

1 Article

2 Sodium Rechargeable Battery with Electrolyte Based 3 on Nafion Membrane

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14 **Abstract:** The possibilities of manufacturing batteries with Nafion 117 membranes in the Na⁺-form
15 intercalated by mixtures of non-aqueous organic solvents used both as electrolyte, separator and
16 binder were investigated. Electrochemical stability of various organic solvent mixtures based on
17 N,N-dimethylacetamide, ethylene carbonate, propylene carbonate, tetrahydrofuran was
18 characterized. It was shown that sodium battery based on Nafion-Na membrane intercalated by
19 mixture of ethylene carbonate - propylene carbonate with Na₃V_{1.9}Fe_{0.1}(PO₄)₃/C positive electrode is
20 characterized by a discharge capacity of *ca.* 110 mAh g⁻¹ (C/10) at room temperature and shows the
21 ability to cycle for a long time. Batteries with Nafion membrane electrolytes, containing N,N-
22 dimethylacetamide were characterized by capacity fading during cycling, which is due to the
23 interaction of N,N-dimethylacetamide and a negative sodium electrode.

24 **Keywords:** sodium rechargeable battery, polymer electrolyte, Nafion, cycle stability,
25 electrochemical stability
26

27 1. Introduction

28 Of late, sodium-ion batteries attract keen attention [1–3]. In such batteries, the positive and
29 negative electrodes are made of materials capable of reversibly inserting sodium without the release
30 of a free metallic phase. This is what ensures their safe functioning. Sodium rechargeable batteries
31 differ from sodium-ion counterparts in that sodium metal is used as a negative electrode in such
32 batteries. The theoretical specific capacity of metallic sodium during its anodic dissolution amounts
33 to 1165 mAh g⁻¹, which is much higher than that of intercalation compounds of the negative electrode
34 of the sodium-ion batteries. For example, sodium titanate (Na₄Ti₃O₇), sodiated hard carbon (Na₆C),
35 sodiated germanium (Na_{1.6}Ge), sodiated phosphorus (Na₃P), have a theoretical specific capacity for
36 sodium extraction of 154, 282, 390, and 804 mAh g⁻¹, respectively [4]. In addition, the potential of
37 sodium metal at its anodic dissolution is noticeably more negative than that of intercalation
38 electrodes during discharge, which contributes to an increase in the discharge voltage of the battery.
39 At the same time, it is known that metallic sodium (as well as metallic lithium) doesn't able prolonged
40 cycling in liquid electrolytes due to encapsulation and dendritic formation. The latter can lead to a
41 shorting and ignition of the battery with metallic sodium.

42 The use of a solid polymer electrolyte, in principle, can create a battery with a metallic sodium
43 negative electrode, the energy density of which will be higher than that of the sodium-ion battery.
44 Another advantage of solid polymer electrolyte consists in their flexibility, which makes it possible
45 to obtain a large area of electrolyte, and to design batteries of different geometries. In addition, the

46 use of polymer electrolytes reduces the known effect of the volume changes of electrode material
47 during sodium intercalation/deintercalation [5,6].

48 To date, quite a lot of work has been published on the creation and investigation of sodium-ion
49 solid polymer electrolytes [7-10]. The most widespread class of polymer electrolytes are true solid
50 polymer electrolytes [7]. They are based on polymer matrices with dissolved in them sodium salts
51 with a bulky anion. In most cases, the polymer basis of such electrolytes is polyethylene oxide [11].
52 Such electrolytes are characterized by low ionic conductivity at room temperature (*ca.* 10^{-5} S cm^{-1}) [12].
53 Replacement of salts with membrane ionogenic groups, such as $-\text{SO}_3^-$, $-\text{COO}^-$, etc., as well as the
54 addition of a low-molecular plasticizer, allows higher conductivity values [9, 13]. The most promising
55 polymer electrolytes at present are Nafion-type membranes. Due to the perfluorinated polymer
56 matrix, they have high thermal and electrochemical stability, as well as a high degree of dissociation
57 of functional groups, which ensures high ionic conductivity [14–16].

58 Initially electrolytes based on the Nafion membrane were proposed for lithium-ion batteries [17–
59 24], and later for their sodium-ionic analogs [8,25,26]. Such electrolytes are obtained by transferring
60 Nafion from hydrogen to sodium form (ion exchange in aqueous solutions of sodium salts), followed
61 by removal of water and impregnation with an aprotic solvent. Thus, in fact, they are gel-polymer
62 electrolytes. The principal possibility of creating a sodium battery is mentioned in [25] using the
63 example of the Nafion membrane in sodium form intercalated by a mixture of ethylene carbonate
64 (EC) and propylene carbonate (PC) and $\text{Na}_{0.44}\text{MnO}_2$ as the active material of the positive electrode.
65 The conductivity of the resulting electrolyte was 0.35 mS cm^{-1} at room temperature and 1.52 mS cm^{-1}
66 at 70°C . The laboratory cell was tested at a temperature of 45°C and demonstrated smaller values of
67 the discharge capacity, but better cycleability than that with liquid electrolyte (1 M NaClO_4 in an EC-
68 PC mixture).

69 Recently, the influence of the nature of organic solvents impregnating the membrane in the
70 sodium form, on the ionic conductivity, was investigated [26]. A certain correlation (but not
71 proportionality) was found between the solvent uptake and the ionic conductivity. Membranes,
72 containing N, N dimethylacetamide (DMA), namely EC–DMA, EC–diethyl carbonate (DEC)–DMA,
73 and PC–DMA–tetrahydrofuran (THF), are characterized by the highest ionic conductivity ($\sim 4 \text{ mS}$
74 cm^{-1} at 30°C).

75 The purpose of this work was to investigate the possibilities of manufacturing batteries with
76 similar polymer electrolytes based on Nafion membranes in the Na^+ -form. It was taken into account
77 that not only their ionic conductivity, but also their electrochemical stability and interaction with
78 electrode materials are important features of a polymer electrolytes.

79 2. Results

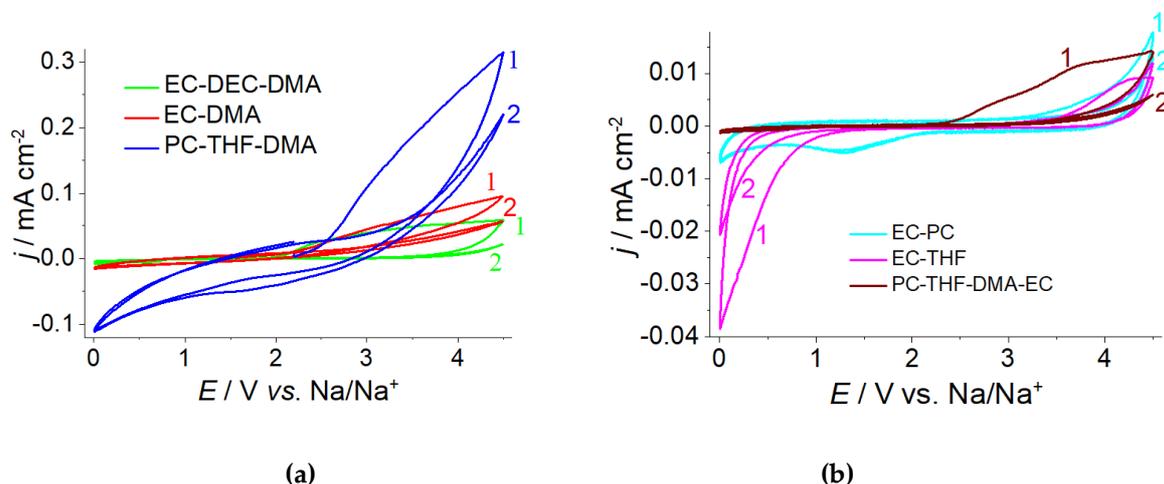
80 2.1. The composition of the materials obtained

81 The IR spectra of the obtained electrolytes are identical to the spectra presented in the
82 Supplementary of the paper [26]. The presence of organic solvents in membranes is revealed by a set
83 of vibrational frequencies inherent in these solvent molecules. In the frequency range $1600\text{--}1800 \text{ cm}^{-1}$,
84 the $\text{C}=\text{O}$ stretching vibrations characteristic of organic carbonates (EC, PC, DEC) are observed; at a
85 frequency of $\sim 1640 \text{ cm}^{-1}$, a band corresponding to the valence vibration of the $\text{C}=\text{O}$ bond in the DMA
86 molecule can be singled out; the presence of the THF molecule can be detected by the characteristic
87 antisymmetric valence vibration of the ring characteristic of cyclic ethers at $\sim 906 \text{ cm}^{-1}$. The absence of
88 vibrations of OH groups at $\sim 3490 \text{ cm}^{-1}$ in the IR spectra of the obtained samples indicates that the
89 membranes containing aprotic solvents and their mixtures contain no water or methanol. According
90 to the X-ray diffraction data, $\text{Na}_3\text{V}_{1.9}\text{Fe}_{0.1}(\text{PO}_4)_3/\text{C}$ is a rhombohedral modification of the NASICON
91 structure ($R\bar{3}c$ space group). The carbon of the composite is X-ray amorphous. According to
92 elemental analysis, the carbon content in $\text{Na}_3\text{V}_{1.9}\text{Fe}_{0.1}(\text{PO}_4)_3/\text{C}$ was 8.9% by weight. According to EDX
93 data this composite contains Na, V, P, O, C and Fe. The ratio of the elements Na:V:P:Fe corresponds
94 to the initial load.

95

96 2.2. The electrochemical stability of polymer electrolyte liquid phase

97 Figure 1 shows CVs for liquid electrolytes based on different solvent mixtures in the potential
 98 range from 0.001 to 4.5 V vs. Na⁺/Na at a potential scan rate of 10 mV s⁻¹. For all electrolytes, the first
 99 two cycles of CV are shown. Attention must be drawn to the difference in scale of the ordinates in
 100 Figures 1a,b.
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 103
 104 **Figure 1.** CVs in 1 M NaClO₄ in different solvents at scan rate 10 mV s⁻¹. Solvents compositions and
 105 cycle numbers are shown at the figures.
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 107

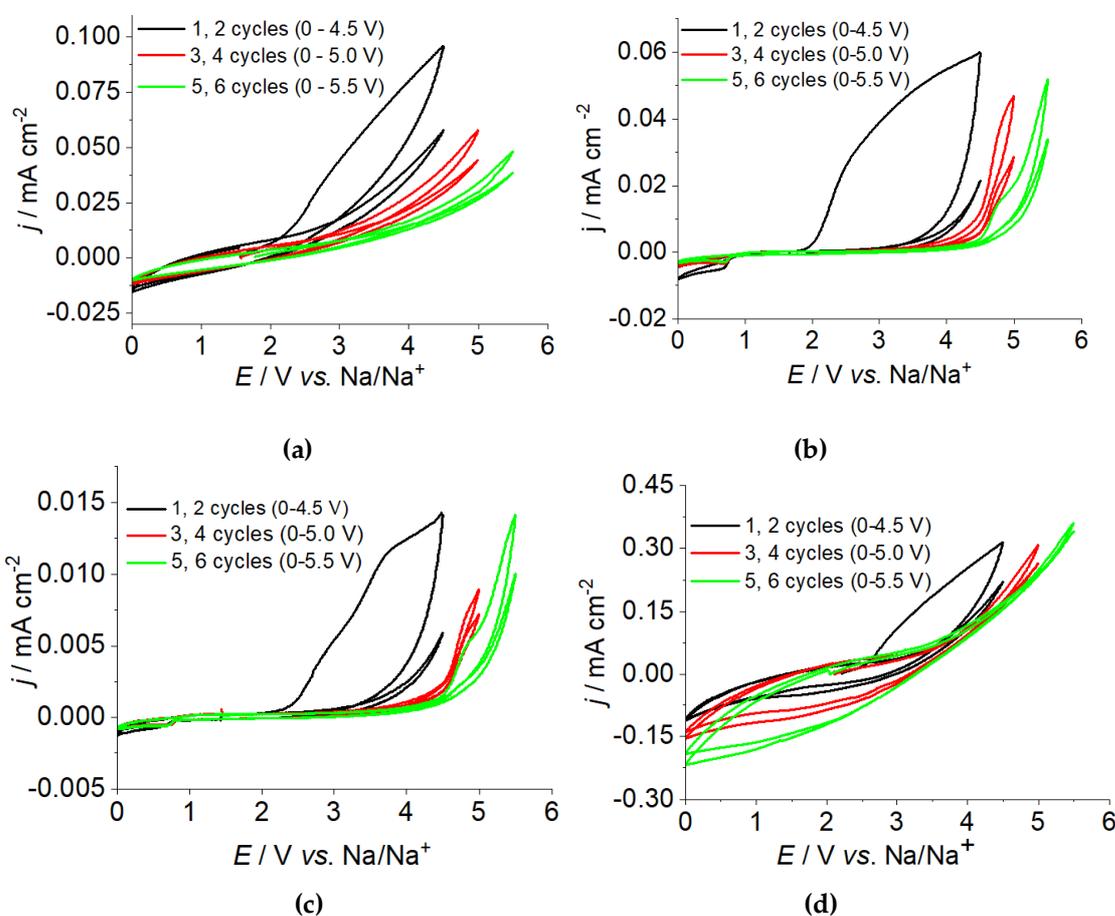
108 The lowest electrochemical stability was noted for 1 M NaClO₄ in a three-component mixture of
 109 PC–DMA–THF (Figure 1a). In this case, the anode process proceeds at potentials somewhat more
 110 positive than 2 V. The nature of the anode process remains uncertain. Undoubtedly, a certain part of
 111 the current is spent for anodic dissolution of aluminum with the possible formation of any complex
 112 compounds, since after the registration of the CVs on the aluminum electrode, certain signs of local
 113 corrosion that were distributed unevenly over the electrode surface were noticeable. At the same
 114 time, an appreciable part of the anode charge is spent on oxidizing the components of the electrolyte,
 115 most likely DMA. Similar, but less intense, anode processes at potentials more positive than 2 V are
 116 observed for all DMA-containing solvents (Figures 1a,b). The cathode process, which takes place in
 117 a 1 M solution of NaClO₄ in a three-component mixture of PC–DMA–THF at potentials more negative
 118 than 3 V, refers to the reduction of oxidation products of DMA in the previous anode semi-cycle,
 119 since at the CVs taken in such a solution in the potential range from 0 to 2 V, cathode currents of less
 120 than 0.002 mA cm⁻² are recorded, i.e. is almost three orders of magnitude smaller than that shown in
 121 Figure 1a.

122 The highest electrochemical stability from all the electrolytes studied refers to 1 M NaClO₄ in a
 123 four-component EC–PC–THF–DMA solvent, as well as to solutions in a binary EC–PC and EC–THF
 124 mixtures (Figure 1 b).

125 The anode processes described above (Figure 1a) are conjugated to a certain passivation of the
 126 aluminum electrode. It is possible to trace the passivation of the aluminum electrode in various
 127 electrolytes by analyzing Figure 2, which shows CVs for the first six cycles with an increasing range
 128 of cycling potentials. As can be seen from the Figure 2a, a 1 M NaClO₄ in the EC–DMA mixture is
 129 susceptible to oxidation at potentials more positive than 2 V and causes passivation of the aluminum
 130 electrode during cycling. A noticeable electrolyte oxidation at potentials more positive than 2 V is
 131 also noted for 1 M NaClO₄ in mixtures of EC–DEC–DMA (Figure 2b). In the solution of NaClO₄ in
 132 the four-component EC–PC–DMA–THF mixture, the rate of anodic oxidation is much lower than in
 133 previous electrolytes (Figure 2c), and a gradual passivation of the electrode is also observed here. The
 134 smallest passivation of the aluminum electrode was noted for a 1 M NaClO₄ in a mixture of PC–
 135 DMA–THF (Figure 2d). When the aluminum electrode is cycled in NaClO₄ solutions in mixtures of
 136 EC–DMA, EC–DEC–DMA and EC–PC–DMA–THF (i.e., in all solutions containing EC), passivation

137 leads to gradual inhibition of the anodic process. This does not occur in a solution of NaClO₄ in the
 138 PC-DMA-THF mixture (Figure 2d), therefore, when using such a solution, a permanent irreversible
 139 capacity loss will appear in the battery, which excludes the use of such a solvent in practical devices.
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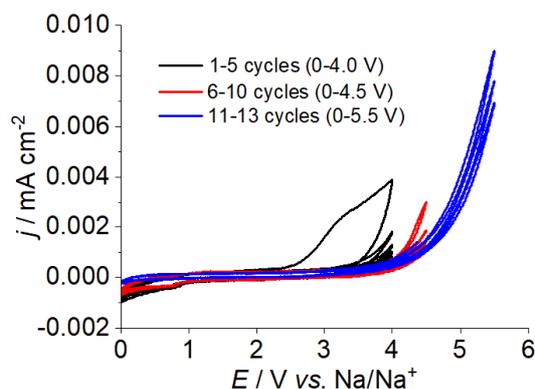
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146 **Figure 2.** Aluminum electrode passivation at cyclic polarization in different electrolytes: (a) 1 M
 147 NaClO₄ in EC-DMA, (b) 1 M NaClO₄ in EC-DEC-DMA, (c) 1 M NaClO₄ in EC-PC-DMA-THF, and
 148 (d) 1 M NaClO₄ in PC-DMA-THF

149 The oxidation rate of DMA depends significantly on which mixture it is in (Figures 1,2). The
 150 oxidation rate (currents at potentials more positive than 2 V) decreases in the series PC-DMA-THF
 151 > EC-DMA > EC-DEC-DMA > EC-PC-THF-DMA. This thesis is also confirmed by the results of a
 152 cyclic voltammetric study of a 1 M solution of NaClO₄ in plain DMA. The corresponding CVs are
 153 shown in Figure 3.



154

155 **Figure 3.** CVs in 1 M NaClO₄ in DMA at enlarging potential range. Cycle numbers are shown

156 The rate of the anodic process in a solution of NaClO₄ in plain DMA is seen to be noticeably
 157 lower than in a 1 M NaClO₄ in a three-component mixture PC–DMA–THF. It can be assumed that in
 158 this case it is precisely THF that has a de-passivating effect on the aluminum surface.

159 When cyclic voltammetric measurements were carried out, one feature of a 1 M solution of
 160 sodium perchlorate in a mixture of PC–DMA–THF solvents was disclosed. When this solution was
 161 brought into a contact with the sodium electrode, the solution became red-brown, and the staining
 162 intensity increased with time. With enough contact time the polymerization of the solution up to
 163 solidification took place. It was found by separate experiments that the active component of the
 164 solvent in this case was DMA. Interestingly, when other solutions containing DMA (solutions of
 165 NaClO₄ in mixtures EC–DMA, EC–DEC–DMA and EC–PC–DMA–THF) come into contact with
 166 sodium, the color change of the solution was much slower. This fact is most likely explained by the
 167 fact that all these solutions contained EC, and when sodium was contacted with such solutions, a
 168 fairly strong passive film (solid electrolyte interphase - SEI) formed on its surface, which significantly
 169 inhibited the interaction of sodium with the solution. A separate publication will be devoted to the
 170 mechanism of chemical interaction of sodium with DMA with a detailed analysis of the products
 171 formed.

172 2.3. The rechargeable battery with polymer electrolyte

173 As already mentioned above, the ionic conductivity of the polymer electrolyte is an important
 174 but not the determining parameter in deciding the applicability of the electrolyte in sodium batteries.
 175 Also, it is essential to operate the positive electrode in contact with a certain polymer electrolyte.
 176 Finally, this issue can be solved only by testing the real batteries. In this work, coin cells with polymer
 177 membranes intercalated by solvents EC–PC and EC–PC–THF–DMA were tested. In the case of using
 178 a polymer membrane intercalated by an EC–PC mixture, it was of interest to compare our results
 179 with the results given in [25], where the electrolyte was also a Nafion membrane in sodium form
 180 intercalated by an EC–PC mixture, and Na_{0.44}MnO₂ was used in positive electrode. It was found by
 181 separate experiments that the membrane intercalated by the four-component mixture of EC–PC–
 182 THF–DMA has an almost an order of magnitude higher electrical conductivity (more than 4 mS cm⁻¹
 183 at 30 °C) compared to the membrane intercalated by EC–PC (ca. 0.7 mS cm⁻¹ at 30 °C) [26], with close
 184 electrochemical stability (Table 1).

185 **Table 1.** Physical properties of membrane electrolytes

Electrolyte	Thickness, <i>mm</i>	Solvent uptake (n(solvent)/n(SO ₃ ⁻))	Conductivity at 30°C, mS cm ⁻¹
Nafion 117-EC-PC	240	19,8	0.7
Nafion 117-EC-PC– THF–DMA	260	24,3	4.1

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187

188 Besides, the selected membranes are characterized by a minimum decrease in conductivity with
 189 decreasing temperature.

190 Figure 4 shows the charge-discharge curves for coin cells with polymer electrolytes based on a
 191 Nafion 117 membrane intercalated by EC–PC (Fig. 4a) and EC–PC–DMA–THF (Fig. 4b) mixtures.

192 The current density was 0.1 mA cm⁻², which corresponded to 10 mA g⁻¹ of active cathode material
 193 (Na₃V_{1.9}Fe_{0.1}(PO₄)₃/C). For comparison, the similar coin cell with a liquid electrolyte (1 M NaClO₄ in a
 194 mixture of EC–PC) was also tested. The positive electrode in such a cell was made of
 195 Na₃V_{1.9}Fe_{0.1}(PO₄)₃/C with a PVDF binder.

196 The charge-discharge curves of coin cells with polymer electrolyte are generally similar to the
 197 charge-discharge curves of a battery with a liquid electrolyte, namely, the charge proceeds at a
 198 voltage of about 3.5 V, discharge at a voltage of about 3.3 V.

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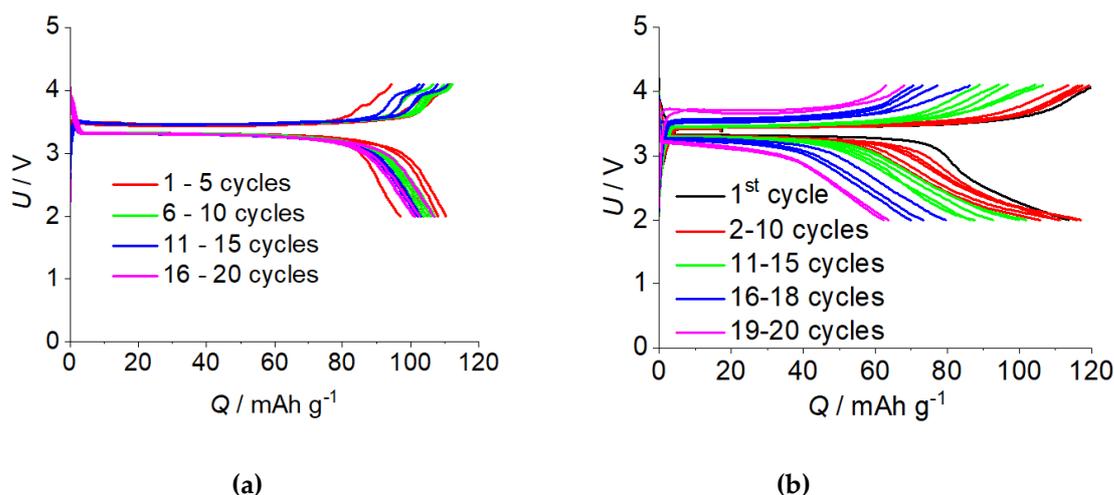


Figure 4. Charge-discharge curves of coin cells with polymer electrolytes based on Nafion 117, intercalated by EC-PC (a) and EC-PC-DMA-THF (b) mixtures. Current density of 0.1 mA cm^{-2} (10 mA g^{-1})

A slight difference consists in the shape of a charging curve on which for a cell with a polymer electrolyte intercalated by the EC-PC mixture, the second plateau is recorded at a voltage higher than 3.9 V. The nature of this plateau is not clear but is unlikely to be associated with the oxidation of solvents. Besides, for a cell with a polymer electrolyte based on a mixture of EC-PC-DMA-THF, the voltage drop at the end of the discharge does not occur so steeply.

Comparison of the charge-discharge curves of three cells (Figure 5) shows that when cycling in such a low rate (C/10), the difference in the voltage of the cells does not exceed the experimental discrepancy. This is not surprising. The ohmic voltage drop in the polymer electrolyte with thickness is 0.4 mm, at a current density of 0.1 mA cm^{-2} is estimated as 8 mV for a cell with polymer electrolyte based on an EC-PC mixture and about 1 mV for a cell with polymer electrolyte intercalated by a four-component solution.

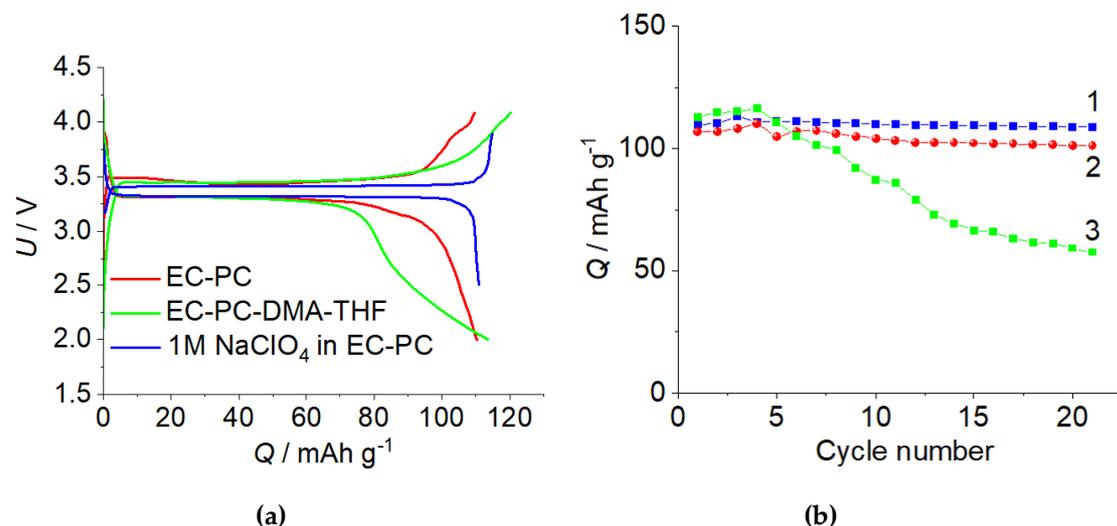


Figure 5. Charge-discharge curves (a) and cycling stability (b) for coin cells with liquid and polymer electrolytes. The capacity is normalized by weight of cathode active material, rate C/10. 1 – 1 M NaClO_4 in PC-EC, 2 – Nafion 117 membrane, intercalated by EC-PC mixture, 3 – Nafion 117 membrane, intercalated by EC-PC-DMA-THF mixture

3. Discussion

It is worth noting that a battery with a polymer electrolyte based on a Nafion 117 membrane intercalated by an EC-PC mixture is fully functional. From the battery described in [25], it is

227 advantageously distinguished by the practical constancy of the discharge voltage, which is explained
228 by the features of the positive electrode from sodium vanado-iron-phosphate. Besides, in the battery
229 in the present work, a polymer electrolyte is used as a binder of the positive electrode, which ensures
230 a more complete utilization of the entire volume of the active material. The initial capacity of a battery
231 with a polymer electrolyte based on a Nafion 117 membrane intercalated by an EC-PC mixture was
232 slightly lower than the corresponding value for a liquid electrolyte battery. However, with further
233 cycling, almost identical values of the discharge capacity were recorded. The specific capacity of the
234 electrode from the composite of sodium vanado-iron-phosphate with carbon, registered in this work
235 when cycling a battery with polymer electrolyte on the basis of a mixture of EC-PC at room
236 temperature in the C/10 mode was about 100 mAh g⁻¹. Taking into account the content of carbon (8.9
237 wt.%) in the Na₃V_{1.9}Fe_{0.1}(PO₄)₃/C composite, the discharge capacitance is close to the theoretical value.
238 Fig. 6 shows the data on coin cells with liquid and polymer electrolytes cycling.

239 The discharge capacity of a coin cell with a polymer electrolyte based on the Nafion117
240 membrane intercalated by the EC-PC-DMA-THF mixture at the initial cycles was slightly higher
241 than that of the cells with a liquid electrolyte and EC-PC-based polymer electrolyte. However, with
242 a further cycling for the coin cell with the Nafion 117 membrane intercalated by the EC-PC-DMA-
243 THF mixture, a noticeable capacity fading was recorded, which is due to the chemical interaction of
244 DMA and metallic sodium. The stable operation of a battery with polymer electrolyte based on the
245 Nafion 117 membrane intercalated by a EC-PC mixture for 20 cycles demonstrates the principal
246 possibility of manufacturing a sodium battery with such a polymer electrolyte and a positive
247 electrode based on Na₃V_{1.9}Fe_{0.1}(PO₄)₃/C, capable of long cycling without passivation and excessive
248 degradation. It is worth noting that one of the important challenges in the design of a solid electrolyte
249 battery is to ensure a good contact at the electrode/electrolyte interface. In the case of inorganic solid
250 electrolytes, this is achieved by making composite electrodes (active material/electrolyte/carbon)
251 followed by high-temperature sintering [30–32]. However, this does not completely solve the
252 problem in the case of a thick layer of electrode material and with multiple
253 intercalation/deintercalation, which is accompanied by a change in volume. The use of polymeric
254 binder and polymer electrolyte promotes good cycling by reducing the effect of changes in the
255 volume of electrode material during intercalation/deintercalation. However, in the case of a non-
256 conductive binder, the capacity of such cells is inferior to that of similar cells with liquid electrolyte.
257 Thus, the initial capacity of the electrode based on Na_{0.44}MnO₂ at 45 °C in the C/20 mode was inferior
258 to the values obtained with the use of a liquid electrolyte and did not exceed 60 mAh g⁻¹. In this work,
259 the perfluorinated membrane in the Na⁺ form was used both as an electrolyte and as a binder. As a
260 result, the capacity of the battery with polymer electrolyte based on the EC-PC mixture is comparable
261 with the corresponding value for a battery with liquid electrolyte. The obtained result indicates a
262 good contact of the polymer electrolyte and particles of the electrode material over the entire
263 thickness of the electrode.

264 The theoretical energy density (based on the weight of active materials only) of sodium battery
265 with a polymer electrolyte and a positive electrode based on the Na₃V_{1.9}Fe_{0.1}(PO₄)₃/C composite
266 amounts to 360 Wh kg⁻¹. With due account for the weight of structural materials and polymer
267 electrolyte of smaller thickness (less than 0.1 mm), one can expect to achieve a practical energy density
268 of 180-200 Wh kg⁻¹, which seems quite optimistic. The use of positive electrodes in a sodium battery
269 with an active material having a higher specific capacity than Na₃V_{1.9}Fe_{0.1}(PO₄)₃ will result in a
270 corresponding increase in the energy density.

271 4. Materials and Methods

272 4.1 Preparation of electrolytes based on Nafion membrane

273 The membranes were made by the same procedure as described in [26]. The commercial Nafion
274 117 membrane manufactured by DuPont was conditioned according to scheme [27], then it was kept
275 for two days in 2 M aqueous NaCl solution with constant stirring. The membrane was then washed
276 several times with deionized water until the chloride ions were completely removed and dried under

277 vacuum at a temperature of 70 °C for 12 hours. After that, the membrane was aged for 6 hours in
278 methanol at a temperature of 60 °C and again dried under vacuum. Such treatment with methanol
279 contributed to an appreciable expansion of the pores in the membrane. The final operation was the
280 soaking of membranes in mixed solvents. This operation was carried out in a glove box with an argon
281 atmosphere containing less than 1 ppm of oxygen and water vapor. In the present study, the
282 following mixtures of aprotic solvents containing equal volumes of components have been studied:
283 EC - DMA, EC - PC, EC - THF, EC - DEC - DMA, PC - DMA - THF, EC - PC - THF - DMA.

284 4.2 The binder preparation

285 A membrane-based binder was prepared by the following procedure: a membrane was casted
286 from a 5 wt% solution of a Nafion in a proton form in a mixture of lower aliphatic alcohols and water
287 (55:45). Then this membrane was transferred to the Na⁺ form by ion exchange in a manner like
288 described above. The resulting Nafion-Na membrane was dried in vacuum at 70 °C. The dry polymer
289 was placed in the calculated amount of dimethylformamide (DMFA) to prepare a 10 wt% solution.
290 Dissolution took place at room temperature for 1 day with constant stirring.

291 4.3 The cathode material synthesis

292 The Na₃V_{1.9}Fe_{0.1}(PO₄)₃/C nanocomposite was synthesized by the modified Pechini method
293 according to the procedure described in [28, 29] using V₂O₅, Fe(NO₃)₃·9H₂O, NaNO₃, NH₄H₂PO₄,
294 oxalic acid (a chelating agent and a reducer), ethylene glycol and citric acid. The polycondensation of
295 thylene glycol and citric acid leads to the formation of a polymer matrix that inhibits the growth of
296 the composite particles.

297 4.4 The materials characterization

298 The infrared (IR) spectra of the obtained electrolytes based on Nafion membranes were recorded
299 with a Nicolet iS5 IR spectrometer with a SpecacQuest attachment in the attenuated total reflection
300 mode with a diamond crystal in the frequency range 500-4000 cm⁻¹. The phase composition of the
301 synthesized cathode material was characterized using a Rigaku D/MAX 2200 diffractometer, CuK_α
302 radiation in the range of 10-60° 2θ. The carbon content of the composite was determined using a
303 CHNS analyzer EuroEA 3000. The chemical composition of the cathode material was determined
304 using a scanning electron microscope Carl Zeiss NVision 40 equipped with an energy dispersive X-
305 ray (EDX) analyzer Oxford X-Max. Ionic conductivity was measured by impedance spectroscopy
306 using an Elins Z-1500J AC bridge (1 kHz–2 MHz) on symmetric carbon/membrane/carbon cells.

307 4.5. The electrochemical studies

308 Cyclic voltammetric measurements in liquid electrolytes, i.e. in 1 M solutions of NaClO₄ in the
309 above-mentioned mixed solvents (paragraph 4.1) were made to assess the electrochemical stability
310 of the liquid phase of polymer electrolytes based on Nafion membranes. The measurements were
311 carried out in three-electrode cells with an aluminum working electrode (foil 50 μm thick, "Rusal"
312 Co., Russia). The auxiliary and the reference electrodes were made from sodium metal, rolled on a
313 stainless steel mesh. To register cyclic voltammograms (CVs), a potentiostat-galvanostat R-20X8 from
314 "Elins" (Russia) was used. The water content in solvents and electrolyte, determined by coulometric
315 titration by K. Fisher method using a coulometric titrator 917 Ti-Touch (Metrohm) did not exceed 20
316 ppm. The potential scan rate was 10 mV s⁻¹.

317 To evaluate the feasibility of using the polymer electrolytes under investigation in real sodium-
318 ion batteries, coin cells with a polymer electrolyte were tested. For the sake of comparison, similar
319 cells with liquid electrolyte (1 M solutions of NaClO₄ in the mixture of EC-PC) were tested as well.

320 For coin cells with polymer electrolyte, positive electrodes contained 80 wt.%
321 Na₃V_{1.9}Fe_{0.1}(PO₄)₃/C, 10% acetylene black as conducting additive and 10% of Nafion-Na dissolved in
322 DMFA as a binder. For coin cells with liquid electrolyte, the positive electrodes contained 80%
323 Na₃V_{1.9}Fe_{0.1}(PO₄)₃/C, 10% acetylene black and 10% PVDF dissolved in N-methylpyrrolidone. The

324 electrodes were dried, pressed with a pressure of 1 ton cm⁻² and further dried at a temperature of 120
325 °C for 8 hours. The amount of active material on the substrate was about 5 mg cm⁻². The coin cells
326 were of the 2016 type. Cyclic galvanostatic tests were carried out using a computerized charge-
327 discharge measuring and computing complex AZRVIK 50 mA-10 V (NTT Buster, Russia). Coin cells
328 were assembled in a glove box with a dry argon atmosphere (JSC Spectroscopic Systems, Russia).
329 The water and oxygen content in the box did not exceed 1 ppm.

330 5. Conclusions

331 In the present work, an estimation was made of the possibility of creating a sodium battery with
332 a polymer electrolyte based on a Nafion membrane intercalated by a mixture of aprotic organic
333 solvents and a positive electrode based on the Na₃V_{1.9}Fe_{0.1}(PO₄)₃/C composite. It has been established
334 that an important factor in the choice of the organic solvent, which impregnates the Nafion membrane
335 in the sodium form, is the electrochemical window. It is shown that sodium batteries with Nafion
336 membrane electrolyte containing dimethylacetamide were characterized by capacity fading during
337 cycling, which is due to the interaction of DMA and a negative sodium electrode. A suitable
338 electrolyte for a sodium battery, in terms of high conductivity and electrochemical stability, is a
339 Nafion membrane in sodium form intercalated by binary solvent ethylene carbonate – propylene
340 carbonate. A battery with this electrolyte showed a discharge capacity of ca. 110 mAh g⁻¹ (C/10) at
341 room temperature and the ability to cycle for a long time.

342 **Author Contributions:** material synthesis and preparation S.V., D.V.; investigation, D.V., T.K. A.C.; data
343 curation, A.C.; writing—original draft preparation, S.V., T.K.; writing—review and editing, A.S. and A.Y.

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345 **Conflicts of Interest:** The authors declare no conflict of interest.

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