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Effect of radiation on the performance of activated carbon base supercapacitor: Part II. Influence of electron irradiation exposure on full cell

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Abstract

This work presents the effect of electron irradiation on the full symmetric cell using the pure polymer base AC material and irradiation on the full cell was analyzed for different exposure times. An improvement of the current response and ideal EDLC behaviour of the full device was also recorded with increased exposure to electron irradiation for up to 48 h. However, after the source of irradiation was removed, the original capacitance of the device was restored. This interesting phenomenon is a novel finding which is being reported for the first time. The recovery of the material after the radiation source terminated is based on the ability of the carbon-based nanostructured material to self-heal itself in a bid to return to its original form. These results suggest that radiation can improve supercapacitor performance permanently or temporary based on the radiation source.

Keywords: Electron irradiation; activated carbon; supercapacitor; radiation activated carbon.

1. Introduction

Energy storage has been pegged to play a major role in successfully addressing the ongoing energy crisis worldwide due to the fact that most renewable energy sources need to have an efficient backup system to adequately manage the as-generated energy for specific applications. In addition, the time dependency of some of these renewable energy technologies (such as solar, wind etc.) necessitates the storage requirement [1]. Supercapacitors (SCs) which is an emerging technology with the potential to solve the drawback of battery technology in use today is

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still set back by low energy densities for specific application requiring high power density. Although they have been able to provide high power with long cycle life coupled with low maintenance cost in some applications, there is still a lot that needs to be done if they are to replace high-performance battery technology or be used in combination with battery systems [2].

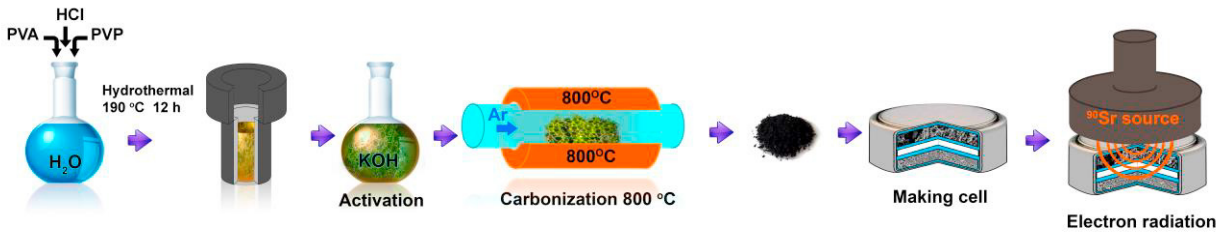
Numerous scientists have attributed the solution to be closely linked to the materials and electrolytes adopted in the supercapacitor devices to obtain novel high-performance devices with high energy density and characteristic high power density. Digressing from the search for new materials and focusing into the existing SC-materials, it is imperative to study in detail their intrinsic properties especially those which have been successfully adopted in commercial electrochemical capacitors (ECs). Most commercial ECs are made up of EDLC-type materials, consisting of activated carbons (ACs), characterized by a hierarchically porous structure and the amorphous disordered structure. Such properties enable it to actively transport ions within the electrolyte and store charges in the process.

For decades, it was the opinion of most scientists that the bombardment of solid materials with specific energetic ion beams or irradiations would generate defects and disorder, therefore, deteriorating the materials in an undesirable manner. However, recent investigations involving benefit of radiation on supercapacitor electrodes material [3]. However, until now, there has been no study on the effect of an electron or ion radiation on a full cell of SCs.

In our study, a complete device was subjected to electron radiation exposure to analyze if there is any restructuring of the material architecture when in operation. It is expected that the radiation could have beneficial effects on the constituent materials within the cell which could provide a positive effect on the entire device electrochemical behavior. The results from this study showed an improvement in the current response from the cyclic voltammetry plots which could be attributed to the formation of extra covalent bonds within the disordered activated carbon structure as seen in earlier reports [4] on similar carbon-based nanostructured materials. The observed improvement in the full device will also be discussed in details with initial propositions made on possible reasons for these observed enhancements. These results can be useful in nuclear power stations, nuclear submarines and hospital radiation facilities. Furthermore, future designs could also include omitting the radiation shields from the components of the entire units containing the supercapacitor devices.

2. Material and methods: Electrode preparation, cell fabrication, and Irradiation

Scheme 1 shows the preparation process of the electron radiation cell. First, activated carbon (AC) from pure polymer (without any additive) was produced and assembled according to reference [5].



Scheme 1. Schematic diagram of the preparation process of the electron radiation cell

Strontium 90 (^{90}Sr) was used as the electron radiation source. The diameter of the ^{90}Sr source was the same as the current collector of the cell. The cell case made of stainless steel 304 with a thickness of 0.2 mm and a diameter of 16 mm. The cell was exposed to the electron source for varying times before being electrochemically tested to obtain the effect of radiation exposure on the cell performance.

The electrochemical tests used to determine the performance of the symmetric cell was carried out in two-electrode cell configuration with a glass microfiber filter paper adopted as the separator in a 6 M KOH aqueous electrolyte solution. All electrochemical measurements namely, cyclic voltammetry (CV), chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS) were carried out using a Bio-logic VMP-300 potentiostat.

The CV tests were carried out in an operating voltage range of 0 - 1 V at different scan rates. Electrochemical impedance spectroscopy (EIS) measurements were conducted in the frequency range from 0.1 Hz to 100 kHz with

an open circuit potential (0 V). The CV, CP and EIS measurements of the supercapacitor device were also carried out before any radiation so that proper comparison can be made with the radiated sample. Thereafter, the cell was exposed to the ^{90}Sr radiation source for 1 h and all electrochemical measurements repeated on it. Subsequently, the same cell was once again exposed to the ^{90}Sr radiation source for another 2 h to give a total exposure time of 3 h and all electrochemical measurements repeated on it again. The supercapacitor device was exposed to the ^{90}Sr radiation source for a total period of 48 h and during each time, the CV, CP and EIS measurements were carried out at specific times. After radiation for 48 h, the cell was removed from the source for 1 h without any radiation and all electrochemical measurements were repeated on the same cell. The measurements were also repeated for varying times up to 36 h after the electron irradiation with the legends reported in negative times and written as -36 h for example.

3. Results and discussion

Figure 1 (a) presents the energy distribution of electrons emitted by a ^{90}Sr radionuclide that was used for irradiating the cell. For clarity, the sum of the Sr and Yttrium (Y) contributions has been displaced by an amount indicated by the arrow [6].

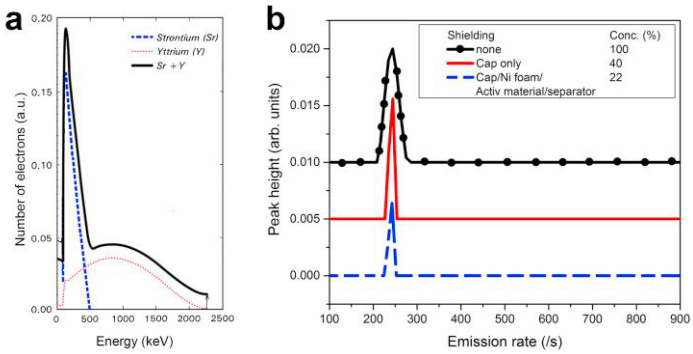


Figure 1. (a) Energy distribution of electrons emitted by a ^{90}Sr radionuclide [25] has been displaced by an amount indicated by the arrow, (b) Laplace DLTS spectra of the radiation-induced E3 defect in GaAs

This section investigates the effects of the stainless steel cap serving as a shield between the samples and irradiating source. This was investigated by analysing the results on the E3 defect of Gallium arsenide (GaAs). Three samples of an n-type GaAs (doped to 1 x 10^{15} cm^{-3} with Si) were irradiated by the electron source, ^{90}Sr, for 4 h. The general electron energy distribution of the ^{90}Sr source is shown in Figure 1 (a) [6]. By irradiating GaAs with high energy electrons we introduce several defects, such as the E3 defects [7]. This defect was detected using deep level transient spectroscopy (DLTS) and high-resolution Laplace DLTS (L-DLTS) [8,9]. DLTS provides information regarding energy level of the defect in a bandgap and its concentration. The top line in Figure 1 (b) shows the L-DLTS peak of the E3 defect without any blocking. The area under the peak is proportional to the E3 concentration.

The first measurement made for the GaAs sample was irradiated without any shields for 4 h and using the L-DLTS, the E3 peak of GaAs was investigated. As shown in Figure 1 (b), a strong peak with a defect concentration of 0.024 arbitrary units was recorded. The second set of measurements was made with the SC stainless steel cap between the electron source and sample prior to irradiation for 4 h. Laplace DLTS showed a decreased defect concentration. Note that the defect concentration is proportional to the area under the curve, this is calculated using the Laplace transient process, and the defect concentration for the second measurement was recorded as 0.017 arbitrary units. Compared to the first measurement, the concentration reduced to 0.017 from 0.042 which is 40% of the initial value. The third measurement was done by putting the SCs cap, Ni foam coated with the active material, and separator (glass microfiber filter paper) between the GaAs sample and radiation source before irradiating for 4 h. The result as displayed in Figure 1 (b) shows a defect concentration of 0.009 arbitrary units and, compared to the first one, is 0.009/0.042 = 20%. From the results obtained, it is observed that by putting the shields between the samples, electrons still go through the shields and create defects, however at lower concentrations. These results confirm that both active materials in the negative and positive side of the cell will be affected by the ^{90}Sr source radiation. Figure 2 (a) shows the CV of the cell at a scan rate of 20 mV s^{-1} during radiation and after radiation time.

It can be clearly seen that the shape of the CV plot for the supercapacitor device becomes more rectangular after radiation with less polarization or oxygen evolution at the maximum operating voltage [10]. A clearer image of the onset of ideality in the CV plot is observed in Figure 2 (b) where the increase in exposure time enhances the EDLC response of the device.

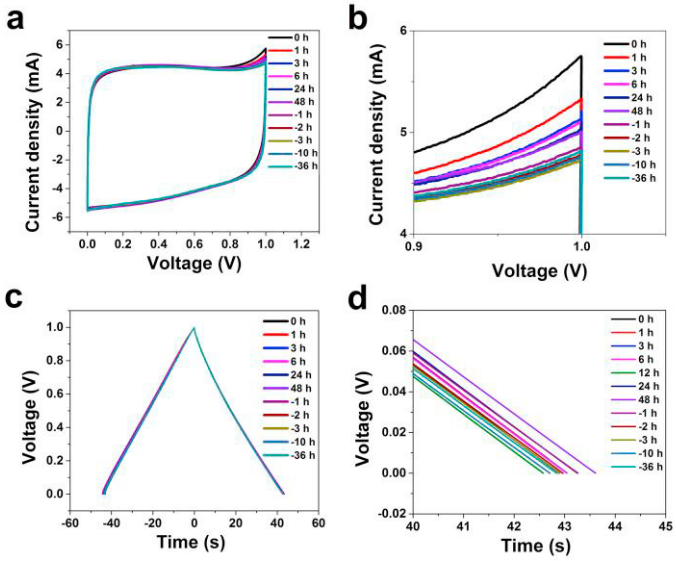


Figure 2. (a) and (b) full and zoom part of CV curves at scan rates 20 m Vs^{-1} and, (c) and (d) full and zoom part of galvanostatic charge/discharge curves from 0.5 A g^{-1} of the PPAC cell during radiation and after radiation time

The associated charge-discharge profile is displayed in Figure 2 (c) with a similar trend observed in the discharge time. The optimum discharge time is observed for the 48 h electron irradiation exposure time with a drop in the discharge time after re-taking measurements for a resting time of 36 h without radiation (-36 h) that can be seen clearly in Figure 2 (d). The observed initial improvement in the electrochemical performance of the symmetric device could be linked to the self-reorganization of the carbon nanostructures [11]. It has been reported previously that electron beams of sufficient energy could improve the nanocrystallinity of activated carbon materials [12]. Based on this assumption, the self-reorganization might be linked to an improvement in the crystallinity of the material which in turn improved the material conductivity. Contrary to most scientific thoughts which link radiation to damage to an entire material, recent studies have shown advantageous effects of tailoring materials to specific applications based on material exposure to moderate doses of electron irradiation [13,14]. The electron radiation exerts a significant influence on the performance of the supercapacitor devices with the results indicating an increase in the value of capacitance and conductance over the period in which the device was exposed to the irradiation source. However, after the source of irradiation was removed, the original capacitance of the device was restored. This improved electrochemical performance behavior could be explained on the basis of the improved conductance of the current collectors and the induced charges introduced due to the irradiation which contributes to the total electrode capacitance. Electron radiation can cause major change in order and disorder on sp^2 states in the carbon materials and the electrical conductivity will be increased by increasing electron dose which is because of tunneling of charge carriers through neighboring conductive chains [15]. The recovery of the material after the radiation source terminated is based on the ability of the carbon-based nanostructured material to “self-heal” itself in a bid to return to its original form. This has been reported in other related carbon materials which have been used extensively for different applications [11,16,17]. The obtained results indicate that the electrochemical properties of the supercapacitors devices can be improved by a small dose of irradiation and the original capacitance of the electrode materials can be restored once the irradiation source is removed. The re-modelling of the defects within the carbon nanostructured electrode material could be responsible for the observed enhancement in its charge storage capability [18]. This reconfiguration of the material nanostructure can be viewed from the alignment of the defects to have a general surface reconstruction of carbon atoms due to the threshold energy for defect formation being reached and produces a highly disordered graphitic material [19]. However, the realignment of defects necessary for efficient electrical conductivity is partial/temporary. Thus with time, there likely exists a gradual reordering of these defects

to its original state which leads to a subsequent drop in the discharge time but not to its original value. Therefore, the electron irradiation more or less improves the carbon material charge storage capability based on the defects re-structuring to aid charge trapping and storage [20].

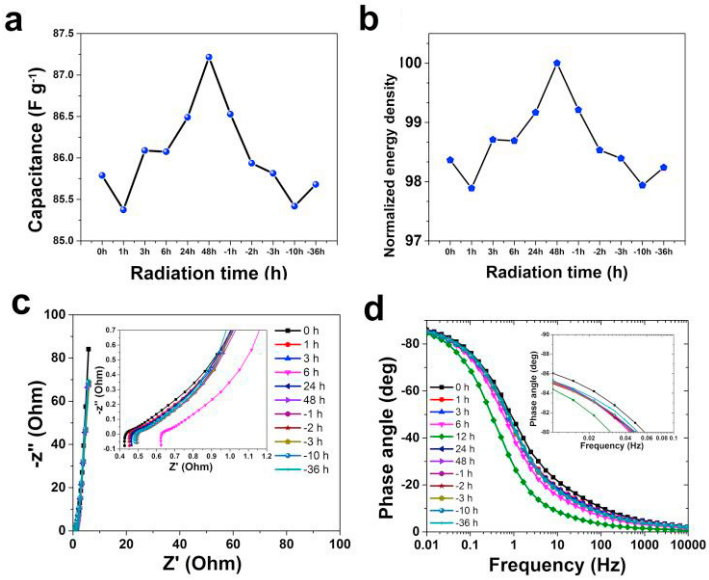


Figure 3. (a) Capacitance versus time, (b) normalized energy density versus time, (c) EIS plot and (d) Bode phase angle of sample during radiation and after radiation time

Figure 3 (a) displays the capacitance variation with exposure time and resting time after final exposure of 48 h. It can be observed from the plot that the specific capacitance initially increased to an optimum value after which it decreased by about 2% of the maximum value. Although this decrease is negligible but the observed decrease could be likened to the re-ordering of the carbon nanostructures after the exposure to the irradiation source is discontinued.

The effect on the energy density of the symmetric cell was also analyzed with the normalized energy density plotted as a function of exposure and relaxation times as shown in Figure 3 (b). A similar improvement in the device energy density is observed with a little loss in energy density to about 97.5% the nominal value. A ~ 3% loss is observed after a 36 h relaxation time has elapsed. The interesting part of the results shown over the entire test period is a further increase in the specific capacitance and energy density which depicts a final re-configuration of the material structure with improving electrochemical performance. Further exposure and relaxation times could yield even much more interesting occurrences but this is out of the scope of the present study.

The EIS plot (Figure 3 (c)) showed a similar trend with a drastic improvement in the ideal behaviour of the Nyquist impedance response at the low-frequency region. The inset to the figure 3 (c) shows the intercept to the real impedance axis at the high-frequency region. A little shift (increased equivalent series resistance, ESR) from the initial value of ~0.45 Ω with no irradiation at 0 h was recorded as compared to the 0.62 Ω series resistance after 6 h radiation. However, with further exposure time up to 48 h, the ESR value decreased to about 0.48 Ω. It is also worthy to note that the ion diffusion length reduced as observed from the set of the Nyquist plots displayed for all exposure and rest times. The Bode impedance plot (Figure 3 (d)) also displays a slight drop in the phase angle from -86° to -85° which can further be linked to the earlier observation of the possible re-ordering of aligned defects within the carbon nanostructure.

4. Conclusions

The results suggest that the exposure of the entire EC device to electron irradiation resulted in the re-ordering of the carbon nanostructure which led to improved charge storage capability during radiation time. However, with the discontinuation of the electron radiation exposure to the symmetric cell, the material naturally tried to re-order itself to its original state. It has been demonstrated that material irradiation both in form of a direct exposure to microwave irradiation to the material as well as exposure of the material fabricated in a symmetric device yielded promising pathways to improving the charge storage capability of the carbon-based electrode materials. Nonetheless, a more

permanent approach to tuning the material properties for suitable energy storage materials with good electrochemical performance lies in directly exposing the active material to irradiation.

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