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Y.A. Maletin, S.I. Chernukhin, N.G. Stryzhakova, S.G. Kozachkov

COMBINATION OF SURFACE WITH BULK: HYBRIDS OF SUPERCAPACITORS WITH Li-ION BATTERIES

Institute for Sorption and Problems of Endoecology of National Academy of Sciences of Ukraine
YUNASKO-Ukraine LLC
13 General Naumov Str., Kyiv, 03164, Ukraine, E-mail: ymaletin@gmail.com

As it turns out, the right combination of Li-ion and supercapacitor ingredients in both the positive and negative electrodes, as well as in the electrolyte, can significantly improve the characteristics of such a hybridized power supply as compared with "parent" systems. While Li-ion components provide large volumetric energy, the high surface area of nanoporous carbon borrowed from supercapacitor technology provides fast charge-discharge of the corresponding electric double layer and facilitates the intercalation-deintercalation processes in the Li-ion components. This full hybridization of the system can increase the energy density by 10 times that of a supercapacitor while maintaining the relatively high power density, long cycle life, and fast charging characteristics of supercapacitors. In addition, charge-discharge curves and low self-discharge currents become similar to those of Li-ion batteries. Such power supplies with a specific energy of 60+ Wh/kg, a full charge within 5–6 minutes and more than 30 K full charge-discharge cycles can be successfully used, for example, in urban transport or robotics in warehouses where the range is less critical than fast charging capability, long service life and safe operation. This article discusses the methods of full hybridization and the achieved characteristics of electrochemical systems "supercapacitor and Li-ion battery". Special attention is paid to the "interaction" of the activated carbon surface with the channels in the bulk lithiated metal-oxide material of the electrodes to accelerate the charge-discharge processes.

***Keywords**: supercapacitors, Li-ion batteries, hybridization, high energy and power, fast charging*

INTRODUCTION

Until recently, electrochemical power supply technologies were developing in two directions: on the one hand, various types of batteries are used, in particular, Li-ion batteries (LIB), which provide high energy density, however, at a relatively low power density. As a result, the use of LIB may become dangerous in high power modes, especially when fast charging with high current. On the other hand, a supercapacitor (SC) is used to obtain short-term super-powerful energy pulses [1] and long service life: up to millions charge-discharge cycles. However, the low energy density usually not exceeding 20 J/g [1] or about 6 Wh/kg in commonly used engineering units, and the relatively fast self-discharge are still obvious disadvantages of SCs compared to batteries. A known approach [2, 3] to increase the SC energy density due to replacing one of the two electrodes with that from a battery technology cannot improve the situation significantly since in such a series connection of two different electrodes the low capacity electrode borrowed from SC technology limits the capacitance thus providing an approximately 2-fold increase in energy, namely, only up to 40–50 kJ/kg or 12–15 Wh/kg in common engineering units. Alternatively, a parallel combination of SC and battery (LIB or fuel cell or both) is a natural and effective solution to this issue, where the battery provides the required energy consumption, while SC covers peak loads [4, 5]. However, the parallel combination of two current sources, each of which contains a number of SC and LIB single cells connected in series to achieve the desired voltage, leads to a corresponding increase in mass and volume caused by a separate packaging of each source, two monitoring and managing systems (BMS), and additional contacts. This increase may be insignificant for some stationary applications, but the weight and/or volume of power supply is very critical for numerous moving or portable objects, such as, e.g., electric vehicles, aircrafts and smart phones. Therefore, other solutions should also be sought, one of which may involve the full internal hybridization of electrochemical systems of SCs and batteries at the level of both positive and negative electrodes and electrolytes. The theoretical justification of such a "parallel" hybrid was proposed by Cericola and Kötz [2] and practically implemented in [6, 7]. Over the past years, our laboratory has developed various versions of the “parallel” SC-LIB hybrid systems and, in cooperation with Yunasko-Ukraine LLC, has manufactured experimental batches of cells with capacities from 1.2 Ah to 3.0 Ah. This article is devoted to their description.

EXPERIMENTAL

System formation methodology. The general approach to a hybrid electrochemical system can be described as follows:

- Both positive and negative electrodes are fabricated by mixing powders of nanoporous carbon material and lithiated transition metal oxide or phosphate; the negative electrode contains nanosized lithium titanate powder, while the positive electrode contains any cathode material(s) known in the LIB technology;
- The nanoporous carbon in the positive and negative electrodes can be different to best match the respective potential ranges with the Li-ion components and prevent going beyond the potential ranges during charge-discharge processes;
- A binding agent and electrically conductive additive (special carbon black and/or graphite) are added to the powdered mixture of the active electrode components; the resulting composite is applied to an aluminum foil (current collector), thus forming an electrode;
- As an electrolyte, it is desirable to use solutions of chemically stable lithium salts common for LIB technology, such as lithium *bis*(trifluoromethanesulfonyl)imide (LiTFSI) in acetonitrile, the solvent widely used in SC technology. To increase the conductivity, it is preferred to use acetonitrile instead of carbonate solvents, which are commonly used in LIB technology.

Anodes in all systems contained the nanosized $Li_4Ti_5O_{12}$ (LTO) produced by Johnson Matthey, Germany. Fabrication of anodes was accomplished as follows: a mixture of 98 g of LTO with 10 g of carbon conductive composite material (SuperP-Li carbon black produced by TimCAL and YP80F carbon powder produced by Kuraray, Japan) and 7 g of polyvinylidenefluoride (PVDF binder produced by KYNAR) was suspended in 170 ml of N-methylpyrrolidone (NMP, CHROMASOLV Plus produced by Honeywell) followed by applying the slurry obtained to the surface of Al foil (a current collector, 20 microns thick). The electrode layer was then dried in vacuum and calendered to obtain the final thickness of 60 microns.

Cathodes of two types were fabricated as follows: a mixture of 102 g of Li-Ni,Co,Al oxide (NCA, produced by TODA AMERICA) or 102 g of $LiMn_2O_4$ (LMO, NANOMYTE produced by NEI Corp.) with 9 g of carbon conductive composite material and 5 g of PVDF binder as specified above was suspended in 130 ml of NMP followed by applying the slurry obtained to the surface of a current collector foil. The electrode layer was then dried in vacuum and calendered to obtain the final thickness of 40 microns in case of NCA or 85 microns in case of LMO.

As an electrolyte, 20 % solution of Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Extra dry from Solvionic) in acetonitrile (CHROMASOLV for HPLC produced by Honeywell) was prepared.

Prototype fabrication and testing methodology. Cathodes and anodes 42×85 mm in size were cut out, followed by the formation of electrode packages of various thicknesses to obtain the required capacity. The current collectors of electrodes in the package were welded to the corresponding positive or negative current leads made of Al foil 0.5 mm thick. Then the stack thus formed was packed in a shell made of laminated aluminum foil, partially sealed and filled with electrolyte through a special tube, aged and degassed followed by final sealing. All the assembly operations were carried out in a glove box filled with dry Ar gas.

The cells thus fabricated were charged in CCCV mode (constant current - constant voltage) followed by discharging them at various current values - see Fig. 1, and at various temperatures – see Fig. 2. Besides, the cells were discharged under constant power conditions in order to observe their energy retention with an increase in load – see Ragone plots in Fig. 3. Finally, the cells were continuously cycled with 10C-rate to determine their service life – see Fig. 4.

RESULTS AND DISCUSSION

Fig. 1 illustrates the capability of hybrid cells to charge and discharge at high current values. Charging current can exceed 10C-rate and in CCCV mode the cells can be fully charged within 6 min. When discharging, the current can exceed 100C-rate while still delivering about 60 %

charge to the load. Another positive effect of the full system hybridization can be seen in Fig. 2, which shows the results of the discharge at various temperatures and current rates. Even at low temperature, hybrid cells are capable to work efficiently, transferring the significant charge to the load at high current values. In addition, the cells are characterized by a fairly low self-discharge retaining at least 90 % of their charge after a month of storage “on the shelf”.

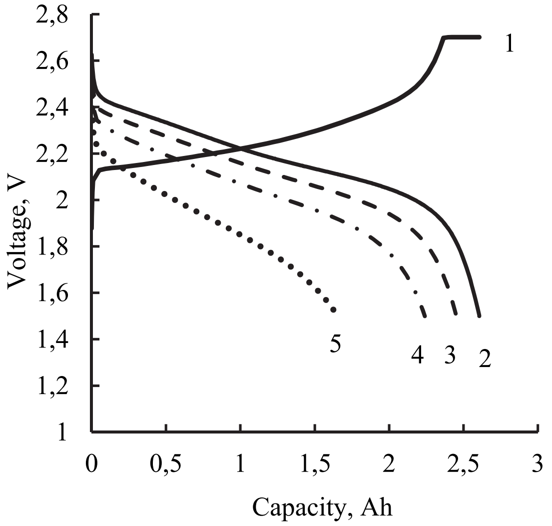

Fig. 1. Charge-discharge curves of a hybrid cell (0.1 kg, 2.8 Ah, NCA-containing cathode) at high loads: *1*, *2* – charge/discharge current 30 A; *3* – discharge current 100 A; *4* – discharge current 200 A; *5* – discharge current 300 A

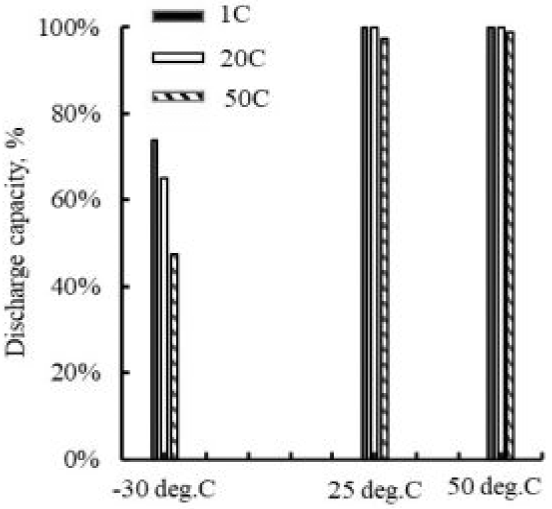

Fig. 2. Discharge capacity retention at various C-rates and temperatures (NCA-containing cathode)

Various energy storage technologies and “electrode chemistries” can be compared using the Ragone plot [8], which shows the decrease in energy density with increasing output power density and is usually presented on a logarithmic scale. The curves can be obtained by discharging a fully charged cell under constant power conditions, and the results for hybrid cells with NCA or LMO composite cathodes are shown in Fig. 3. This Figure illustrates some advantage of NCA containing cells compared to those with LMO in both energy and power capabilities. To get even more comprehensive comparison of the performance of these materials, we have also tested their cycle life. In the tests the cells were continuously cycled with 10C-current rate at room temperature and their degradation (a decrease in capacity and an increase in resistance in %) was monitored. Horizontal dashed lines show acceptable limits according to international standards [9], namely, 20 % decrease in capacity and/or 100 % increase in resistance.

If the data of Figs. 3, 4 are compared, one can see the possible options for electrode chemistry with their pro and contra. As an example, the use of NCA in cathode can provide higher energy and power density than LMO, while LMO can provide much longer cycle life than NCA. It is worth also noting that even after the acceptable level of degradation is reached at 30K-40K cycles the LMO-based system continues to work further with a smooth degradation. This can help to select the best material combination for a particular application.

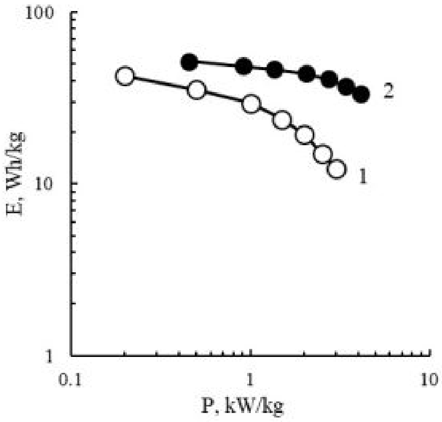

Fig. 3. Ragone plots for hybrid cells with LMO (*1*) or NCA (*2*) material in cathode

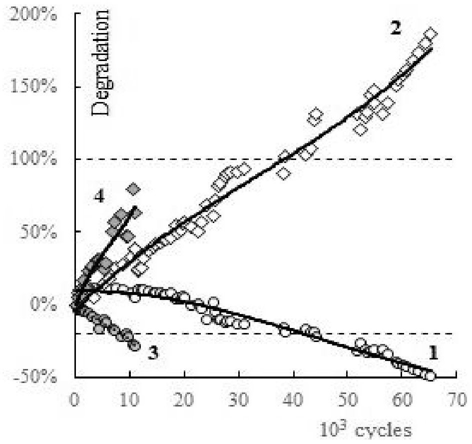

Fig. 4. Degradation of hybrid cell capacity and resistance over cycling: 10C charge-discharge current; LMO (*1* – capacity; *2* – resistance) or NCA (*3* – capacity; *4* – resistance) material in composite cathode

Now the question can arise how a small amount of YP80F nanoporous carbon (about 5 wt. %) is able to increase significantly the specific power of composite electrodes in a hybrid cell. A possible explanation may be as follows. Despite the small mass of nanoporous carbon in the composition of the electrode, an increase in the surface area of the electrode is enormous. This is easy to see if we compare the specific surface area of carbon (~ 2100 m^2/g) with the specific surface area of LTO (~ 8 m^2/g), LMO (~ 1 m^2/g) or NCA (~ 1 m^2/g). In addition, the bulk density of YP80F carbon used in this study is approximately an order of magnitude lower than that of Li-ion components, and, therefore, the volume fraction of nanoporous carbon in the electrode composition is significant. Still, the electrode capacity is obviously due to the accumulation of Li^+ ions in the ion-conducting channels in the bulk of the metal oxide component, while the carbon surface can contribute a small part of the capacity only. On the other hand, the rate of intercalation-deintercalation processes is approximately proportional to the concentration of Li$^+$ ions near the channels and, therefore, a huge additional surface in the immediate vicinity of the Li-ion components, easily accessible to the electrolyte and quickly replenished, can serve as a reservoir to facilitate the transfer of ions back and forth during charging and discharging the corresponding electrode.

To check this hypothesis, a hybrid system was modeled[1] with a parallel combination of SC and LIB if their mass or capacity ratio corresponds to that in a hybrid composite electrode. Fig. 5 illustrates the simulation result, which can be explained by the well-known expression relating the capacitance C to current I: $C = I\Delta t/\Delta U$, where Δt is the discharge duration, and ΔU is the change in voltage during the discharge. Correspondingly: $I = C\Delta U/\Delta t$, and with a small change in voltage (since the voltage is maintained by a battery connected in parallel with a SC – e.g., see Fig. 5), a high current can be expected in a very short time. With a long duration of time, the current flowing through the SC becomes very low. On the other hand, the obvious effect of SC component connected in parallel with a LIB component in a hybrid electrode may be due to the "relay effect" when the former provides its huge and rapidly charged-discharged surface to facilitate the corresponding discharge-charge processes in the bulk of the LIB component. In addition, no charge or mass transfer occurs across this additional surface, but only the charge-discharge of the electrical double layer, and therefore this electrolyte reservoir is not blocked by the formation of SEI. This effect may be the reason for the extended service life of the hybrid system.

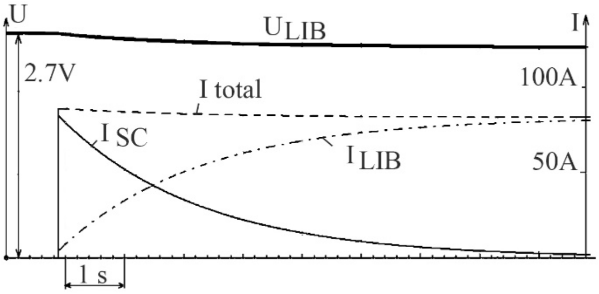

Fig. 5. Currents I flowing through a SC and LIB along with the total current through the circuit if SC and LIB cells of the same voltage of 2.7 V are connected in parallel

CONCLUSIONS

- Internal parallel or full hybridization of supercapacitors and Li-ion batteries can significantly improve some of the performance of both systems and allows to fill the gap between the two technologies.
- This full system hybridization allows for 10 times the energy density of a supercapacitor while maintaining a much higher power density than a Li-ion battery.
- Hybrid power supplies with a specific energy of 60+ Wh/kg, a full charge within 5–6 minutes and up to 60K+ full charge-discharge cycles can be successfully used, for example, in charging stations, in urban transport or robotics in warehouses where the range is less critical than fast charging capability and long lifespan.

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[1] The authors are grateful to A.A. Slezin for simulating such a hybrid system with the use of Multisim

Комбінування поверхні з об’ємом: гібриди суперконденсаторів з Li-іонними акумуляторами

Ю.А. Малєтін, С.І. Чернухін, Н.Г. Стрижакова, С.Г. Козачков

Інститут сорбції та проблем ендоекології Національної академії наук України
ТОВ Юнаско-Україна
вул. Генерала Наумова, 13, Київ, 03164, Україна, ymaletin@gmail.com

Як виявилося, правильна комбінація Li-іонних і суперконденсаторних компонентів як у позитивному, так і в негативному електродах, а також в електроліті може значно покращити характеристики такого гібридного джерела живлення в порівнянні з «батьківськими» системами. У той час як Li-іонні компоненти забезпечують велику об’ємну енергію, висока площа поверхні нанопористого вуглецю, запозичена з технології суперконденсаторів, забезпечує швидкий заряд-розряд відповідного подвійного електричного шару та полегшує процеси інтеркаляції-деінтеркаляції в Li-іонних компонентах. Ця повна гібридизація системи може збільшити питому енергію в 10 разів, ніж суперконденсатор, зберігаючи при цьому відносно високу питому потужність, тривалий термін служби та характеристики швидкої зарядки суперконденсаторів. Крім того, криві заряд-розряд і низькі струми саморозряду стають подібними до Li-іонних акумуляторів. Такі джерела живлення з питомою енергією понад 60 Вт·год/кг, з можливістю повного заряду протягом 5–6 хвилин і понад 30 тисяч повних циклів заряду-розряду можуть успішно використовуватися, наприклад, в міському транспорті або робототехніці на складах, де довжина пробігу після одного заряду є менш критичною, ніж можливість швидкої зарядки, тривалий термін служби та безпека експлуатації. У статті розглядаються методи повної гібридизації та досягнуті характеристики електрохімічних систем «суперконденсатор і Li-ion акумулятор». Особливу увагу приділено «взаємодії» поверхні активованого вугілля з каналами в об’ємі літійованого металооксидного матеріалу електродів для прискорення зарядно-розрядних процесів.

***Ключові слова**: суперконденсатори, Li-іонні батареї, гібридизація, висока енергія та потужність, швидка зарядка*

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