

# Propylene carbonate based organic electrolytes for supercapacitors used in portable electronics power sources

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## Abstract

Results of a systematic study of propylene carbonate (PC) based organic electrolytes with alkylammonium tetrafluoroborates for use in supercapacitors (SC) for portable electronics and self-charging power sources have been presented. The importance of the study is dictated by the requirement to combine SC high power capacity, electrochemical stability over a wide temperature range, and operation safety, especially in independent miniaturized devices. Unlike acetonitrile (AN) conventionally used in SC electrolytes, PC is not noxious and non-flammable, but its high viscosity limits the electrical conductivity of electrolytes thus making the choice of optimum ionogenic salt a critical task. The properties of PC-based electrolytes with tetraethylammonium (TEA·TFB), methyltriethylammonium (TEMA·TFB), spiro-(1,1')-bipyrrolidinium (SBP·TFB), and 1,1-dimethylpyrrolidinium (DMP·TFB) tetrafluoroborates, differing in the size and structure of cations (acyclic and cyclic) have been studied. All the test salts deliver approximately similar capacities of SC cells, but TEA·TFB demonstrates somewhat lower capacity due to the large size of its cation. Ionogenic salts with cyclic cations (SBP·TFB and, especially, DMP·TFB) provide a far greater range of operation voltage at elevated temperatures to 85 °C, whereas TEA·TFB and TEMA·TFB electrolytes degrade at above 60 °C. Durability tests (up to 70,000 cycles at 50–95 °C) confirmed the electrochemical and thermal stability of DMP·TFB+PC: SC cells with the latter electrolyte retain 80 % of initial capacity after 50,000 cycles of galvanostatic charging/discharging (GCD) and provide for an operation voltage of 3.0 V. The recommended operation temperature range for SC with DMP·TFB+PC electrolyte is 0 to 85 °C, with the possibility of short-time temperature growth to 95 °C, whereas at below 0 °C the growing viscosity of the electrolyte causes a dramatic degradation of SC capacity. Thus, DMP·TFB+PC electrolyte is promising for SC used in portable electronics.

## Keywords

supercapacitor, energy storage systems, rechargeable power sources, portable electronics devices, spiro-(1,1')-bipyrrolidinium tetrafluoroborate, 1,1-dimethylpyrrolidinium tetrafluoroborate, propylenecarbonate

## 1. Introduction

Among advanced energy storage systems, electrochemical capacitors or supercapacitors (SC) find increasing application, their key advantages being high power density allowing rapid accumulation and energy release, long service life, and high performance over a wide temperature range, including extremely low temperatures [1, 2]. Due to their good performance, SC have found application in alternative power devices, including independent power sources for use in Arctic regions, as backup power sources for essential consumers, in electric vehicle braking energy recuperation systems, and in hybrid vehicles [3–6]. The use of SC is of special importance for peak load conditions, and therefore their operation in combination with batteries and fuel cells is a critical requirement, allowing one to increase the stability of energy systems, reduce network loads, and provide for the integration of renewable energy sources into power supply systems [7, 8].

## 2. Main development trends of energy accumulation systems

In recent years, the attention of researchers has been focused on the development of energy accumulation systems for portable electronics devices, i.e., portable, lightweight, and comfortable accessories which people wear and use for intellectual assistance, navigation, communication, health monitoring, and other purposes. Such devices can be worn outside such as rings, badges, watches, glasses, bijouterie, shoes, or clothes, or inside in implants, such as cardiac pacemakers or neuroprosthetics [4, 6, 9–11]. Special attention is paid to portable devices used for health monitoring, testing, and recording of metabolic changes in human body, i.e., blood sugar, temperature, arterial pressure, heart rate, health condition during sleep etc., which can be vitally important for a large number of people. Great possibilities are expected to emerge in the field of remote health monitoring due to the involvement of the so-called Internet of Things, i.e., systems of interconnected devices which can automatically collect and transfer data through wireless networks. It is believed that the Internet of Things will play a decisive role in supporting stable health parameters of patients in hospitals and in their everyday life. Due to the permanently increasing energy consumption by portable devices, there is the need for self-charging power sources which could use the energy of light, mechanical motion, human body heat etc. for recharging by converting them to electric power. A separate and quite actual trend of this research is the development of power sources for bionic robotic prosthetics and neuroprosthetics [4, 9, 12, 13]. Energy accumulation systems which are unalienable part of such power sources should meet a number of requirements: along with the main criteria related to energy and

power performance, there are additional requirements, including non-toxicity and fire safety, mechanical impact stability, high temperature tolerance, pulsed mode operation capability, charging mode variability, and flexibility. It was shown that SC meet the above requirements the most completely, and furthermore exhibit a lower tendency to the degradation of energy and power performance in miniaturized options, in comparison with lithium-ion batteries [3, 9, 10]. It should be stressed that for this application, of key importance is the capability to give back and receive current pulses, which is required for data collection and transfer and for the mechanical motion of robotic prosthetics, rather than the power capacity of the storage system.

The wide practical implementation of SC is still hindered by their relatively low specific power capacity as compared to batteries. Therefore it is an important task to develop SC and micro-SC having the highest specific power capacity for this range of devices (about 10–20 (W·h)/kg) and also meeting the above requirements. There are different approaches to increasing the power capacity of SC. In conventional symmetrical two-layered SC consisting of two porous conducting electrodes separated by an electrolyte-impregnated spacer, energy is accumulated in the form of double electric layer (DEL) charge at the electrode/electrolyte boundary. Since achieving the highest specific capacity requires the greatest possible contact area between the electrolyte and the electrode, the latter are typically made from nanoporous carbon materials with a specific surface area of above 1000 m<sup>2</sup>/g. The development of carbon materials with optimized porous structure hierarchy and the use of new carbon materials such as carbon nanotubes, including those doped with heteroatoms, graphene-based electrode materials, and activated carbon fiber and tissues allows one to achieve a specific capacity of up to 200 F/g for water-based electrolytes [14–17]. Another approach is to modify the electrolyte by adding so-called pseudo-capacity materials capable of rapid reversible oxidation-reduction processes during SC charging and discharging, transition metal oxides, electrically conducting polymers, and metal-organic skeleton structures with embedded chemically active and functional elements. To increase the electrical capacity, one can also use asymmetrical structures in which the positive and negative electrodes and made from different materials. This allows one not only to make the pseudo-capacity to contribute to the overall capacity of SC but also to increase its operation voltage, thus significantly increasing the charge density and power. Theoretically, pseudo-capacity electrode materials can allow one to increase the power capacity of SC by several times, but in practice one can rarely achieve a more than two-fold increase [18–22].

Taking into account that the specific energy of SC increases as the square of the difference of potentials between the electrodes, a promising strategy of increasing the power performance of SC is to increase the operation voltage of the cell, which is mainly

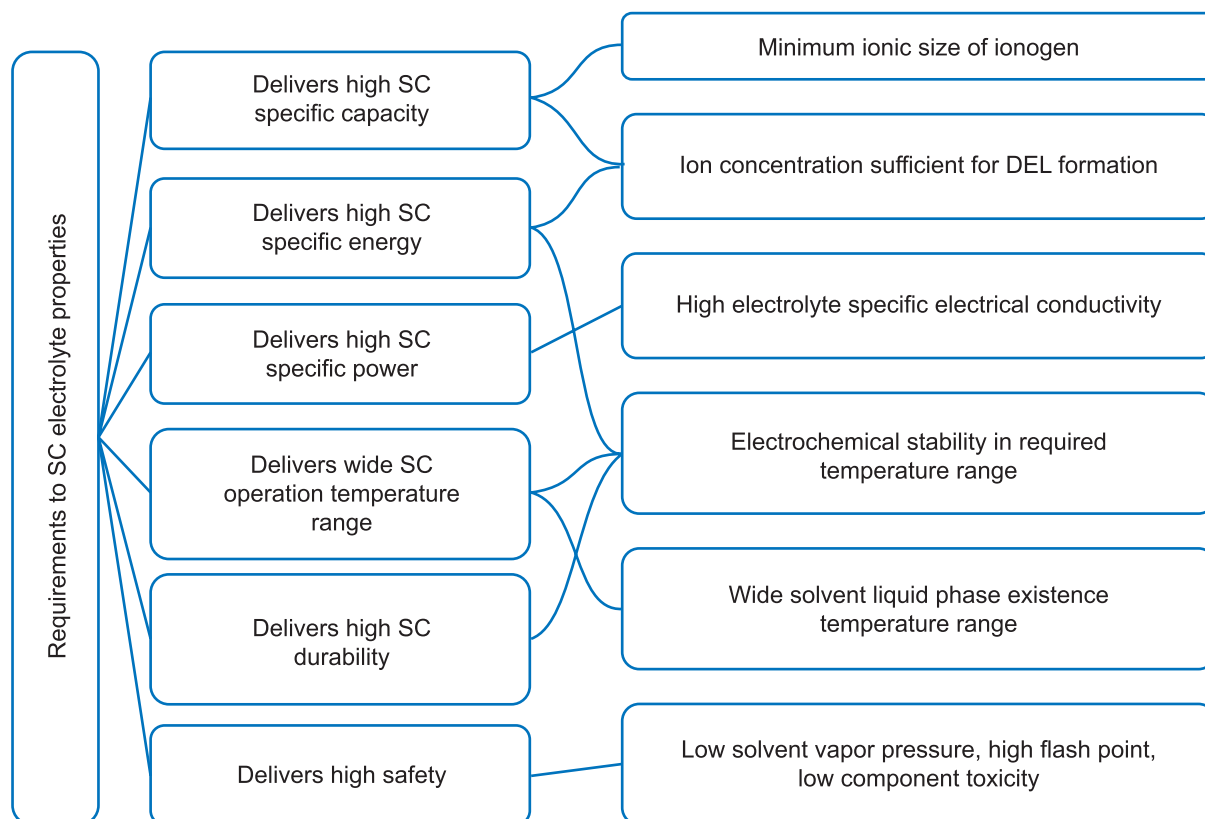
limited by the electrochemical stability of the electrolyte. Whereas for water-based electrolytes (salts, alkalis and acid solutions) the electrochemical window is 1.23 V, that of organic electrolytes and ionic liquids can be increased to 2.7–3.0 V, and therefore most SC manufacturers use organic electrolytes, most typically acetonitrile-based ones (AN). AN-based electrolytes have the highest electrical conductivity among organic electrolytes, thus providing for sufficiently high power performance and efficiency of high-power SC, i.e., up to 10 kW/kg and 95–98 %, respectively [2, 23]. However, the use of electrolytes on the basis of AN or other nitriles requires taking into account safety aspects, since these materials are noxious, volatile, and inflammable liquids with high vapor pressures and low flash points. Incidental damage or overheating of AN-based electrolyte devices to above 60 °C, e.g. by direct sunlight, can cause SC depressurization due to high vapor pressure, AN vapor emission, and flashing, resulting in a release of extremely noxious products.

Considering the above requirements to SC electrolyte for use in portable devices, one should bear in mind that the electrolyte should deliver the highest possible capacity and energy parameters of SC, along with a number of performance characteristics, i.e., sufficiently wide range of operation temperatures combined with minimum toxicity and maximum fire safety. Generalized relationship between the required SC electrolyte properties and the physicochemical parameters of its components that are required for the achievement of the above properties

is shown in Fig. 1. Using the data presented in the illustration, one can justify the choice of solvents for SC electrolytes and set out requirements to the properties of the ionogenic salt used.

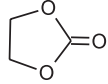
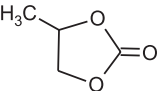
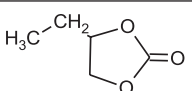
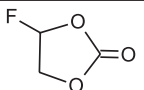
To provide for the highest electrochemical stability and electrical conductivity, the electrolyte solvent should be an aprotic high-polarity liquid with a sufficiently wide liquid phase existence temperature range. The solvent should be chosen from liquids having high dielectric permeability providing for sufficient solubility and degree of dissociation of ionogenic salts into ions, as well as low viscosity for achieving the highest electrical conductivity of the electrolyte. Taking into account that the minimum viscosity is achieved if the sizes of molecules are small, the range of solvents complying with the above requirements is limited to nitriles and cyclic alkylcarbonates with sufficiently low molecular weights [23, 24]. From the viewpoint of physicochemical parameters, nitriles (AN, propyl nitrile, and methoxyacetonitrile (Table 1)) meet the above requirements the most completely. Those solvents are quite rarely used in electrolytes of lithium-ion batteries due to their insufficient stability against reduction, but they are the optimum solvents for high-power SC electrolytes.

However, taking into account SC operation safety requirements for portable devices, a viable alternative for nitriles can be another group of high-molecular organic solvents, i.e., cyclic alkylcarbonates, such as ethylenecarbonate (EC), PC, butylenecarbonate, vinylencarbonate (VC), and fluoroethylenecarbonate (FEC), Table 1.



**Figure 1.** Relationship between required SC electrolyte properties and physicochemical properties of electrolyte components

**Table 1.** Properties of SC electrolyte solvents (shown is specific electrical conductivity of 0.65 M TEA·BF<sub>4</sub> solution in appropriate solvent) [24]

| Name (Abbreviation)           | Chemical formula                                                                  | $T_m$ (°C) | $T_{boil}$ (°C) | $H$ (MPa·s, (at 25 °C)) | $\epsilon$ (at 25 °C) | $\sigma$ (mS/cm) | $T_f$ (°C) |
|-------------------------------|-----------------------------------------------------------------------------------|------------|-----------------|-------------------------|-----------------------|------------------|------------|
| Acetonitrile (AN)             | CH <sub>3</sub> CN                                                                | −49        | 82              | 0.3                     | 36                    | 49.6             | −1         |
| Propionitrile                 | C <sub>2</sub> H <sub>5</sub> CN                                                  | −93        | 97              | 0.5                     | 26                    | Insoluble        | 6          |
| Metoxyacetonitrile            | CH <sub>3</sub> −O−CH <sub>2</sub> −CN                                            | −35        | 120             | 0.7                     | 21                    | 21.3             | 31.7       |
| Ethylenecarbonate (EC)        |  | 36.4       | 248             | 1.09 (at 40 °C)         | 90                    | –                | 160        |
| Propylenecarbonate (PC)       |  | −48.8      | 242             | 2.53                    | 65                    | 10.6             | 132        |
| Butylenecarbonate             |  | −53        | 240             | 3.2                     | 53                    | 7.5              | –          |
| Vinylenecarbonate (VC)        |  | 15         | 168             | –                       | 126                   | –                | 80         |
| Fluoroethylenecarbonate (FEC) |  | 23         | 212             | 4.1                     | 107                   | –                | 102        |

Alkylcarbonates are non-toxic and have low vapor pressure and high boiling and flash points. In SC, alkylcarbonate-based electrolytes are mainly contained in spacer and electrode pores, and electrolyte leakage will not occur even if the container is damaged.

However, the uniquely high dielectric permeability of alkylcarbonates is combined with their high viscosity and melting point, and therefore they are rarely used alone as electrolyte solvents. The best candidate is PC which has moderate viscosity and the widest liquid phase existence temperature range. Note that PC is used quite rarely in lithium-ion battery electrolytes with graphite anodes because it can cause graphite corrosion. Most typically, lithium-ion battery electrolytes are made from EC mixed with co-solvents, and VC and FEC are used as additions favoring the formation of an interphase contact layer.

According to literary data [24], direct replacement of AN for PC in electrolyte with TEA·BF<sub>4</sub> ionogen leads to an almost five-fold decrease in the specific electrical conductivity due to the high density of PC (Table 1), which, in turn, has a negative effect on the power performance of SC. This drawback can be corrected by optimizing the electrolyte components and their concentrations by selecting an alternative ionogenic salt, choosing optimum component concentrations, and introducing additions to electrolyte.

Regarding ionogen choice, the primary requirement to this salt is good solubility in PC (at least 1.5–2 mole/l at 25 °C), high electrochemical stability, and stability against moisture. Inorganic salts having the required solubility in PC are lithium and sodium hexafluorophosphates, and among organic ones, such are alkylammonium and alkylphosphonium tetrafluoroborates

and hexafluorophosphates. According to literary data [24–26], the most electrochemically and hydrolytically stable materials are alkylammonium tetrafluoroborates. Furthermore, the electrical conductivity of their solutions in PC is higher than those of inorganic salts.

For the formation of DEL having the highest capacity, ionogen cations and anions should have the smallest possible size. At the same time, reaching sufficient salt solubility in organic solvents, high dissociation degree, and high electrical conductivity requires choosing ionogens having lower crystalline lattice energy and hence large ions. For example, tetramethylammonium tetrafluoroborate that has a smaller cation has a solubility of within 0.1 mole/l and therefore cannot be used for solutions with sufficient electrical conductivity. Analysis [25, 26] suggests that the best ionogens can be tetraethylammonium tetrafluoroborates which contain 6–8 carbon atoms in the cation.

The most commercially available ionogen which is often used in AN-based electrolytes is TEA·TFB. However, the solubility of that salt in PC is limited, even at room temperature (Table 2), which is insufficient taking into account that the optimum ionogen concentration in electrolyte should be 1.0–1.5 mole/l. With a decrease in temperature, electrolyte components can start to crystallize in electrode pores and on its surface.

In this work, four ionogenic salts were studied: TEA·TFB, TEMA·TFB, SBP·TFB, and DMP·TFB, of which two contain anticyclic cations and the other two are formed by cyclic cations (see Table 2). All the test salts have high solubilities in PC. Furthermore, there are indications that the cyclic structure of the SBP·TFB cation can favor higher electrochemical stability of electrolyte. In recent years, data have been published on the use

**Table 2.** Parameters of ionogenic salts for organic electrolytes

| Abbreviation | Chemical formula                 | Solubility in PC<br>(at 25 °C) (mole/l) | Specific electrical<br>conductivity of<br>1 M solution in PC<br>(at 25 °C) (mS/cm) | Cation or molecule<br>diameter (nm) |
|--------------|----------------------------------|-----------------------------------------|------------------------------------------------------------------------------------|-------------------------------------|
| LPF          | $\text{LiPF}_6$                  | ~4.6                                    | 5.6                                                                                | 0.15                                |
| TEA·TFB      | $\text{BF}_4^-$                  | 1.15**                                  | 13.1**                                                                             | 0.68                                |
| TEMA·TFB     | $\text{BF}_4^-$                  | ~3.2                                    | 13.5*                                                                              | 0.66*                               |
| SBP·TFB      | $\text{BF}_4^-$                  | 3.6**                                   | 11.7**                                                                             | 0.65**                              |
| DMP·TFB      | $\text{BF}_4^-$                  | 3.0**                                   | 12.1**                                                                             | 0.61**                              |
| TMA·TFB      | $\text{BF}_4^-$                  | ~0.1                                    | 2.7 (0.1 M)*                                                                       | 0.57*                               |
| TFB          | $\text{BF}_4^-$                  | —                                       | —                                                                                  | 0.46**                              |
| PC           | $\text{C}_4\text{H}_6\text{O}_3$ | —                                       | —                                                                                  | 0.55**                              |

Note: \* [26], \*\* [27].

of the DMP·TFB salt, which also contains a five-member cycle and has the smallest cation size [26–30].

Although PC-based electrolytes have already been used in a number of commercial SC, the available literary data on their capacity and performance, e.g. maximum operation voltage, permissible operation temperature range, and durability are insufficient for a comprehensive evaluation of their potential practical applications in the field considered. Furthermore, SC parameters depend largely on the type of ions constituting ionogenic salts, because they participate directly in DEL formation, but there are only scarce literary data on the possibility of using other salts than TEA·BF<sub>4</sub> for SC electrolytes [31, 32].

The aim of this work was to systematically study the electrochemical properties and performance of PC- and alkylammonium tetrafluoroborate-based SC electrolytes containing both non-cyclic and cyclic cations, i.e., TEA·TFB, TEMA·TFB, SBP·TFB, and DMP·TFB, for understanding their effect on the properties of electrolytes and choosing an ionogenic salt which can deliver the optimum combination of SC parameters for portable electronics applications.

## 3. Experimental

### 3.1. Materials

The electrodes of SC cells were made from commercial electrode ribbon LMSS consisting of 20 μm thick

aluminum foil with an applied active layer of activated charcoal having a thickness of about 120 μm. Industrial electrode ribbon fabrication conditions guarantee homogeneous active layer properties and provide for the stability of electrode material properties such as moisture content and resistivity, and hence for a more accurate assessment of electrolyte contribution to the equivalent serial resistivity of the cell. The active layer of the carbon ribbon has a specific area of 1290 m<sup>2</sup>/g and specific mesopore and micropore volumes of 0.25 and 0.36 cm<sup>3</sup>/g, respectively, with 1.25 nm sized micropores making the main contribution to the overall micropore volume. It was also shown that electrode materials having this type of porosity are optimum for use in SC with organic electrolytes [2].

The ionogenic salts were tetraethylammonium tetrafluoroborate (TEA·TFB), methyltriethylammonium tetrafluoroborate (TEMA TFB); and spiro-(1,1')-bipyrrolidinium tetrafluoroborate (SBP·TFB) from CapChem, China. *N,N*-dimethylpyrrolidinium tetrafluoroborate (DMP·TFB) was synthesized as follows. 7 ml (0.084 mole) of pyrrolidine dissolved in 50 ml tetrahydrofuran was added to a round-bottomed flask. The reaction mixture was placed in an ice bath, and 13 ml (0.21 mole) methyl iodine was added by drops. The mixture was stirred for 3 h at room temperature, and after solvent evaporation unpurified 1,1-dimethylpyrrolidinium iodide was in the form of semi-hard pale-orange substance. The product output was 8.19 g (43%). Then 2.27 g (10 mmole) of 1,1-dimethylpyrrolidinium iodide solved in 10 ml acetonitrile was mixed with 1.1 g (10,6 mmole) ammonium

tetrafluoroborate, and the reaction mixture was stirred at room temperature for 24 h. After the completion of the reaction, the solution was filtered, evaporated in a rotary evaporator, and the product crystals were purified for two times from isopropanol by recrystallization. After vacuum drying at 80 °C for 24 h, DMP·TFB was in the form of white powder. The product output was 1.28 g (68 %). The composition and structure of the product were verified using elemental analysis, <sup>1</sup>H NMR spectroscopy, and Fourier spectroscopy [23].

Before electrolyte production, the ionogens were dried at 1 kPa and 120 °C for 12 h. The electrolytes were produced by solving the required quantity of ionogenic salt in the respective quantity of PC to achieve a 1 M concentration. All the works were carried out in a glove box in an argon gas atmosphere. The moisture content in the solvents and electrolytes was measured by Fisher's controlled-current calorimetry using a Coulometric KF Titrator C20S (Mettler Toledo). The moisture content in the electrolytes was within 20 ppm.

For electrochemical measurements, laboratory SC cells were manufactured in the form of aluminum foil bags with two symmetrical 3×3 cm<sup>2</sup> electrodes inside (active layer weight 0.0594 g for an active surface area of 9 cm<sup>2</sup> and a specific coating weight of 6.6 mg/cm<sup>2</sup>), separated with a cellulose-based spacer. Before electrolyte filling, the cells were dried at 120 °C and 1 kPa for 72 h, following which argon gas was supplied to the drying chamber.

The SC cells were transferred to the argon gas filled glove box directly from the drying chamber, without exposing to ambient atmosphere. The SC cells were then filled with 1.5 ml electrolyte and impregnated at a reduced pressure for 10 min, following which the cells were pressurized using a vacuum solder. After complete pressurization the cells were removed from the glove box and electrochemically tested.

### 3.2. Electrochemical tests

The electrochemical parameters of the cells were studied using galvanostatic charging/discharging (GCD) on a BTS4008-5V6A charging/discharging test bed from Neware, China, and cyclic voltammetry (CVA) on a P-20X8 potentiostatic galvanostat from Electrochemical Instruments, Russia. Durability tests were carried out using multiple (to 70,000 cycles) GCD in continuous mode at 1.35 to 2.7 V and a current density of 10 mA/cm<sup>2</sup>. The capacity of the SC cells ( $C_{\text{cell}}$ ) was calculated based on the GCD data using the following formula:

$$C_{\text{cell}} = \frac{I \Delta t}{\Delta U}, \quad (1)$$

where  $I$  is the discharge current (A),  $\Delta t$  is the discharge duration (s), and  $\Delta U$  is the change in the cell voltage over the discharge time  $\Delta t$  (V).

When calculating the specific parameters of the electrode material in combination with the electrolyte used,

one should bear in mind that the test SC cell is asymmetric and consists of two DEL capacitors connected in series. In this case, the specific capacity normalized to the unit weight of the electrode material active layer  $C_{\text{sp}}$  (F/g) is calculated using the following formula:

$$C_{\text{sp}} = \frac{4C_{\text{cell}}}{m_1 + m_2}, \quad (2)$$

where  $C_{\text{cell}}$  is the cell capacity (F), and  $m_1$  and  $m_2$  are the weights of the active electrode material layer for the first and second electrodes, respectively.

The specific capacity normalized to the unit surface area  $C_{\text{surf}}$  (F/cm<sup>2</sup>) is calculated using the following formula:

$$C_{\text{surf}} = \frac{2C_{\text{cell}}}{S}, \quad (3)$$

where  $S$  is the surface area of one electrode (cm<sup>2</sup>).

The specific energy  $E_{\text{sp}}$  ((W·h)/kg) of the SC cells was calculated using the following equation:

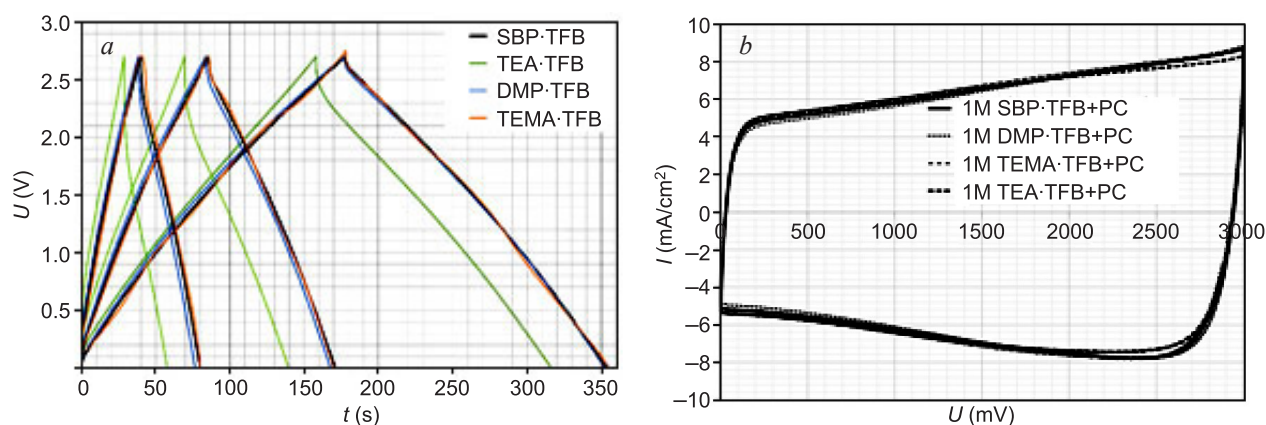
$$E_{\text{sp}} = \frac{C_{\text{sp}} \Delta U^2}{2 \cdot 3.6}, \quad (4)$$

where  $C_{\text{sp}}$  is the specific capacity of the active material (F/g),  $\Delta U = (U_b - U_e)$  is the voltage range determined by the difference of voltages at the beginning  $U_b$  and at the end  $U_e$  of SC discharge (V), and 3.6 is the multiplier for the conversion of seconds to hours and grams to kilograms.

## 4. Results and discussion

The first stage of our study was aimed at understanding the effect of ionogenic salt type on the specific capacity and specific energy of SC. To this end, laboratory SC cells with 1 M solutions of SBP·TFB, DMP·TFB, TEA·TFB, and TEMA·TFB salts in PC as electrolytes were studied using the GCD and CVA methods (Figs. 2a and 2b). The shapes of the GCD curves are close to equilateral triangles, suggesting the implementation of a double-layer energy accumulation mechanism (Fig. 2a). The CVA curves are also almost perfect close-to-trapezoidal, typical for double-layer SC (Fig. 2b). The specific energy and capacity of the SC cells with electrolytes containing the test ionogens, as calculated on the basis of the GCD data, are generally close, suggesting quite minor differences between the test ionogens from the viewpoint of their capability to form DEL (Table 3). The TEA·TFB salt electrolytes have slightly lower capacity due to a large size of the salt cations.

The next stage of the study was the estimation of the electrochemical stability window for SC cells with the test electrolytes at 25, 55, and 85 °C. Based on the CVA curves measured in a voltage range of 2.5 to 4 V (Fig. 3), the electrochemical stability window for all the test electrolytes at 25 °C can be estimated to be 3.5 V. With an increase in the operation voltage to above that point, redox



**Figure 2.** (a) GCD and (b) CVA curves of SC cells with electrolytes (room temperature, GCD current density 5, 10, and 20 mA/cm<sup>2</sup>, CVA voltage sweep rate 20 mV/s)

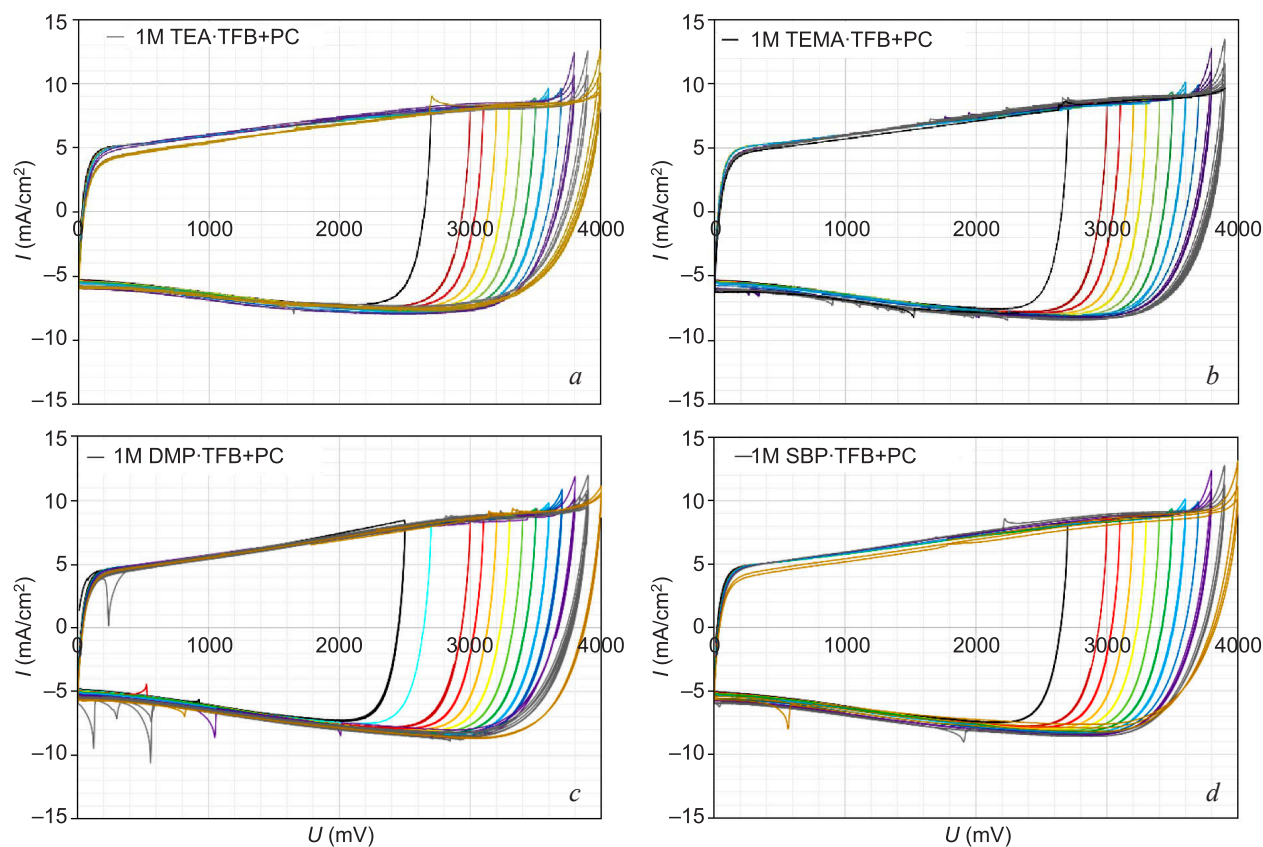
**Table 3.** Electrochemical parameters of SC cells with PC-based electrolytes

| Electrolyte | $C_{\text{cell}}$ (F) | $E_{\text{sp}}$ ((W·h)/kg) | $C_{\text{sp}}$ (F/g) | $C_{\text{sp}}$ (F/cm <sup>2</sup> ) |
|-------------|-----------------------|----------------------------|-----------------------|--------------------------------------|
| TEA·TFB+PC  | 2.70                  | 23.0                       | 91                    | 0.60                                 |
| TEMA·TFB+PC | 3.00                  | 30.9                       | 122                   | 0.70                                 |
| DMP·TFB+PC  | 3.00                  | 30.4                       | 120                   | 0.70                                 |
| SBP·TFB+PC  | 2.90                  | 29.4                       | 116                   | 0.60                                 |

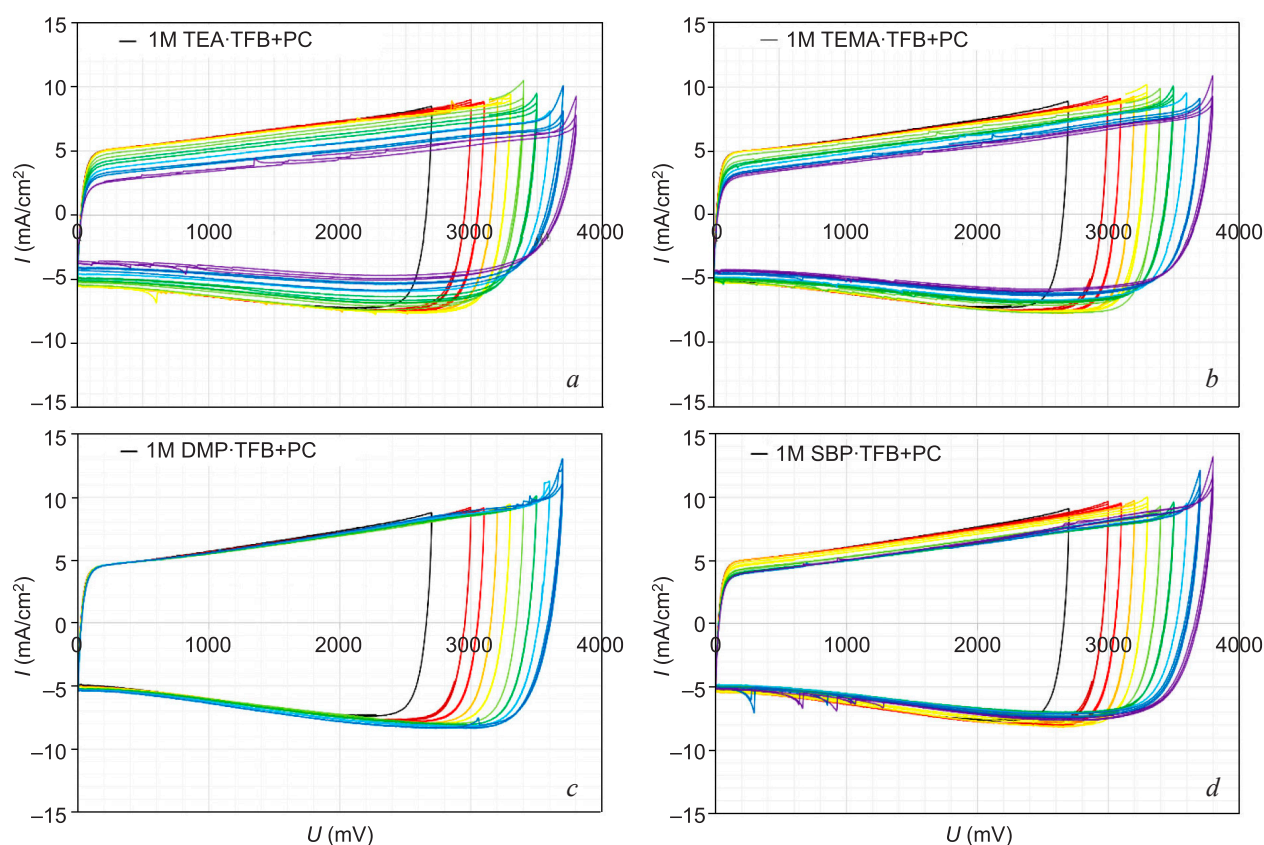
Note: Electrode active layer weight 0.0504 g.

processes of electrolyte components are initiated, which can be seen in the CVA curves as an abrupt increase in the current density.

At 55 °C the electrochemical stability window for SC with the test electrolytes is narrower (Fig. 4). Whereas at room temperature there is almost no difference



**Figure 3.** CVA curves for SC cells with (a) TEA·TFB+PC, (b) TEMA·TFB+PC, (c) DMP·TFB+PC, and (d) SBP·TFB+PC electrolytes in 2.5–4.0 operation voltage range at 25 °C, voltage sweep rate 20 mV/s



**Figure 4.** CVA curves for SC cells with (a) TEA·TFB+PC, (b) TEMA·TFB+PC, (c) DMP·TFB+PC, and (d) SBP·TFB+PC electrolytes in 2.5–3.8 operation voltage range at 55 °C, voltage sweep rate 20 mV/s

between the electrochemical stability of the electrolytes, an increase in the temperature to 55 °C and, especially, to 85 °C clearly demonstrates the advantages of the ionogens containing cyclic cations, i.e., SBP·TFB and DMP·TFB (Table. 4). The CVA data suggest that, in the whole test temperature range, the electrochemical stability window is the widest for the SC with the SBP·TFB ionogen (3.3 V); for the DMP·TFB electrolyte, the 3.5 V operation voltage range is retained at 55 °C but decreases to 3.0 V at 85 °C. Thus, according to the CVA data, the highest electrochemical stability over the whole test temperature range is observed for the ionogens with cyclic cations: SBP·TFB and DMP·TFB.

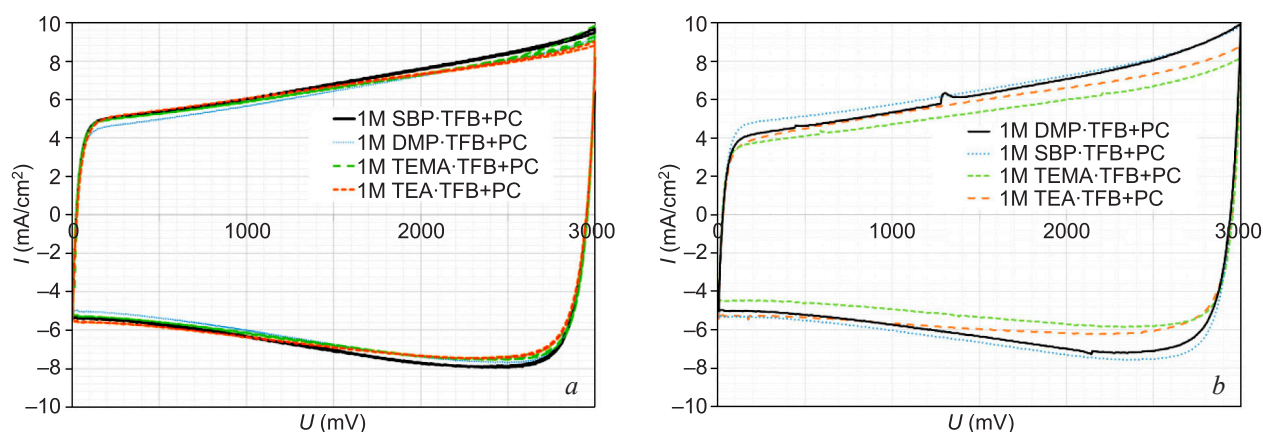
From the viewpoint of practical applications, one of the most important SC parameters is high durability, evaluated as the number of charging/discharging cycles after which the SC still has acceptable performance.

**Table 4.** Electrochemical stability of SC cells with PC-based electrolytes at different temperatures

| Electrolyte | $\Delta U$ (V) |       |       |
|-------------|----------------|-------|-------|
|             | 25 °C          | 55 °C | 85 °C |
| TEA·TFB+PC  | 3.5            | 3.3   | 2.7   |
| TEMA·TFB+PC | 3.5            | 3.4   | 2.7   |
| SBP·TFB+PC  | 3.5            | 3.3   | 3.3   |
| DMP·TFB+PC  | 3.5            | 3.5   | 3.0   |

As a rule, double-layered SC can withstand more than 500,000 charging/discharging cycles without specific capacity reduction by more than 20 %. Durability tests under close-to-real SC operation conditions require very long time, and hence the stability of SC cells and their components is tested using various accelerated durability testing methods imitating SC operation in different modes. One of such testing methods, which characterizes the degradation susceptibility of electrolyte components during storage in a charged condition, implies SC cell exposure to DC voltage for a long time with periodical capacity measurements. For this test, SC cells with the test electrolytes were exposed for 2 h at 55 °C and then for 2 h at 85 °C at a 1.35 V DC voltage, with CVA curves in a 0 to –3 V range being recorded after each stage (Fig. 5). It can be seen from Fig. 5 that after 55 °C exposure, cells with all the test electrolytes demonstrate almost identical electrochemical behavior. At 85 °C, the situation changes for SC cells with the TEA·TFB and TEMA·TFB salts: they exhibit a decrease in the current density, and hence the capacity, over the whole voltage range, most probably due to the electrochemical decomposition of ionogens at elevated temperatures. For SC cells with the SBP·TFB and DMP·TFB salts, 85 °C exposure reduces the capacity but slightly.

After the latter stage of the study, based on the overall scope of experimental data, more specifically, due to its low specific capacity and energy, as well as low thermal

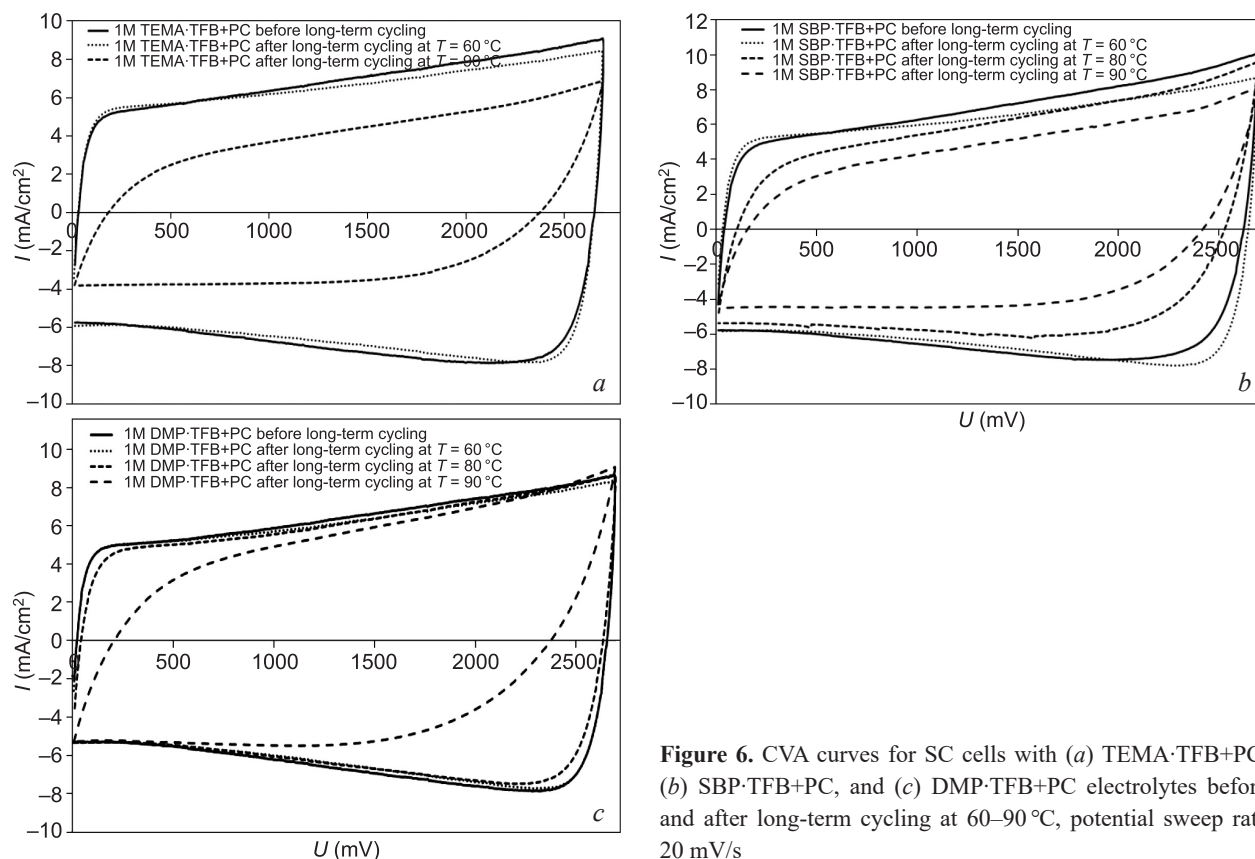


**Figure 5.** CVA curves of SC cells with TEA·TFB+PC, TEMA·TFB+PC, DMP·TFB+PC, and SBP·TFB+PC electrolytes after exposure at 1.35 V and (a) 55 and (b) 85 °C

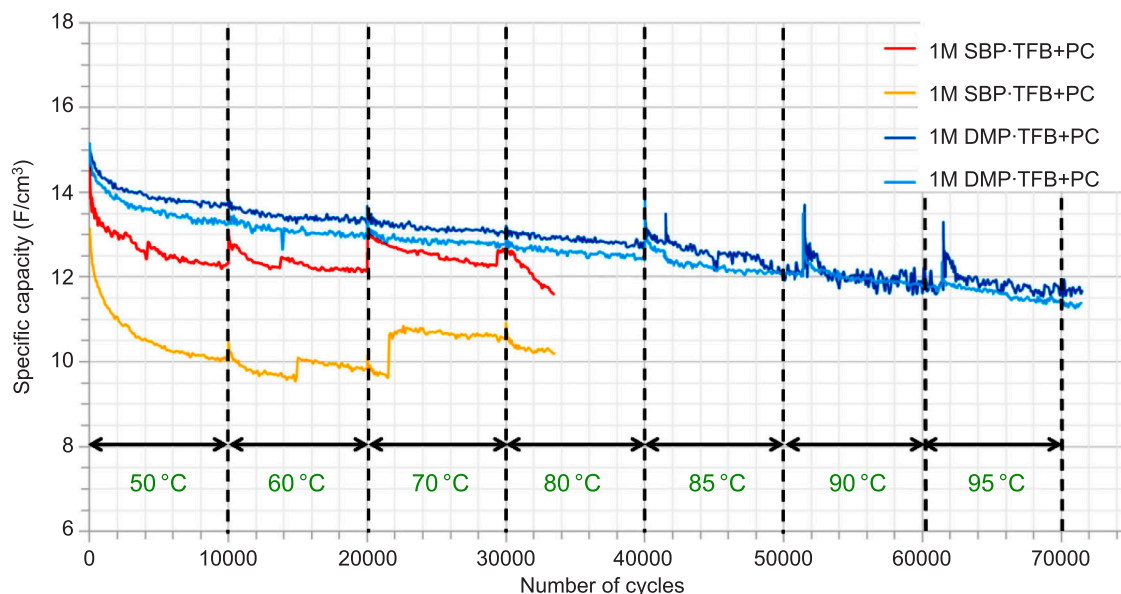
stability, TEA·TFB salt electrolyte was discontinued from further study as the least promising one.

Further durability tests of SC cells were carried out in continuous GCD mode in a voltage range of 1.35–2.7 V at 25 to 90 °C. The cells were preliminarily cycled for a certain time at room temperature, and then GCD tests were run for 1000 cycles at 60, 80 and 90 °C each. After 1000 cycles at the above temperatures, the cells were cooled down to room temperature and studied using the CVA method. This allowed us to identify a specific temperature range for each electrolyte in which intense degradation processes onset. The experimental data confirm the conclusions made on the basis of the previous test

series. The TEMA·TFB salt electrolyte lost performance even before the completion of the 80 °C tests, which was indicated by significant changes in its CVA curves after cycling at that temperature (Fig. 6a). At 90 °C the cells filled with that electrolyte did not work. The capacity of the SC cells with SBP·TFB salt electrolyte declined after each cycling stage (Fig. 6b), but they retained some performance even at 90 °C. Finally, the DMP·BF<sub>4</sub> salt electrolyte proved to be electrochemically stable at 80 °C (Fig. 6c), its CVA curves changing but slightly after cycling at that temperature. A decrease in the capacity and an increase in the resistivity were only observed after cycling at 90 °C. Thus, the DMP·BF<sub>4</sub>+PC electrolyte



**Figure 6.** CVA curves for SC cells with (a) TEMA·TFB+PC, (b) SBP·TFB+PC, and (c) DMP·TFB+PC electrolytes before and after long-term cycling at 60–90 °C, potential sweep rate 20 mV/s



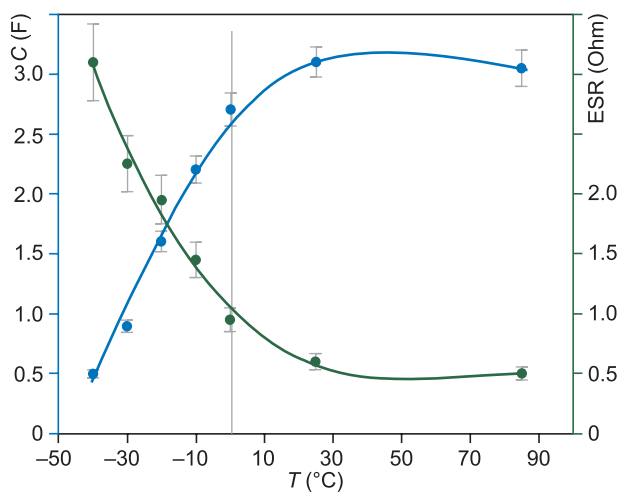
**Figure 7.** Results of long-term cycling for SC with SBP·TFB+PC and DMP·TFB+PC electrolytes in 50 to 95 °C range (data are shown for two cells with each electrolyte type)

proved to be the most electrochemically stable over the whole test temperature range.

Finally, the SC cells with SBP·TFB+PC and DMP·TFB+PC electrolytes, which demonstrated the highest thermal and electrochemical stability during the previous test stages, were exposed to long-term cycling in the 50 to 95 °C range in continuous charging/discharging mode at 1.35–2.7 V for 10,000 cycles at each test temperature. The SC specific capacity vs number of cycles curves for different temperatures (Fig. 7) prove the high stability of the DMP·TFB+PC electrolyte: SC with this electrolyte retained 80 % of the initial capacity after 50,000 charging/discharging cycles at 50 to 85 °C and 77 % of the initial capacity after 70,000 cycles at 50 to 95 °C. Under these conditions, the SC with the SBP·TFB+PC electrolyte behaved in a less stable manner: one of the cells lost 20 % of capacity at as low as 50 °C, and the other cell, at 80 °C. The capacity vs number of charging/discharging cycles curve has a “saw-like” pattern which is typically attributed to electrolyte components degradation processes accompanied by gas release.

Thus, the durability tests confirm the electrochemical stability of the DMP·TFB+PC electrolyte at up to 95 °C. At up to 85 °C, SC with that electrolyte can be operated at 3 V, indicating a high specific energy reaching 30 (W·h)/kg. The choice of ionogen is a key factor in increasing the durability of SC. Alkylammonium tetrafluoroborates with cyclic cations, especially DMP·TFB, demonstrate high electrochemical stability at elevated temperatures, which is unachievable with conventional TEA·TFB and TEMA·TFB. It should be stressed that the possibility of SC operation at such elevated temperatures is one of the key advantages of the PC-based electrolytes over their AN-based counterparts which are not recommended for operation at above 60 °C.

In order to find the lower limit of the DMP·TFB+PC electrolyte SC operation temperature range, we measured the capacity of the cells at low temperatures, down to –40 °C. It can be seen from Fig. 8 that the SC capacity decreases significantly with a decrease in temperature. At 0 °C, the cell capacity is 80 % of the 25 °C figure, at –20 °C the capacity decreases twofold as compared to the room-temperature one, and at –40 °C the SC with that electrolyte loses 83 % of the initial capacity, which is accompanied by an increase in its equivalent serial resistivity by 360 % (Fig. 8). The high resistivity at low temperatures is caused by an increase in the electrolyte viscosity which abruptly decreases the ion migration rate and hinders the formation of DEL. Based on the criterion according to which SC should retain at least 80 % of its rated capacity, one can conclude that the DMP·TFB+PC electrolyte has an operation temperature range of 0 to 85 °C.



**Figure 8.** DMP·TFB+PC electrolyte SC capacity and equivalent serial resistivity as a function of temperature

## Conclusion

The study showed that the PC-based electrolyte with DMP·TFB ionogen containing cyclic cation is the most suitable from the viewpoint of requirements to electrolytes of energy storage devices used in portable electronics. Due to its good electrochemical stability, this electrolyte provides for an operation voltage of 3.0 V thus achieving a specific energy of about 30 (W·h)/kg.

As compared with its counterparts, DMP·TFB has the highest electrochemical stability at elevated temperatures of up to 85 °C, which was experimentally confirmed

by continuous GCD tests for 70,000 cycles. The recommended operation temperature range for SC with DMP·TFB+PC electrolyte at 3.0 C is 0–85 °C, with the possibility of short-term temperature growth to 95 °C.

Further studies should be carried out aimed at developing multicomponent co-solvent systems which would increase the electrical conductivity of PC-based electrolytes over the whole operation temperature range and improve their negative-temperature performance, as well as exploring the possibility of using new-generation electrode materials in combination with the electrolytes developed herein.

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