

Current sources based on supercapacitors with β -active isotopes*

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Abstract

In asymmetric supercapacitors, electric charges are separated and accumulated in conditions of neutron irradiation. The paper presents the results of studying current sources with radioactive isotopes (CSRI) based on supercapacitors of 100 F made by neutron activation of the elements of the substances (BN or SrO) introduced to the electrodes. Following the neutron irradiation with a dose of up to 400 Gy, the supercapacitors turn into CSRI and have a charging rate of up to 7.8 $\mu\text{V}/\text{day}$. The CSRI charging rate increases in proportion to the activation with a neutron dose up to 14 kGy. This is explained by the production of β -active isotopes as a result of the $^{14}\text{N}(n, p)^{14}\text{C}$ and $^{88}\text{Sr}(n, \gamma)^{89}\text{Sr}$ reactions in the supercapacitor electrode materials. Estimation of the radiation-induced charge accumulation rate, with regard for the energy released during β -decay of ^{14}C and ^{89}Sr , excludes the known mechanisms of charge separation in a condensed environment due to the ionization and production of secondary electrons, the production of electron-hole pairs, etc. The electric charge separation and accumulation in CSRI take place as a result of non-equilibrium thermoelectric phenomena in the near-electrode nanoregions. Nuclear reactions in nanoscale regions produce “temperature gradients” of up to 10⁵ K/nm, this leading to up to 10¹³ electrons “evaporating” from nanocrystallites at times of $\sim 10^{-11}$ s.

Keywords

Current sources with radioactive isotopes (CSRI), supercapacitor, neutron irradiation, radiation-induced electric charge

Introduction

The most promising as readily available sources of current with a long autonomous operating life are sources based on direct conversion of nuclear to electric energy in which

the decay of radioactive isotopes leads to radiation-induced separation of electric charges. Many types of direct nuclear to electric energy converters have been developed and manufactured for the past six decades (Stepanov and Chernov 2019). Apart from ensuring the radiation

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safety requirements, the use of direct energy conversion is held back by the variety of the currently marketable conversion devices being highly expensive. High cost is explained by the expensiveness of the required isotopes (β - or α -active) and by the complexity of radioactive material handling. For this reason, such energy sources have had application where these can be used regardless of costs, say, in spacecraft or military hardware.

Supercapacitors with internal induced radioactivity can be effective alternative sources of current. The required effect from direct nuclear to energy conversion is achieved thanks to an extremely large interphase area in which radiation-induced separation of charges takes place. Expensive fabrication of systems with radioactive substances is substituted by nuclear doping in the neutron field of the normally factory-made semi-finished item when, as a result of the interaction with neutrons, the elements introduced to the electrode material turn into radioactive isotopes and the supercapacitor turns into a current source with a radioactive isotope (CSRI).

Physical simulation of the electric charge separation processes in a CSRI was performed earlier by measuring the electrophysical characteristics of supercapacitors in which the role of the radioactive isotope was played by continuous penetrating neutron radiation (Chernov et al. 2016). This paper presents the investigation results for irradiated asymmetric electrodes of supercapacitors with a solid inorganic electrolyte (Ag_4RbJ_5), and (Stepanov et al. 2018a, 2018b, 2018c) for those with an organic electrolyte (TEATFB solution in propylene carbonate). The electric charge separation and accumulation on the electrodes was observed immediately in the process of neutron irradiation. It was shown that the charge accumulation depended on the electrode asymmetry, did not depend on the neutron flux, and was defined by the absorbed radiation dose. The CSRI performance can be estimated using the ratio of the electric charge surface density value on the metal-dielectric-metal (MDM) conductor, $\rho \sim 10^{-8} \text{ C}/(\text{Gy} \cdot \text{m}^2)$, obtained experimentally in (Chernov et al. 2016, Stepanov et al. 2019) to the absorbed dose rate. This value is constant irrespective of the MDM structure type and the radiation type (electron, neutron or ion radiation).

It turned out that the voltage between the electrodes and the capacity of the supercapacitors increased also after the irradiation was over. This is connected with the induced radioactivity resulting from the neutron activation of the inorganic and organic electrolytes and of the electrode's carbon material. An active isotope with a half-life of $T_{1/2} = 18.642$ days (β –1.8 and 0.7 MeV, γ –1.08 MeV) is produced in the solid electrolyte as a result of the $^{85}\text{Rb}(n, \gamma)^{86}\text{Rb}$ reaction, and an isotope with a half-life of $T_{1/2} = 10.776(3)$ years (β – 0.72 MeV, and γ –0.54 MeV) results from the $^{85}\text{Rb}(n, p)^{85}\text{Kr}$ reaction (EXFOR). A β -active (0.155 MeV) isotope, ^{14}C , with a half-life of $T_{1/2} = 5700$ years is produced in organic electrolytes and in the electrode material, as a result of the (n, γ) -reaction, from ^{13}C which is present in natural uranium in the amount of 1.07%, and from dissolved nitrogen as a result of the $^{14}\text{N}(n, p)^{14}\text{C}$ reaction.

The paper presents the investigation results for the CSRI mockups in the form of supercapacitors with β -activity of one of the electrodes which results from the neutron activation of the preliminarily introduced substances.

Measurement procedures and results

The supercapacitors (SC) and the CSRI mockups with a capacity of 100 F and an internal resistance of $\sim 1 \text{ k}\Omega$ were manufactured at JSC “ELECOND”. The area of the electrodes was $\sim 40 \text{ cm}^2$, and the effective area was $\sim 2000 \text{ m}^2$. The electrodes consisted of absorbent carbon with a binding agent (fluoroplastic, butadiene-styrene latex, carboxymethyl cellulose). The organic electrolyte represented the TEATFB solution in propylene carbonate with a varying molar concentration in a range of 0.01 to 1 mol. One of the CSRI electrodes contained nanoparticles of either BN or SrO in the amount of $1 \text{ mg}/\text{cm}^2$, unlike the SC in which both electrodes were identical.

The SC and CSRI mockup specimens with BN and SrO were irradiated with neutrons with a dose rate of $0.1 \text{ Gy}/\text{s}$ in a leak-tight container with preliminarily annealed silica gel. Fig. 1 shows the results of measurements immediately in the process of neutron irradiation for $\sim 5500 \text{ s}$. Following the neutron irradiation, as a result of the $^{14}\text{N}(n, p)^{14}\text{C}$ and $^{88}\text{Sr}(n, g)^{89}\text{Sr}$ reactions, β -active carbon or strontium isotopes were produced in the electrode material. The results of measuring the differences of potentials on the SC and CSRI specimens with BN and SrO after 15 days of irradiation are presented in Fig. 2

In the process of irradiation for $5.5 \cdot 10^3 \text{ s}$, the residual potential on the specimens ($\sim 20 \mu\text{V}$) decreases to 40% of the initial value. The residual potential reduction is likely to be explained by the partial ionization in the double near-electrode electric layer in the electrolyte, its shorting and, as a sequence, the SC and CSRI discharge. It can be seen from Fig. 2 that the difference of potentials grew to

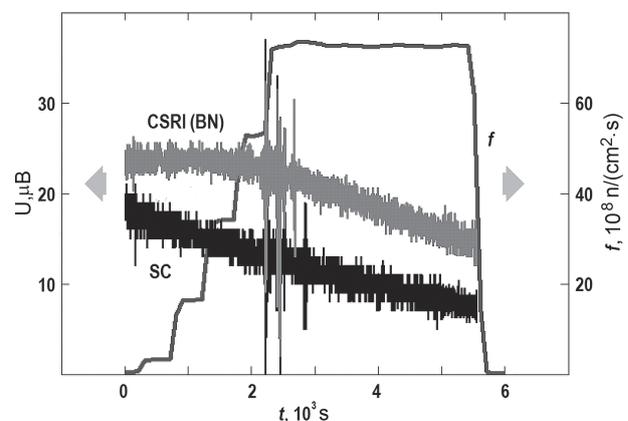


Figure 1. Intensity of neutrons, f , and difference of potentials, U , for a supercapacitor (SC) and a CSRI mockup in the process of irradiation.

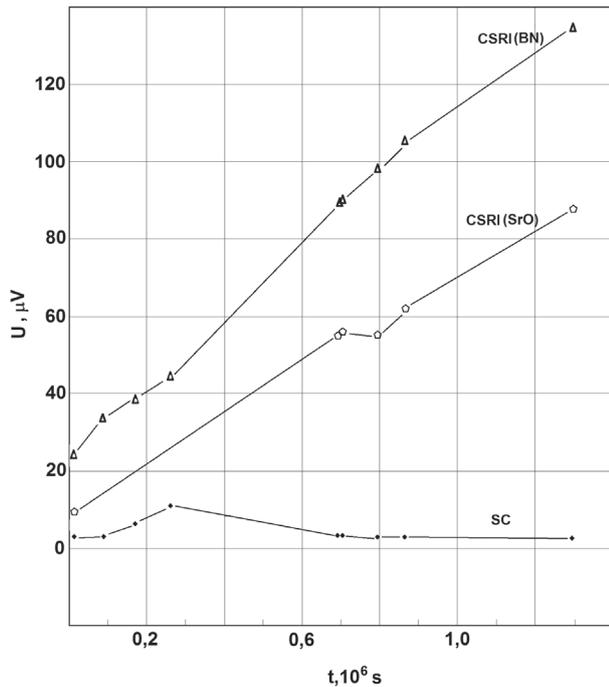


Figure 2. Difference of potentials as a function of time for the current source (CSRI) and supercapacitor (SC) specimens irradiated with neutrons with a dose of $2.9 \cdot 10^{13}$ n/cm².

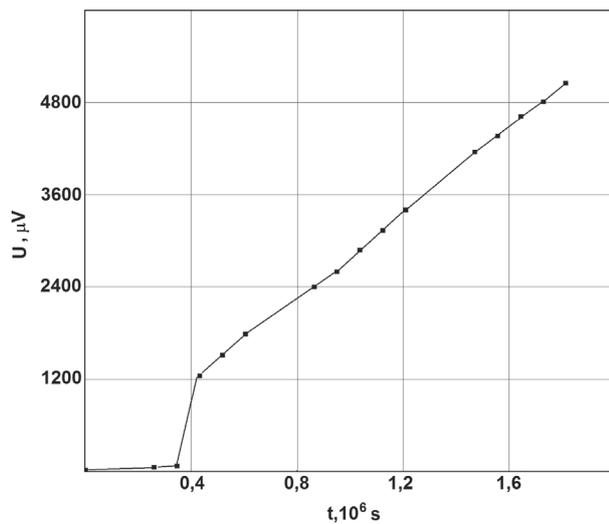


Figure 3. Change in the difference of potentials for the CSRI (BN) specimen irradiated with neutrons to a dose of $1.0 \cdot 10^{15}$ n/cm².

70–130 μV after the neutron irradiation with a dose of $2.9 \cdot 10^{13}$ n/cm² in a CSRI for $1.3 \cdot 10^6$ s. The difference of potentials on the SC does not change with an accuracy of 5 μV during the same time.

To study the effect of the exposure dose and the content of β -active isotopes on the variation rate of the difference of potentials on the electrodes, the CSRI (BN) was additionally irradiated to a dose of $1.0 \cdot 10^{15}$ n/cm². Prior to this, the mockup electrodes were shorted for 10^4 s. Following the irradiation, after 17 days of holding for the short-lived gamma activity from the CSRI structural components to decay, the CSRI (BN) electrodes were

also shorted for four days ($3.5 \cdot 10^5$ s). The results of further 21-day ($1.8 \cdot 10^6$ s) measurements for the difference of potentials are shown in Fig. 3. By the measurement time, the difference of potentials was 20 μV , and after $3 \cdot 10^5$ s, as can be seen in the figure, the voltage growth changed from slow to rapid.

Discussion of the measurement results

An important experimental result to confirm the feasibility of a supercapacitor-based CSRI is the measurement data for the charging rate variation with an increase in the neutron activation dose. A comparison of the diagrams in Figs 2, 3 shows that the CSRI (BN) specimen charging rate increased by a factor of 31, from 7.8 to 240 $\mu\text{V}/\text{day}$, with the neutron irradiation dose increased by a factor of 34.5. This proves the charge separation rate proportionality to the quantity of β -active ^{14}C isotopes in the supercapacitor electrode.

Certain conclusions with respect to the microscopic mechanisms of charge separation in the CSRI mockups can be made from analyzing the kinetics of the potential difference variation on the specimen electrodes. For 10^6 s, the difference of potentials increases by ~ 100 μV (see fig. 2), this corresponding to the charge accumulation rate of $\sim 10^{-8}$ C/s. On the other hand, one can estimate the number of decays per unit of time resulting from the neutron activation of isotopes. With regard for the known data on the $^{14}\text{N}(n,p)^{14}\text{C}$ reaction cross-section (EXFOR) and the neutron energy in the energy range from thermal to 10^4 eV, we obtain that the fraction of active ^{14}C nuclei with a dose of $2.9 \cdot 10^{13}$ n/cm² is $\sim 10^{-11}$. The content of BN is 40 mg, which corresponds to $5 \cdot 10^{20}$ atoms of nitrogen throughout the electrode and $5 \cdot 10^9$ carbon isotopes formed. The nuclei of ^{14}C experience β -decay with a half-life of 5700 years ($1.8 \cdot 10^{11}$ s), this meaning approximately one decay for 100 s throughout the CSRI (BN) electrode. Assuming that all nuclear reactions lead to the charge separation between the electrode and the electrolyte, one decay leads to $\sim 10^{13}$ electrons moving through the double near-boundary electric layer.

A similar result is obtained for the CSRI (SrO). The effective average cross-section of $^{88}\text{Sr}(n, \gamma)^{89}\text{Sr}$ (EXFOR) for the neutron spectrum is three barns, so the fraction of activated isotopes is also $\sim 10^{-11}$. With regard for the total number of Sr atoms ($5 \cdot 10^{19}$) and the ^{89}Sr half-life of 54 days ($4.7 \cdot 10^6$ s), we have an estimate of several tens of decays per second. This corresponds to the movement of up to 10^9 – 10^{10} electrons through the *carbon layer–electrolyte* boundary as the result of one nuclear transformation.

Such estimate, given the energy of 0.155 MeV (^{14}C) and 1.5 MeV (^{89}Sr) released during β -decay, excludes the mechanisms of charge separation as the result of the secondary electron ionization and production, the electron-hole pair formation, etc. Actually, the number of sec-

ondary electrons, with the ionization energy being over 1 eV, cannot exceed 10^6 . Besides, the estimates for the CSRI with electrodes with BN and SrO differ by three or four orders of magnitude, while the experiment produces an approximately similar result. The mechanisms of the electric charge separation and accumulation in CSRI are most likely connected with microscopic non-equilibrium phenomena of thermionic transport through a double electric layer with a thickness of several interatomic distances on the boundary with the electrolyte.

The energy released during β -decay leads to the temperature of electrons in nanoregions on the surface of the conducting graphitized carbon electrode increasing to 1–2 eV. At times of up to 10^{-13} s, the lattice temperature increases to the same values, and the so-called thermopeak occurs which can exist in nanosize crystallites at times of up to 10^{-6} – 10^{-7} s. Estimations in accordance with (Stepanov 1998), using gas-dynamic ratios of transport in conditions occurring in the nanometer scale of the “temperature gradients” of up to 10^{14} K/m, lead to the values of the electron “evaporation” rate from nanocrystals at a level of up to 10^{13} at times of up to $\sim 10^{-11}$ s.

The process is stochastic and highly nonhomogeneous along the interface, the driving force for which is local “temperature” surges to 1–2 eV. Up to 10^{13} electrons move through the double electric layer during such “thermopeaks”. Nonhomogeneity of the charge distribution along the surface (nonhomogeneity of the double electric layer formed) leads to lengthy processes of charge flowing and equalization in the near-surface electrolyte layer, which probably causes the initial slowdown of the CSRI

charging process for $3 \cdot 10^5$ s, as can be clearly seen in Fig. 3. Long-term relaxation in the supercapacitor recharging processes is a well-known fact (Uchaykin et al. 2016, Bertrand et al. 2010).

Conclusion

Mockups of current sources with radioactive isotopes (CSRI) based on supercapacitors have been made by neutron activation of the elements of the substances introduced to the electrodes (BN, SrO). Following the neutron irradiation with a dose of $2.9 \cdot 10^{13}$ n/cm² for $1.3 \cdot 10^6$ s, the difference of potentials grew to 70–130 μ V with no changes in the test specimens within 5 μ V.

It has been shown that the CSRI charging rate increases in proportion to the neutron activation dose of up to $1.0 \cdot 10^{15}$ n/cm². The CSRI charge accumulation rate is proportional to the number of the β -active ^{14}C isotopes produced as the result of the (n,p)-reaction on the BN noncrystalline nitrogen introduced to one of the electrodes.

Estimating the radiation-induced charge accumulation rate, with regard for the energy released during β -decay of ^{14}C and ^{89}Sr , excludes the known mechanisms of charge separation in a condensed environment as a result of the secondary electron ionization and production, the electron-hole pair formation, etc. The electric charge separation and accumulation in a CSRI is most likely caused by non-equilibrium thermionic phenomena in near-electrode nanoregions.

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