

Continuing Quest for High Temperature Electrochemical Capacitors

KUI 11/2005
Received August 16, 2004
Accepted January 10, 2005

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Progress is described in the development of small electrochemical capacitors that would be capable of high current pulses when in parallel with high energy density primary batteries used at present in oil and gas drilling operations. Difficulties were experienced initially in passivation of electrode substrate materials in presence of minute amounts of water related impurities and with an unacceptable leakage current at full charge at maximum temperature of up to 150 °C prevailing in most oil services applications. While the problem of electrode substrate passivation has been successfully resolved by choice of material and of a surface pre-treatment in preparation of electrodes the excessive leakage current has only recently been sufficiently reduced to consider hybrid power sources with batteries and electrochemical capacitors practical. A tentative conclusion has been reached that the electrolyte components, otherwise stable alone or in rechargeable batteries, are subject to decomposition in presence of high surface area carbon creating an internal electrochemical shuttle responsible for self-discharge.

Keywords: *Capacitors, electrochemical, double layer, high temperature*

Introduction

The application of primary batteries at high temperatures such as those prevailing in oil and gas drilling and exploration is still, 23 years since introduction, carried out only with the electrochemical systems involving metallic lithium and oxyhalide electrolyte depolarizers. With the energy density of up to 15 times that of zinc/carbon batteries, the high power type cells of this kind lead to a violent explosion whenever the melting point of lithium was reached, either by internal self heating caused by accidental short circuit or by external overheating. One of these causes of hazardous behavior could be totally eliminated if only the low rate cells are used, those which could not heat up to the melting point of lithium by their own power under short circuit heating alone. For reasons of safety we have steadfastly refused to fabricate high power cells for this application during all these years. Standard safety devices such as vents were not practical in this application. However, newcomers to this business could not resist the temptation of new business opportunities and are currently supplying the industry with these dangerous high power batteries.

The goal of this effort over the last several years has been to provide the industry with safe low power cells that would, in parallel with electrochemical capacitors, enable the high power pulsing discharge without the potential for hazardous behavior. The rate capability of such hybrids can easily be projected from the nominal discharge rate of low rate batteries and the strength and duration of the high power pulses required, but the satisfactory operation of electrochemical capacitors at elevated temperature has not been achieved and appeared a task more formidable than expected. The fact that one can discharge AA size electrochemical capacitor at higher rate than that possible for ten to twelve times larger safe primary battery, on the one

hand, and that most down hole applications require a pulsing power, on the other, justify this quest and holds a promise of safer solution for down hole power sources.

Prototype design and fabrication

The test vehicle in this investigation was built using hermetically sealed AA size stainless steel hardware with glass sealed feedthroughs as originally designed and developed by Marinčić¹ for use in cardiac pacemaker batteries thirty years ago. The electrode structure comprised a pair of identical carbon electrodes and glass fiber separators in wound electrode configuration. Two types of carbon were investigated, one with the BET surface area of 1500 m²g⁻¹ and the other with 2000 m²g⁻¹. Several metallic current collector substrates were investigated, both in foil and in expanded screen form. The choice was quickly limited to titanium and aluminum before the aluminum was left as the only alternative for this high temperature application.

The carbon electrodes were formed by sandwiching the current collector between carbon foils formed by extrusion of cured mix of carbon powder and Teflon binder, just as in the case of lithium oxyhalide batteries except with an increased content of the binder needed to hold together this high surface area carbon. A typical electrode was 4.00 × 1.50 × 0.02 inches (10.16 × 3.81 × 0.051 cm) and contained 0.5 g of carbon. Certain surface mismatching, intrinsic in the wound electrode structure made with relatively short electrodes, was tolerated in this initial phase of development.

Following the dry assembly the test units were subjected to an extensive drying at 150 °C under high vacuum before the electrolyte was admitted under closed system conditions and the fill ports closed by welding. A proper level of

electrolyte content was determined in advance in order to avoid bulging of cell containers at test temperatures. This cell housing appeared sound and remained superficially unaffected by exposure to high temperature throughout the tests.

Electrolyte preparation and evaluation

The electrolytes were based on either propylene carbonate (PC) or acetonitrile (AN) solvents and were dried by passing through a column of freshly regenerated molecular sieve at room temperature after the electrolyte salt, tetraethylammonium tetrafluoroborate (TEATFB), was dissolved. Some proprietary electrolytes were tested as received from suppliers under the conditions of nondisclosure stipulating further arrangements if the initial tests indicated the potential for use in this application.

Cyclic voltammetry in the electrolytes was carried out at room temperature using narrow strips of titanium current collector foil as working and reference electrodes and a larger counter electrode of the same material. The goal was to verify that the voltage window was free of significant Faradaic transients in the range of interest. Assembling the voltammetric cell with carbon electrodes was attempted but was found impossible without contaminating the electrolyte with oxygen and water even in the dry room atmosphere. Typical cyclic voltammogram is shown in Fig. 1.

The clear voltage window indicated by Fig. 1 would not necessarily be so clear with carbon electrodes, even with the best drying and de-gassing procedures, due to the extreme tendency of this carbon to adsorb gases of which oxygen and water vapor would be indicated by Faradaic transients at their respective specific potentials. However, such voltammograms even without carbon show the onset of hydrogen evolution and/or oxygen reduction at the extreme negative end of the voltage window, even after most extensive pretreatment of carbon electrodes. Backing off that extreme of the voltage window would mean reducing the voltage for the capacitor at full charge and an exponential reduction of the energy storage capability of the system.

Commercially available electrolytes were tested as received except for the final closed system drying procedure. We have developed this procedure for nonvolatile electrolytes such as organic ionic liquids for use in stainless steel hardware. The dry cells and the electrolytes were heated separately under vacuum at 150 °C until no gas bubbles were visible coming either out of the cell or out of the liquid. The liquid was then admitted into the cell as the pressure in the vacuum oven

was slowly brought to normal. Quick closing by plugging and welding the fill port was carried out before the unit was cooled down to room temperature.

Prototype testing in PC and AN electrolytes

A symmetric carbon capacitor in AA size hardware and with the electrolyte made of 1 mole/l TEATFB in PC was tested in order to establish the sensitivity to elevated temperature before further steps were taken to improve the performance. The electrochemical system tested here was no different from that used in building very large units for load leveling application as reported by Marinčić² earlier. Fig. 2 shows the single cycle at increasing temperature and a fair performance up to a 100 °C. An increase in the internal resistance and a rapid deterioration at 110 °C indicated a need for further improvement in the system. We wished to investigate other means of improvement needed in high temperature application before we would consider reducing the voltage window below 3V.

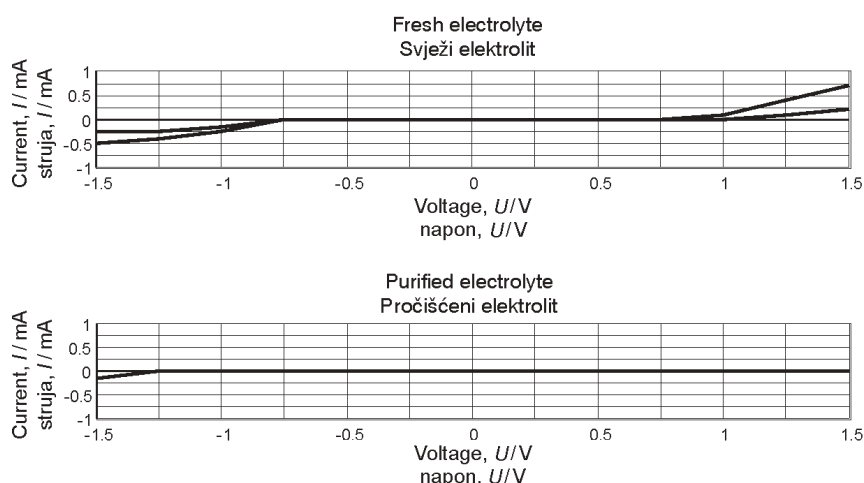


Fig. 1 – Cyclic voltammetry in 1 mol dm⁻³ TEATFB in PC
Slika 1 – Ciklička voltametrija u 1 mol dm⁻³ TEATFB u PC

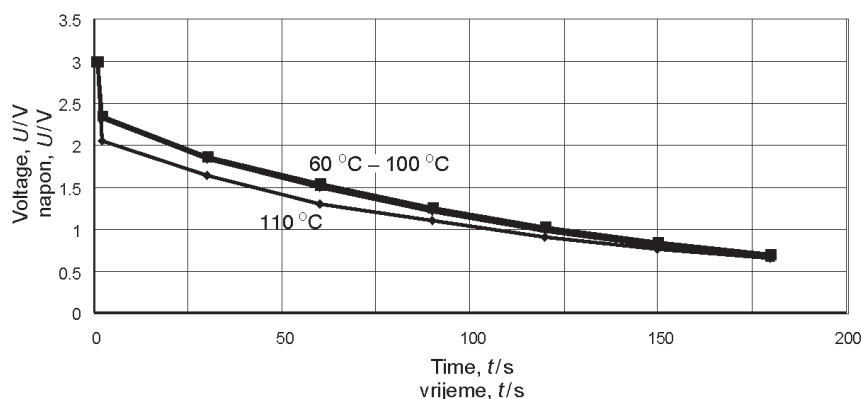


Fig. 2 – Discharge with constant load of 3 Ω at gradually increasing temperature
Slika 2 – Pražnjenje kroz stalni otpor od 3 Ω pri postupnom povišenju temperature

The voltage window could be extended in the anodic direction by partial lithium intercalation of the anode, which would shift its rest potential in negative direction. We have developed our own *in situ* method of precise electrochemical intercalation to the desired level of lithium content in the anode. The first significant improvement step is illustrated in Fig. 3 using 32 F, AA size unit at 50 °C. The capacitance decayed to 28 F after 1 100 cycles and to 23 F after 4 600 cycles but that was far superior to the initial performance without lithium intercalation.

The internal resistance of the cell with AN based electrolyte is less than half of that with PC based electrolyte but AN is more volatile, more difficult to contain at elevated temperature and, also, represents a far greater health hazard than PC. The conductivity of both of these electrolytes is greatly improved by substituting methyl triethyl ammonium tetrafluoroborate (MTEATFB) for TEATFB due in part to a

greater solubility of MTETFB in these solvents. Also, by replacing AN with propionitrile (PN) we would increase the boiling point of the solvent to 97 °C from 81 °C for AN. However, the reduced solubility of MTETFB in PN would carry another penalty in conductivity. In order to overcome this we have developed a procedure for filling cells with hot PN saturated with MTETFB at 60 °C which had the conductivity comparable to that of AN electrolyte. Improved cycling behavior is illustrated with the 10th cycle at 100 °C in Fig. 4 showing somewhat reduced *iR* drop relative to that in PC based electrolyte. The highest capacitance of almost 40 F on charging and discharge was achieved with this electrolyte but the losses due to self-discharge were unacceptable even at only 100 °C. A steady floating (leakage) current of 200 mA at full charge of 3.1 V was estimated from the voltage drop at the end of the 6 min cccv charge, and before the onset of discharge.

By this point of the program it has become clear that neither of these improvements was sufficient to enable the operation at 120 to 150 °C required in oil and gas drilling operations.

High rate lithium ion battery systems

The rate capability of various lithium ion rechargeable battery systems has been steadily improving for several years since their introduction in early 1990s. The discharge rates capability became almost comparable to that of early electrochemical capacitors. Based on the most recent claim by *Desilvestro*³ we were tempted to switch our attention to a newly developed rocking chair lithium ion system for use in parallel with the high energy density primary batteries for oil and gas exploration. Several different rocking chair type electrode systems were constructed and tested. These electrodes were made with a capacity as low as 2 mA h cm⁻² but capable of supporting the discharge rate as high as 80 mA cm⁻². Unfortunately we had to modify the standard electrode structure for application at higher temperature. The 0.001 inch thick polypropylene separator, Cellguard, had to be replaced with a 0.005 inches thick glass fiber separator since Cellguard would fuse well below our intended application temperature. This increased the internal resistance of the cell and thus reduced the efficiency of discharge. We used the common (Mitsubishi Chemical) electrolyte made for lithium ion batteries and based on lithium hexafluorophosphate solution in a mixture of organic carbonate solvents.

The typical 1 A constant current discharge at room temperature is shown in Fig.

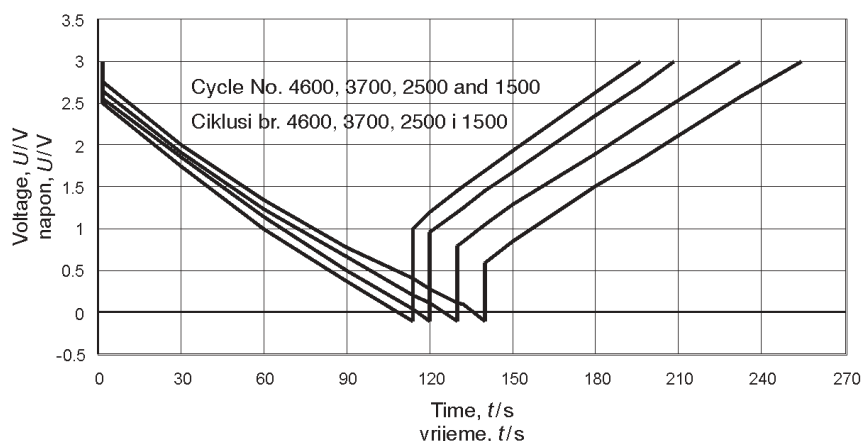


Fig. 3 – 0.5A cccv cycling of AA size capacitor with lithium intercalated anode at 50 °C

Sl i k a 3 – Pražnjenje i punjenje AA kondenzatora s anodom aktiviranom litijem, 50 °C i 0,5 A

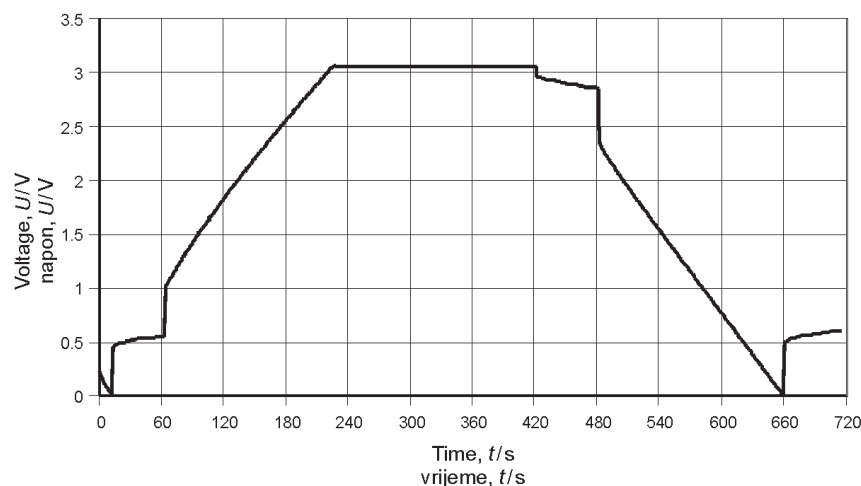


Fig. 4 – Tenth cycle at 100 °C for MTETFB / BN electrolyte with 0.5 A

Sl i k a 4 – Deseti ciklus pri 100 °C za elektrolit MTETFB / PC sa 0,5 A

5. The estimated energy recovered during discharge appeared over three times as large as that of carbon based capacitors. However, the slow heating of the cell in charged state to 70 °C resulted in a sudden decay of cell voltage caused by a large increase in self-discharge current. The cell could be charged again only after cooling to room temperature but the repeated heating showed progressive deterioration as the voltage began to decay at only 50 °C. Typical results of the repeated heating are illustrated in Fig. 6.

We have experienced these kind of difficulties some years ago with PC based lithium hexafluorophosphate electrolyte and we were able to show that hexafluorophosphate began to decompose upon heating at around 90 °C leading to fast self-discharge through an internal shuttle mechanism similar to that reported by Conway.⁴ We were hoping that the particular combination of solvent in Mitsubishi electrolyte might slow down this process and, combined with the particular lithium ion electrodes, might lead us to some success. Based on these latest tests, however, using various lithium ion electrode systems and electrolytes, we are inclined to pronounce these electrolytes unsuitable for use in the range of temperatures prevailing in oil and gas drilling operations.

Prototype testing with ionic liquid electrolytes

Two types of ionic liquids, Type A and Type B, were procured from the Covalent Associates⁴ in Woburn, Massachusetts, USA, under the conditions of confidentiality in order to verify if a potential existed for the high temperature application before more elaborate arrangements were made to protect intellectual property of the supplier. The initial results are represented in Fig. 7 showing the voltage decay after full charge.

It is obvious that the Type A electrolyte was not appropriate for this application. However, the Type B showed promise at 120 °C, particularly since the overall voltage decay appear slower if the maximum voltage was reduced from 3.0 to 2.75 V. Further illustration of this potential is shown in Fig. 8 in which the leakage current was plotted as a function of voltage after charging to various voltage levels at 90 °C. We understood the chemical nature and differences between Type A and Type B electrolyte and hoped that we

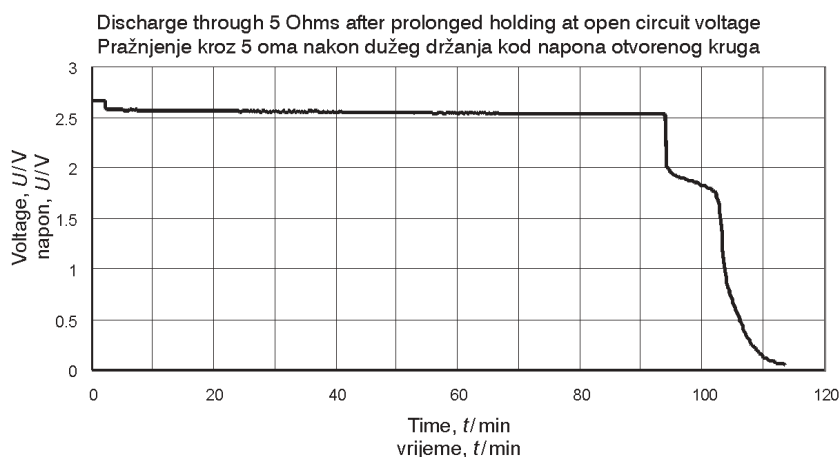


Fig. 5 – Discharge of manganese dioxide/lithium titanate lithium ion battery at room temperature

Slika 5 – Pražnjenje litij-ionske baterije manganov dioksid/litijev titanat pri sobnoj temperaturi

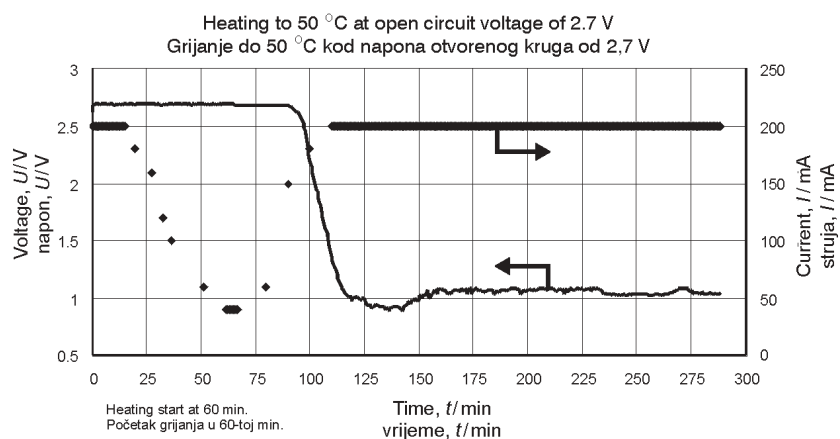


Fig. 6 – Voltage decay caused by heating of a rechargeable lithium ion battery

Slika 6 – Opadanje napona prouzrokovano grijanjem sekundarnog litij-ionskog članka

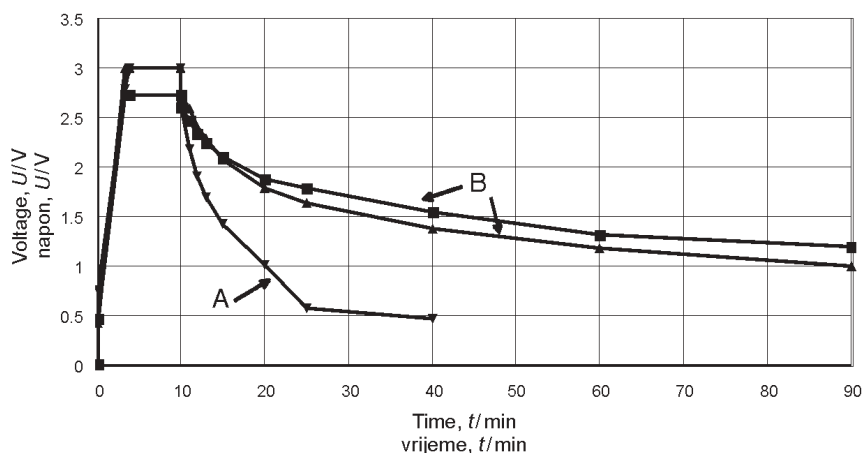


Fig. 7 – Voltage decay after full charge for two ionic liquid electrolytes at 120 °C

Slika 7 – Opadanje napona nakon punog punjenja za elektrolite s dvije različite ionske kapljevine pri 120 °C

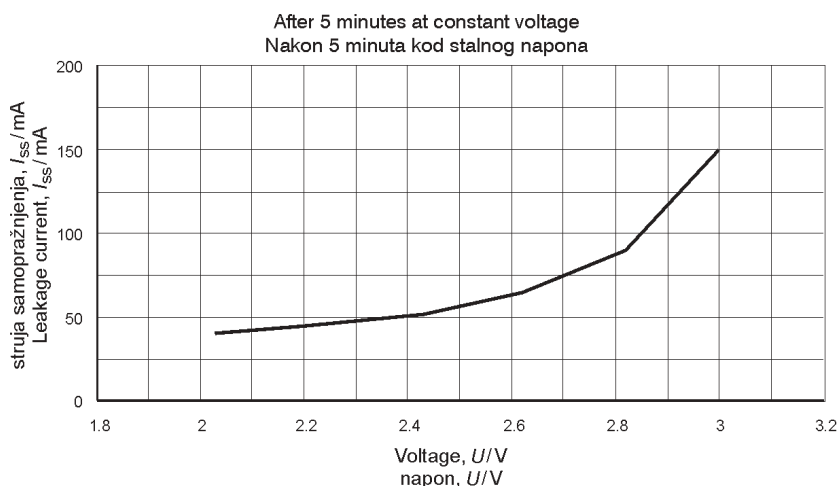


Fig. 8 – Leakage current at various voltages for Type B ionic liquid electrolyte at 90 °C

Slika 8 – Struja samopražnjenja kod raznih napona za ionsku kapljevinu tipa B na temperaturi od 90 °C

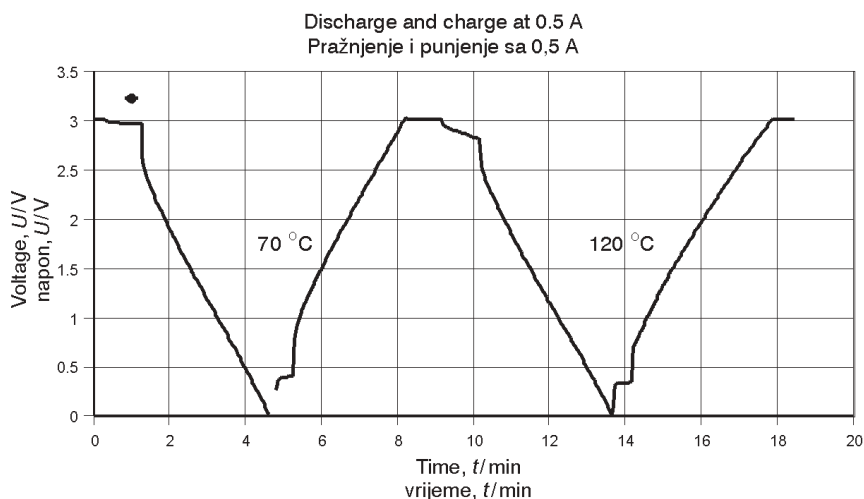


Fig. 9 – Single cycles at 70 and 120 °C with N-methyl-N-butyl pyrrolidine hexafluorophosphate as an electrolyte

Slika 9 – Pojedinačni ciklusi kod 70 i 120 °C s N-metil-N-butil-pirolidin-heksaflorofosfatom, kao elektrolitom

would be allowed to identify these ionic liquids at some future date. A lower maximum cell voltage might be a viable solution for higher temperature applications, even with the penalty in energy density, since no other system tested so far appeared promising for use in this application.

Further promise of high temperature double layer capacitors based on ionic liquids was demonstrated using an identifiable compound from a commercial source of analytical chemicals. Fig. 9 shows two single cycles, one at each selected temperature, with prototypes using N-methyl-N-butyl pyrrolidine hexafluorophosphate as an electrolyte.

This ionic liquid appeared quite stable when heated in vacuum up to 160 °C for many hours which suggested that, in our closed system filling procedure, we could completely remove water impurities both from the assembled electrode system and from the electrolyte before the electrolyte was admitted into the cell. The discharge to zero V from full

charge of 3.0 V with 0.5 A at 120 °C, after a brief period at open circuit, lasted almost 200 seconds which translated into the capacitance of over 40 F – the most remarkable result up to this point under these conditions in the program. The voltage stability at open circuit at 70 °C would have been acceptable but at 120 °C the leakage current became too large for any performance projection in parallel arrangements with primary batteries in oil well application.

We have still suspected that the excessive leakage current in ionic liquid electrolytes might be caused by impurities in carbon itself. We have improved the overall picture significantly by exposing, separately, the dry assembled cell and the electrolyte to 150 °C at high vacuum over a prolonged period of many hours before the cell was filled and closed. Only a brief exposure to the dry room atmosphere with 1% relative humidity was needed in order to rearrange the closed system filling fixtures before another period of high temperature exposure was started, ending with forcing the electrolyte into the cell. The single cycle with a cell so assembled using Type B ionic liquid electrolyte is shown in Figure 10.

The leakage current of only 47 mA, observed at the end of a prolonged charging at constant voltage and at 120 °C, appeared most encouraging. This is only a third of the value obtained in preliminary test at only 90 °C as shown in Fig. 8. This suggests that one might further reduce this value by further refinements in the purification and assembly procedures. In addition, we have contemplated a reduction in maximum voltage to which the unit is charged in order to reduce the leakage current knowing that the energy density of the unit would be also reduced. A test data in Fig. 11 show the magnitude of the leakage current reduction at various values of the voltage reduction.

Conclusions

Neither the lithium ion battery electrolytes nor the common organic electrolytes used in electrochemical capacitors for room temperature application are suitable for high temperature application due to the decomposition leading to an excessive leakage current at full charge. These electrolytes begin to decompose visibly and irreversibly at already 90–100 °C, as illustrated by increased coloration of the solution. We speculate that the products of the electrolyte decomposition are involved in establishing a steady state shuttle type self-discharge, although the impurities in the system might also be contributing to the self-discharge.

Some ionic liquids, stable by themselves, must be subject to a rapid decomposition at elevated temperature in presence of very high surface area carbon and, also, leading to the formation of internal shuttle mechanism of self-discharge.

There is a potential for constructing high temperature capacitors using Type B ionic liquid electrolyte, proprietary to Covalent Associates of Woburn Massachusetts, if combined with our close system dehydration, purification and assembly procedures. With further refinement of preparation and purification of carbon electrodes, we should soon be able to fabricate electrochemical capacitors which would enable the use of safe low rate high energy density primary batteries in high pulse power applications such as Measurement While Drilling (MWD). The quick data acquisition and transmission between the drilling periods might be supported by the electrochemical capacitors alone when the tools include down-hole electric generators to keep the capacitor banks charged during the drilling periods.

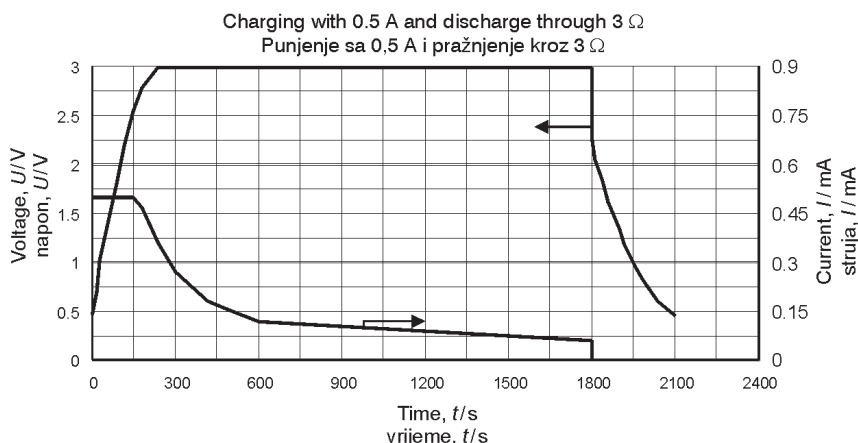


Fig. 10 – A cell with Type B ionic liquid electrolyte after a modified purification procedure

Slika 10 – Članak s ionskom kapljevinom tipa B poslije preinačenog postupka pročišćavanja

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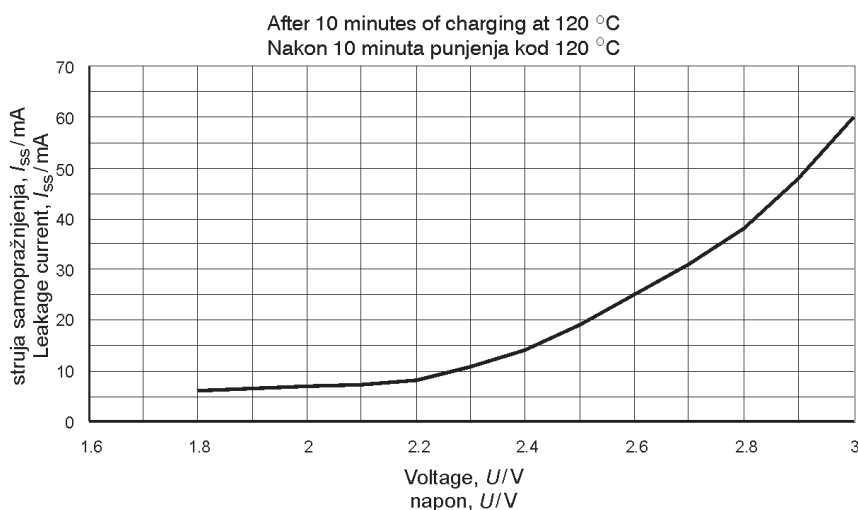


Fig. 11 – Leakage current as a function of voltage for Type B ionic liquid electrolyte

Slika 11 – Struja samopražnjenja kao funkcija napona za elektrolit s ionskom kapljevinom tipa B

SAŽETAK

Neprekidna potraga za visokotemperaturnim elektrokemijskim kondenzatorima

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Opisan je napredak u razvoju malih elektrokemijskih kondenzatora sa sposobnošću dobave jakih strujnih impulsa u paralelnom spoju s primarnim baterijama visoke energetske gustoće kakve se primjenjuju u naftnim i plinskim bušotinama. Početne teškoće bile su u pasivaciji podloga za elektrode s niskim udjelima vlage i drugih onečišćenja kao i u neprihvatljivoj brzini samopražnjenja pri temperaturi do 150 °C kakve prevladavaju u bušotinama. Dok je problem pasivacije uspješno riješen odabirom materijala i prethodnom obradom u procesu proizvodnje elektroda, prekomjerna brzina samopražnjenja je tek nedavno dovoljno snižena tako, da elektrokemijski kondenzatori u kombinaciji s baterijama omogućuju konstrukciju praktičnih hibridnih izvora struje. Došlo se do privremenog zaključka da sastojci elektrolita koji su sami za sebe stabilni pri visokim temperaturama, podliježu razgradnji u prisutnosti aktivnog ugljena visoke specifične površine i potpomažu zatvoreni krug samopražnjenja.

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Prispjelo 16. kolovoza 2004.
Prihvaćeno 10. siječnja 2005.