolution reveals a rapid increase for the EC-PC electrolyte as opposed to a minor increase for our magic  
265 A electrolyte, reminiscent of the formation of a stable CEI.

266 Next we explored the  $O_{1s}$  spectra (Fig. 5b), and observed the presence of three signals: two located  
267 at 532.2 eV (blue) and 533.6 eV (orange) associated to oxygenated carbon species previously spotted with  
268 the  $C_{1s}$  spectra, and another one at 531.4 eV (red) corresponding to the oxygen pertaining to the  
269 phosphate group in  $Na_3V_2(PO_4)_2F_3$ . Interestingly, the amplitude of this signal remains constant upon  
270 cycling for magic A electrolyte, while it decreases to the expense of the blue and orange ones for the EC-  
271 PC electrolyte, indicating its copious growth. We also collected the  $P_{2p}$  and  $V_{2p}$  core spectra for cycled  
272 NVPF electrodes and further confirm the same trend (see supplementary figure 8). Altogether, these  
273 results indicate a much greater stability of the CEI in magic A than in EC-PC electrolyte.

274 To grasp some light on the growth and nature of SEI forming at the negative electrode we next  
275 collected the  $F_{1s}$  and  $P_{2p}$  core spectra as shown in Fig. 5c and 5d respectively. From the  $F_{1s}$  spectra, we  
276 observe the presence of a peak at 684.6 eV after the 1<sup>st</sup> cycle that we can ascribed to NaF derived from  
277 the decomposition of  $NaPF_6$  with its amplitude in EC-PC being more than 10 times larger than the one  
278 observed for magic A. Moreover, the  $C_{1s}$  core spectra of the carbon electrode for magic A revealed signals  
279 located at 290.7, 284.1, 286.6, and 288.8 eV and corresponding to C-F, C-H, C-O and O=C-O functional  
280 groups, respectively, with nearly the same groups appearing for the EC-PC electrolyte at the exception of  
281 C-F (see supplementary figure 9 and table 1, respectively). Lastly, from the  $S_{2p}$  core spectra (see  
282 supplementary figure 10), we could nicely spot the emergence of a signal at 169.0 eV and corresponding  
283 to sodium sulfate ( $Na_2SO_4$ ) which originated from the decomposition of the PS. These differences clearly  
284 indicate the key role played by the additives in controlling the composition and growth of the SEI.

285 Altogether, these results indicate that the SEI forming at the negative electrode cycled in EC-PC  
286 electrolyte is composed of large amounts of NaF, alkyl carbonates and PO/POF<sub>y</sub>. The SEI formed in  
287 presence of magic A contains nearly the same amount of alkali carbonates or phosphate species, but  
288 drastically differs by the lower amount of NaF and the presence of sulfate and B-based species (see  
289 supplementary note 1), hence justifying the use of PS and NaODFB additives. We believe that the positive  
290 attribute of the NaODFB additives is similar to what had been previously observed, to form deposits of  
291 NaF nanocrystallites forming thin and dense SEI layer (See EDS mapping in supplementary Figure 11). In  
292 contrast, the composition of the CEI layer forming at the positive electrode upon cycling mainly consists of

293 organic compounds with its thickness being quite thinner (supplementary Figure 11) in presence of magic  
294 A as compared to EC-PC electrolyte.

295 Overall, complementary XPS and EIS measurements have shown that the gained electrochemical  
296 performances display by magic A with respect to EC-PC based electrolyte is mainly rooted in the  
297 composition of the formed CEI at the NVPF positive and SEI formed at the carbon negative electrodes. We  
298 could identify the role played by individual additives NaODFB or PS while having no clues regarding their  
299 synergy. Motivated by the added knowledge and efficiency that predicting additive synergies could  
300 provide in designing new electrolytes, we next conducted further DFT calculations to shed further light on  
301 the effect of the four additives. Indeed, although the results provided in supplementary figure 1 (Figure  
302 isolated molecules) are instructive, they were performed on single molecules in a polarizable continuum  
303 to represent the solvent and therefore do not account for eventual synergetic interactions between  
304 electrolyte and additive molecules. We therefore investigate the entire electrolyte system—with the  
305 presence of all additives and an explicit solvent— following the example of Ong *et al.*<sup>[20]</sup> In short, DFT-  
306 based molecular dynamics (DFT-MD) is used to simulate a NaPF<sub>6</sub> electrolyte in EC/PC solvent with the  
307 molecular additives at the same concentrations as in experiments in order to more closely examine the  
308 electronic structure of individual molecules and relate this to the average reactivity of each molecule. This  
309 is done by projecting the density of states (DOS) onto an atomic orbital basis set for ten different atomic  
310 configurations spaced 2 picoseconds apart throughout the molecular dynamics simulations. The  
311 electrochemical windows were determined by identifying the band edges (HOMO and LUMO) nearest to  
312 the computed Fermi energy, as shown on [Figure 6](#).

313 In agreement with the isolated molecules calculations, we notice that the ODFB anion and the VC are  
314 likely to be the more electrochemically active of the additive molecules and to participate in the SEI layer  
315 formation at the electrode interface. The condensed phase calculations also show that the PS and SN  
316 levels now are aligned with the ones of the solvent, which suggests that this molecules will not react  
317 directly but rather in a second step with the newly formed species at the SEI.

318 **Conclusions:**

319 We have reported the design of a new electrolyte formulation 1 mol L<sup>-1</sup> NaPF<sub>6</sub> in EC-PC + 0.5%  
320 NaODFB + 3% PS + 1 % SN + 3% VC, which we have implemented into the assembly of practical 18650 Na-  
321 ion batteries that displays attractive high temperature performances (55 °C) in terms of self-discharge and  
322 cycling (Supplementary Figure 12). The search for optimum electrolyte formulation still relies on trial and  
323 error approaches, as theory presents limitations that we could not presently account for the synergetic  
324 effect between the various additives. Over the years, with the knowledge gained so far, several robust  
325 empirical rules have emerged such as for instance the synergy between double and triple bond that we  
326 have used herein together with theoretical guidance to identify our best electrolyte formulation. In the  
327 near future, let's hope the development of artificial intelligence and robotics lines for rapidly conducting  
328 surveys, based on the rich existing data bank, will ingress the battery field and provide robust trends non-  
329 identified yet for selecting additives working in synergy.

330 Besides the right choice of additives, we have shown that their amounts can be critic. VC is for  
331 instance needed to create a stable SEI at the negative electrode but its role in large excess can be counter-  
332 productive because of its oxidative decomposition leading to copious deposits at the positive electrode.  
333 Equally, we found that amounts of NaODFB > 3% were leading, because of parasitic decomposition  
334 reactions were leading to the growth of thick deposits at the positive electrode and hence a drastic  
335 increase in the cell impedance. Through XPS measurement, the role of PS was identified as an enrichment  
336 of the SEI layer in sulfates, which is an ingredient known to be beneficial for SEI at least in Li-ion batteries.  
337 Lastly, SN in combination with VC appears to be beneficial for the CEI formed at the NVPF positive  
338 electrode although we could not explain by which mechanism it happens.

339 Application-wise, it is worth mentioning that a weakness of our magic A electrolyte is nested in its  
340 poor wettability which complicates its use with today's commercial celgard separators. Linear carbonates  
341 (DMC, DEC...) or fluorinated ethers (HFE) solvents having good wettability could alleviate this issue, but to  
342 the expense of poor high temperature performance as we demonstrated by adding DMC to magic A  
343 (Supplementary Figure 13). Obvious improvement of this work calls for the development of an electrolyte  
344 with greater wettability while preserving all other figures of merits and also for the use of a fewer number  
345 of additives. Although this seems like squaring a circle, this new type of electrolyte is being successfully

346 developed and will be the subject of an upcoming paper, which further widens the implications of our  
347 findings.

348

## 349 **Methods**

350 **Electrolyte preparation.** The electrolytes were prepared by dissolving one molar NaPF<sub>6</sub> (Stella, Japan) in a  
351 battery-grade solvent selected from DMC, PC (BASF, USA), and EC (Mitsubishi chemical, Japan) in the Ar-  
352 filled glovebox (MBraun MB200B), prior to adding the certain amount of additives that was purchased  
353 from Sigma-Aldrich except the home made NaODFB. All solvents and additives were dried by adding  
354 molecular sieve (4 Å, Sigma) till their water contents become lower than 10 ppm as determined by Karl-  
355 Fisher titration (Metrohm 899 coulometer).

356 **Electrochemical measurements of NVPF/C cells.** Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3</sub> (NVPF, 12.0 mg/cm<sup>2</sup>) tapes were casted  
357 by spreading the slurries (NVPF materials, polyvinylidene difluoride and carbon black (the weight ratio is  
358 90:4:6) within N-methyl-2-pyrrolidone) onto Al foil. For the hard carbon (C, 6.0 mg/cm<sup>2</sup>) tapes, it were  
359 casted by spreading the slurries (hard carbon materials, carboxymethyl cellulose and carbon black (the  
360 weight ratio is 95:2:3) within deionized water) onto Al foil. All of the electrodes were dried in a Buchi oven  
361 under vacuum (lower than 100 mbar) at 80 degrees for 24 h prior to be transferred into glovebox. The  
362 electrochemical performance of NVPF/C full cells were evaluated in 2032-type coin cells separated by one  
363 layer of glass fiber containing 150 μL of desired electrolytes. All cells were galvanostatically cycled by  
364 using VMP3 or MPG2 potentiostat (Bio-Logic, France) at 55 °C or 25 °C, and the cycling rates were  
365 calculated on the basis of NVPF material (1 C =128 mA g<sup>-1</sup>). The impedance measurements of the NVPF/C  
366 cells after 1<sup>st</sup>, 10<sup>th</sup>, 11<sup>th</sup>, and 61<sup>st</sup> in discharged state were conducted by Bio-Logic MPG2 between 100 kHz  
367 and 10 mHz with an amplitude of 10 mV signal at 55 °C, and the following 62<sup>nd</sup> cycle at 25 °C.

368 **X-ray photoelectron spectroscopy measurements.** To carry out the XPS measurements, another series of  
369 NVPF/C cells were cycled, which were disassembled after the 1<sup>st</sup>, 10<sup>th</sup>, 11<sup>th</sup>, and 61<sup>st</sup> cycled in the glove  
370 box to recover the NVPF and C electrodes. The obtained electrodes were washed with DMC to remove the  
371 residual electrolyte, and dried prior to being packed into a hermetically sealed aluminum plastic bag for  
372 transportation. XPS measurements were carried out with a Kratos Axis Ultra spectrometer, using focused  
373 monochromatic Al K $\alpha$  radiation (h $\nu$  = 1486.6 eV). The XPS spectrometer was directly connected through a

374 transfer chamber to an argon dry box, in order to avoid moisture/air exposure of the samples. The  
375 analyzed area of the samples was  $300 \times 700 \mu\text{m}^2$ . Peaks were recorded with constant pass energy of 20 eV.  
376 For the Ag  $3d_{5/2}$  line the full width at half-maximum (FWHM) was 0.58 eV under the recording conditions.  
377 The pressure in the analysis chamber was around  $5 \times 10^{-9}$  mbar. Short acquisition time spectra were  
378 recorded before and after each normal experiment to check that the samples did not suffer from  
379 degradation during the measurements. The binding energy scale was calibrated using the C 1s peak at  
380 285.0 eV from the hydrocarbon contamination for the negative electrodes HC, and using the C 1s peak at  
381 290.9 eV from the PVdF  $\text{CF}_2$  functions, for the positive electrodes NVPF. Core peaks were analyzed using a  
382 nonlinear Shirley-type background<sup>[21]</sup>. The peak positions and areas were optimized by a weighted least-  
383 squares fitting method using 70 % Gaussian, 30 % Lorentzian line shapes. Quantification was performed  
384 on the basis of Scofield's relative sensitivity factors<sup>[22]</sup>. The curves fit for core peaks were obtained using a  
385 minimum number of components in order to fit the experimental curves.

386 **Single-Molecule Calculations.** To compute the HOMO and LUMO levels of EC, PC, VC, PS, SN and ODFB<sup>-</sup>,  
387 we perform density functional theory calculations using the CP2K code using the Quickstep algorithm.<sup>[23]</sup>  
388 The relaxed geometry of each molecule was computed using the self-consistent continuum solvation  
389 (SCCS) model.<sup>[24]</sup> The dielectric constant used in the SCCS model was set to 75, a value that falls roughly  
390 halfway between pure EC (90.5 at 40°C) and pure PC (65.5 at 25°C).<sup>[25]</sup> TZV2P-MOLOPT-GTH basis sets<sup>[26]</sup>  
391 were used to construct the Kohn-Sham wave functions, and an energy cutoff of 600 Rydberg was used. A  
392 GGA and a hybrid exchange-correlation functional (PBE<sup>[27]</sup> and B3LYP<sup>[28]</sup> respectively) were each tested to  
393 compare the computed HOMO and LUMO energies as well as their relative positions between solvent and  
394 additive molecules. Goedecker-Teter-Hutter pseudopotentials<sup>[29]</sup> were used to describe core electrons.

395 **Molecular Dynamics Calculations.** i) Classical Molecular Dynamics. Classical MD simulations were  
396 performed using LAMMPS code<sup>[30]</sup> to generate the initial atomic structure for two electrolyte systems.  
397 The first electrolyte system without additives contains 38 EC molecules, 30 PC molecules, 7  $\text{NaPF}_6$  pairs,  
398 while the system with additives consists of 38 EC molecules, 30 PC molecules, 3 VC molecules, 2 PS  
399 molecules, 1 SN molecule, 1 ODFB anion, 6  $\text{PF}_6$  anions, and 7 Na cations. The simulation cells were  
400 constructed to match the experimental density. An all-atoms model was used for each of the two



401 systems, in which the OPLS force field<sup>[31]</sup> was used for EC, PC and NaPF<sub>6</sub> molecules. The additive molecules  
402 were treated as rigid bodies without considering any intra-molecular interactions. Simulations were  
403 conducted in NVT ensemble with Nose- Hoover thermostat. All the systems were equilibrated at 353.15 K  
404 for 15ns with a timestep of 1fs. ii) Density Functional Theory. We performed first-principles simulations  
405 using density functional theory molecular dynamics. NVT simulations were performed using the Perdew-  
406 Burke-Ernzerhof (PBE) generalized gradient approximation (GGA).<sup>[27]</sup> The Quickstep algorithm as  
407 implemented in the CP2K code was employed with an energy cutoff of 280 Ryd. Van der Waals  
408 corrections were included at the level of DFT-D3.<sup>[32]</sup> The temperature of the simulation was regulated  
409 using canonical sampling through velocity rescaling (CSVR) at a temperature of 328 K. The timestep used  
410 was 0.5 fs. The simulation cells were identical in dimensions to those used in the classical simulations  
411 along with periodic boundary conditions, and the final state of the classical MD was used as a starting  
412 configuration. The large size of the simulation cells allows us to perform calculations using only a single  $\Gamma$   
413 k-point. Simulations for both systems were run for a total of 20 ps.

414 To perform the analysis of the projected density of states (DOS) calculations, we identify ten  
415 different atomic configurations spaced 2ps apart throughout the molecular dynamics simulations. For  
416 each set of configurations, we used Quantum Espresso code<sup>[33]</sup> to compute the ground state electron  
417 density in order to be projected onto an atomic orbital basis set. We verify the completeness of the  
418 atomic orbital basis using the computed spilling parameter. The projection onto the atomic orbital  
419 basis<sup>[34]</sup> has a corresponding spilling parameter between 0.0126 and 0.0127 for the electrolyte system  
420 with additives and between 0.0123 and 0.0124 for the electrolyte system, and thus we concluded that  
421 this projection can be used to sufficiently construct the density of states. This projection scheme allows us  
422 to parse contributions of individual molecules. Therefore, we can approximate the contribution of an  
423 individual molecule to the total density of states or alternatively determine the average contribution of a  
424 single type of molecule. The electrochemical windows were determined by identifying the band edges  
425 (HOMO and LUMO) nearest to the computed Fermi energy. These values for the ten configurations were  
426 used to determine the average and standard deviations for  $\epsilon_{HOMO}$  and  $\epsilon_{LUMO}$ . Mean values and their  
427 standard deviations are reported for HOMO and LUMO levels for each molecule.

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433

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511 **Figure captions**

512 **Figure 1** The electrochemical performance of NVPF/C cells using electrolytes with single additives cycled  
513 at 55 °C: **a.** the voltage-capacity curve with the corresponding dQ/dV plot as inset. The positive current  
514 shown in the dQ/dV plot of the full cells correspond to the reduction process in the hard carbon electrode;  
515 **b.** the voltage-time curves of NVPF/C cell at 11<sup>th</sup> cycle (self-discharge cycle) and 12<sup>th</sup> (recovery cycle), and  
516 the corresponding  $C_S$  ( $Q_{11th-dis}/Q_{11th-cha}$ ), and  $C_R$  ( $Q_{12th-dis}/Q_{11th-cha}$ ) value; **c-d.** the capacity-retention  
517 and direct current resistance evolution during the cycling at C/10 respectively.

518 **Figure 2** The electrochemical performance of NVPF/C cells cycled in the two or three additives added  
519 electrolyte at 55 °C. **a.** the  $C_S$  and  $C_R$  values at 11<sup>th</sup> cycle (self-discharge cycle) and 12<sup>th</sup> (recovery cycle); **b-c.**  
520 the capacity-retention and direct current resistance evolution during the cycling at C/10.

521 **Figure 3** The electrochemical performance of NVPF/C cells having electrolytes with four additives with  
522 varying amount of VC cycled at 55 °C. **a.** the  $C_S$  and  $C_R$  values at 11<sup>th</sup> cycle (self-discharge cycle) and 12<sup>th</sup>  
523 (recovery cycle); **b.** the representative voltage-capacity curve at 10<sup>th</sup>, 20<sup>th</sup>, and 30<sup>th</sup> cycle; **c-d.** the  
524 capacity-retention and direct current resistance evolution during the cycling at C/10. Notes: to avoid  
525 overwhelm describe the detailed compositions of electrolyte samples, we formatted that one color  
526 represents one sample in Fig. 3 a, b, and d.

527 **Figure 4** The change in impedance of NVPF/C cells with cycling. The cells were cycled at 55 °C for 61 cycles  
528 and cooled to 25 °C. The EIS data were recorded in discharged state for 1<sup>st</sup>, 10<sup>th</sup>, 11<sup>th</sup>, and 61<sup>st</sup> cycle at 55  
529 °C and at the following 62<sup>nd</sup> cycle at 25 °C. The Nyquist plots of NVPF/C cells using **a.** EC-PC electrolyte, **b.**  
530 magic electrolyte. The empty circles show the experimental data and the solid line represents the fitting  
531 results using the equivalent circuit model in (d). The red and blue semi-circles in (a) and (b) gives the  
532 deconvoluted surface film ( $R_{sf}$ ) and charge transfer ( $R_{ct}$ ) resistance values and their evolution on cycling  
533 with different electrolyte formulation are shown in c and e respectively.

534 **Figure 5** The XPS spectra of pristine NVPF and C electrodes, and those cycled electrodes at 1<sup>st</sup>, 10<sup>th</sup>, 11<sup>th</sup>,  
535 and 61<sup>st</sup> under 55 °C by using EC-PC or magic A electrolyte. **a.** the  $C_{1s}$  spectra of NVPF electrode with  
536 corresponding atomic ratio underneath; **b.** the  $O_{1s}$  spectra of NVPF electrode with corresponding atomic  
537 ratio underneath; **c.** the  $F_{1s}$  spectra of carbon electrode; **d.** the  $P_{2p}$  spectra of carbon electrode.

538 **Figure 6** The computed HOMO and LUMO energy levels of ten snapshots throughout a 10ps density  
539 functional theory based molecular dynamics simulation of the Magic A electrolyte. Energies are  
540 represented as box and whisker plots, and are aligned with respected to the Fermi energy of each  
541 snapshot. The filled box represents the HOMO energy levels, and the hollow box show the LUMO energy  
542 levels.













