Advanced development of chemical sources of current (CSC) and ultra high-volume capacitor structures (UCS) for energy storage devices

V V Sleptsov, S N Kulikov, D Yu Kukushkin and A O Diteleva

1 Moscow Aviation Institute (National Research University), Volokolamskoe Shosse, 4, 125310, Moscow, Russia

E-mail: 08fraktal@inbox.ru, anna.diteleva@mail.ru

Abstract. This paper addresses advanced development of chemical sources of current (CSC) and ultra-high-volume capacitor structures (UCS) for energy accumulation. For estimated specific energy, CSC with the lithium anode ranks first. Recently, along with the CSC, the ultra-high-volume capacitor structures (UCS) are intensely developing. The most advanced area for a drastic improvement of batteries properties is the use of nanomaterials that acquire unique physical and chemical properties due to the nanoscale level structurization. To implement development of nanomaterials and nanostructures-based CSC and UCS, conventional microelectronics thin-film technologies are used.

CSC based on lithium materials is the champion in energy intensity. Lithium has the highest specific energy: 11760 W × h/kg [1]. First lithium electric cells (LEC) entered the world market in the early 1970s, and this was due to the development of non-aqueous electrolyte solutions, and the use of high-performance and low-cost thick-layer technology for their production only [2].

Regarding estimated specific energy (one of the key parameters for the electrochemical cells energy efficiency) CSC with the lithium anode hit the first place. Real energy advantages of current sources with lithium anodes are evident in the following comparison. Specific energy value of one of the widely spread in practice energy-intensive Clark cell systems is 80 to 100 W × h/kg, among other standard (silver-zinc and magnesium silver-chloride) systems it does not exceed 120 to 130 W × h/kg, and with various lithium anode based current sources specific energy value amounts to 300 to 500 W × h/kg. Advanced CSC developments can provide obtaining specific energy about 1000 W × h/kg. Discharge voltage values of lithium anode based electro-chemical couples used amount to about 3 to 4.8 V. This is more than twice the voltage of components widely used in household appliances. (1.5 V).

The last steps in developing LIB was the discovery by Japanese scientists the possibility of using not lithium metal but chemically-inactive carbon capable of reversible intercalation of Li + ions as anode and subsequent combination with lithiated transition metals oxides in organic electrolytes. Specific characteristics of modern anode materials produced by using the thick layer technology are shown in table 2. Advanced developments in the area of CSC is energy intensity increase, operating safety improvement and production and operation costs reduction. The major carbon materials used in the LIB compositions are graphite and amorphous carbon [8].

The history of LIB development and improvement goes to show that emergence of new LIB potential uses coincided with the development of new active materials, while the innovations maturity
processes starting with the laboratory study via RTD to real applications took several years. However, it should be noted that since the time of development and over more the last twenty years the lithium-ion batteries capacity underwent no massive improvement. That is because both anode and cathode materials in fact remained the same many laboratories around the world are developing new materials for electrodes, batteries, and numerous breakthrough results are being reported, but commercial applications are hardly in evidence. This is due to the wide range of requirements for such materials - except that they should contain larger amount of lithium than compatibles used, their behavior in batteries should not differ from that of existing electrodes. The most advanced area of drastic batteries properties improvement is the use of nanomaterials that acquire unique physical and chemical properties due to the nanoscale level structurization.

| Material       | Average potential (V) | Specific capacitance (mA × h/g) | Specific energy (W × h/kg) |
|----------------|-----------------------|---------------------------------|---------------------------|
| LiCoO2         | 3.8-3.9               | 140-145                         | 546                       |
| LiNi0.8Co0.15Al0.05O2 | 3.7-3.8              | 180-200                         | 680-760                   |
| LiNi0.33Co0.33Mn0.33O2 | 3.7-3.8            | 160-170                         | 610-650                   |
| LiMn2O4        | 4.1                   | 100-120                         | 410-492                   |
| LiFePO4        | 3.4-3.45              | 150-170                         | 518-587                   |

In more recent times, along with the CSC, the ultra-high-volume capacitor structures (UCS) are intensely developing. At the first stage of UCS development high capacitance of capacitor structures was ensured by developing electrode materials with highly developed surface impregnated with electrolytes. Such capacitor structures are called supercapacitors. The surface quantity of carbon-based electrode materials amounts to 2000–2500 m²/g. The thick-film technology for supercapacitors differs from the CSC technology solely in that instead of a chemically-active material a highly porous carbon mixture is applied onto the current collector in the form of a thin metal (15-20 μm) foil.

At the second stage of development with the aim of improving energy intensity by way of increasing operating voltage polymer electrolytes became to be used that allowed operating voltage (U) increase from 1 ÷ 1.2 V to 4 V. The next stage of development is the electrical capacitance C and operating voltage U increase by way of using dielectrics. Dielectrics with high dielectric permeability, which among nanostructured materials amounts to 107 and higher (Ɛ ~ 104 for the monolithic ferroelectrics), can enable to considerably increase not only capacitance (200F/g and more), but also UCS operating voltage to the level of 4 V and higher. In this case the layer, in which electrical energy is accumulated, has a thickness on nanometer scales and is called double-electric layer (DEL).

The most advanced areas for drastic improvement of battery properties are the use of nanomaterials that due to the nanoscale level structurization acquire unique physical and chemical properties. To development of nanomaterials and nanostructures based CSC and UCS traditional microelectronics thin-film technologies are used (layers thickness changes from micro- to nanometers) [2]. The UCS technical standards are primarily determined by electrode materials and electrolytes design.

Being inferior to the chemical sources of current as for specific energy the supercapacitors significantly outperform them for the specific capacitance and charge-discharge characteristics stability in a wide temperature range. In addition, the ultracapacitors today exceed chemical sources of current by the number of charge-discharge cycles by an order of magnitude [9].

The amount of energy stored in the supercapacitors is determined by the sum capacitances:
1. - the electrochemical capacitance of double-electric layer [9], which is generated at the electrode-electrolyte interface;
2. - the pseudocapacitance, caused by chemical reactions between the electrode and electrolyte [10]
[10]. In this case, the electrons are formed by oxidative reactions and transferred across the border electrode-electrolyte interface region.
In addition to this, among the metals potentially usable for the capacitance increase there are RuO₂, MnO₂, NiO, Co₃O₄, SnO₂, ZnO, TiO₂, V₂O₅, CuO, Fe₂O₃, WO₃, etc. [11,12].

Capacitor structures-based power sources are mainly presented in the market by supercapacitors which capacitance under industrial conditions is 8 to 12 W·h/kg and 15 to 25 W·h/kg under laboratory ones, but they have significantly higher characteristics of power, charging time and the number of charge-discharge cycles (see table 2) [13]. Ceramic capacitors and hybrid power sources that integrate CSC and UCS properties are under laboratory studies. Hybrid power sources allow attaining energy intensity of about 40 to 200 W·h/kg [14]. Such power sources are also called pseudo capacitors, they store energy through reversible Faraday charges that assume rapid and reversible electrochemical redox reactions at the electrodes and electrolyte interface.

**Table 2.** Specific DEL (double-electric layer) capacitance in capacitor structures.

| Electrode | Electrolyte | Specific capacitance (F/g) | Specific capacity (W/kg) | Specific energy (W·h/kg) | Retention ability |
|-----------|-------------|----------------------------|--------------------------|--------------------------|------------------|
| Single-wall nanotubes (SWNTs) | 1 M propylene carbonate tetrafluoroborate/acetonitrile (EMIMBF₄/AN) | 160 F/g at 4 V | 24 kW/kg | 17 W * h/kg | 96.4% after 1000 cycles |
| Peeling reduced graphene oxide (rGO) | 1 M tetraethanolammonium tetrafluoroborate | 250 kW/kg | 70 W * h/kg | 97% after 10000 cycles |
| Nitrogen doped graphene | 0.5 M H₂SO₄ | 280 F/g at 20A/g in 6 M KOH | 800 kW/kg | 48 W * h/kg | 99.8% after 230000 cycles |
| Graphene aerogel | Non-soluble ionic liquid EMIMBF₄ | 151/3 F/g at 0.1 A/g | 10 kW/kg | ~42 W * h/kg | ~98% after 5000 cycles |
| 2D microscopic covalent triazine-based structure | | | | | |
| Co - Polyaniline (PANI) (poly (aniline - Co - 3 - fluoroaniline)) | 6 M KOH | 989 F/g 2 mV/s | 1.581 kW/kg | 352 W * h/kg | 79% after 10000 cycles |
| Co(OH)₂/ graphene film layers | 1 M KOH | 622 F/g at 2 A/g | 15.8 kW/kg | 86.6 W * h/kg | 80% after 10000 cycles |
| Ni(OH)₂/ graphene | 1 M KOH | 1335 F/g at 2.8 A/g | 10 kW/kg | 37 W * h/kg | 100% after 2000 cycles |
| MnO₂/ reduced graphene oxide (rGO) (hydrogel and aerogel) | 1 M Na₂SO₄ | 242 and 131 F/g at 1 A/g | 0.82 kW/kg | 212 W * h/kg | 89.6% 1000 cycles |
| Polyaniline (PANI)-graphene/Carbon nanotube (CNT) | 1 M KCl | 271 F/g with 0.3 A/g | 2.7 kW/kg | 188.4 W * h/kg | 82% after 10000 cycles |
| Patronite (VS₄)/ single-wall nanotube (SWNT)/reduced graphene oxide (rGO) | 0.5 M K₂SO₄ | 558.7 F/g at 1 A/g | 13.85 kW/kg | 174.6 W * h/kg | 97% after 1000 cycles |
| Polyaniline (PANI)/Graphene oxide (GO)/graphene | 2 M H₂SO₄ | 793.7 F/g at 1 A/g | 2.14 kW/kg | 50.2 W * h/kg | 80% after 10000 cycles |

[1] Patonite (VS₄) / reduced graphene oxide (GO) / graphene

[2] Patent (VS₄) / single-wall nanotube (SWNT) / reduced graphene oxide (rGO)

[3] Polyaniline (PANI) / graphene / Carbon nanotube (CNT)

[4] Co - Polyaniline (PANI) (poly (aniline - Co - 3 - fluoroaniline))

[5] MnO₂/ reduced graphene oxide (rGO) / graphene (hydrogel and aerogel)

[6] Polyaniline (PANI) / graphene / Carbon nanotube (CNT)

[7] Patronite (VS₄) / single-wall nanotube (SWNT) / reduced graphene oxide (rGO)

[8] Polyaniline (PANI) / graphene / Carbon nanotube (CNT)

[9] MnO₂/ reduced graphene oxide (rGO) / graphene (hydrogel and aerogel)

[10] Polyaniline (PANI) / graphene / Carbon nanotube (CNT)

[11] Patent (VS₄) / single-wall nanotube (SWNT) / reduced graphene oxide (rGO)

[12] Polyaniline (PANI) / graphene / Carbon nanotube (CNT)

[13] MnO₂/ reduced graphene oxide (rGO) / graphene (hydrogel and aerogel)

[14] Polyaniline (PANI) / graphene / Carbon nanotube (CNT)

[15] Patronite (VS₄) / single-wall nanotube (SWNT) / reduced graphene oxide (rGO)

[16] Polyaniline (PANI) / graphene / Carbon nanotube (CNT)

[17] MnO₂/ reduced graphene oxide (rGO) / graphene (hydrogel and aerogel)

[18] Polyaniline (PANI) / graphene / Carbon nanotube (CNT)

[19] Patronite (VS₄) / single-wall nanotube (SWNT) / reduced graphene oxide (rGO)

[20] Polyaniline (PANI) / graphene / Carbon nanotube (CNT)
Graphene structures (figure 1) with the hierarchical porous structure, high ion-accessible surface area, effectiveness of the electron and ion transfer routes allow developing electrode materials with a capacitance of 298 F/g or 212 F/cm³ in organic electrolyte [13].

Figure 1. Schematic illustration of graphene and porous graphene foams: (a), (b) - initial 3D macro-porous Graphene foam (a) and (b) - porous Graphene foam; (c), (d) - thin films (e) Graphene foam and (d) - porous Graphene foam; (e), (f) - closed type (e) Graphene and (f) porous Graphene film. Arrows indicate ions transfer routes [13].

Lithium-ion capacitor entirely on the basis of graphene, formed by reduced graphene oxide with the oxide nanoparticles coating (SnO₂-rGO), and on the other hand, anode - capacitor electrode based on activated reduced graphene oxide (a-TEGO). The power density of this supercapacitor is about 200 Wh/kg. CNT-NiO composite synthesized by way of nickel oxide nanoparticles growth in suspension with carbon nanotubes during the hydrothermal process demonstrated capacitance increase from 122 F/g to 1600 F/g at the scan rate of 2 mV/sec in the alkaline electrolyte as compared to pure nickel oxide. The specific capacity increase was also observed with V₂O₅ composite nanoconductors and multi-walled carbon nanotubes, which demonstrated 450 F/g specific capacity at current density of 1 A/g, which is much higher (100 F/g) than the characteristics of pure V₂O₅ nanoconductors [12].

Thin-film technologies produce not only new and advanced structures for CSC and UCS but provide for significant improvement of characteristics of standard structures by thick-film technologies [14].

On the basis of the CSC and UCS development analysis it was shown that the development prospect in this area is the development of new nanomaterials and nanotechnologies. Therefore, the development of advanced CSC and UCS design should be carried out in the following areas:
- development of a uniform nanostructurized electrode material for the CSC and UCS;
- development of an active nanostructurized mass for the CSC;
- development of ceramic and polymer-ceramic materials of high inductive capacitance;
- development of uniform electrolytes and separators.

The breakthrough and foremost goals should be considered development of new electrochemical systems, structures and technologies that provide developing current sources with wider charge-discharge cycles range (over 2000-10 000) and higher specific energy (over 500-1000 W·h/kg).

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