Analyses of time-related performance of betavoltaic batteries using Ti\textsubscript{T2}

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Abstract
The time effect of tritium silicon p–n junction betavoltaic batteries is considered in this work. For a titanium tritium (Ti\textsubscript{T2}) source, the processes of decaying, tritium leaking, swelling and \textsuperscript{3}He releasing are contained in the calculation, and expressions of component and density changes are obtained. As time goes by, the self-absorption rate has a downward trend, while all electrical performances decrease, especially the short-circuit current (\textit{I}_{SC}) and the maximum output power (\textit{P}_{\text{max}}). At about 3.5 a, the battery begins to release gaseous \textsuperscript{3}He, and the expiry date of the battery is about 10.7 a, shorter than the half-life of tritium. The result indicated that for a tritium source, the time leads to a significant reduction in the electrical performance of the battery, which cannot be ignored in simulations and experiments.

Keywords: betavoltaic battery, Monte Carlo simulation, time, titanium tritium, electrical performances

(Basic figures may appear in colour only in the online journal)

Betavoltaic batteries are a promising candidate that supplies power to micro-electro mechanical systems (MEMS). It has many advantages including high energy density, long service life and ease of maintenance [1–3]. In recent decades, theoretical calculations [1, 3] and experimental tests [4, 5] have been extensively reported with various kinds of semiconductors [6, 7] and beta sources [7–9]. However, there are few reports about the time effect of a betavoltaic battery’s electrical performance. In fact, with the beta source decaying, the radioactivity declines continually, and the impact on the battery’s electrical performance should not be neglected.

\textsuperscript{3}H(T), \textsuperscript{63}Ni and \textsuperscript{147}Pm are the most widely applied pure beta emitters in betavoltaic batteries, and a solid tritium source has a relatively high specific activity, low shielding requirements and low cost [10]. Among all kinds of metal tritides, titanium tritide is especially preferred because of its stability in air [11, 12]. In this study, we consider three major factors related to time, namely the leakage, the decay and the swelling effect, which will affect the radioisotopes’ energy utilization of the battery. The density, component changes and time-related self-absorption rate of the radioisotope is considered. Based on the Monte Carlo method and numerical calculation, the performance degradation of the battery is obtained.

For a Ti\textsubscript{T2} source, under normal temperature and pressure, about 7.4 \times 10^{9} Bq of tritium desorbed within 10 years [13]. Meanwhile, the remaining tritium decays continually, which reduces the specific beta power along with the leaking process. At ambient temperature, Ti\textsubscript{T2} can store the gaseous decay product (\textsuperscript{3}He) in its lattice, and the maximum retaining
where \( v \) is the expansion rate.

Introduce \( u = \frac{\ln 2}{\tau_{1/2}} \Delta t \), and the amount of remaining \(^3\text{He}\) equals to the amount of non-decaying \(^{1}\text{H}\) minus the amount of leaked \(^3\text{He}\). At \( t = \Delta t \), we obtain the following equations by applying the exponential decay law:

\[
x_1 = 2e^{-\frac{u t}{\tau_{1/2}}} - 2e^{-\frac{u t}{\tau_{1/2}}} \Delta t, \quad \frac{u \Delta t}{A_0} \cdot e^{\frac{-u t}{\tau_{1/2}}} = 2e^{-u} - \frac{2u \Delta t}{A_0}
\]

\[
y_1 = 2 - 2e^{-\frac{u t}{\tau_{1/2}}} \Delta t = 2 - 2e^{-u}
\]

(4)

where \( u \) is the leakage rate. Similarly, at \( t = 2\Delta t \), we have:

\[
x_2 = x_1 e^{-\frac{u t}{\tau_{1/2}}} - x_1 e^{-\frac{u t}{\tau_{1/2}}} \Delta t
\]

\[
x_2 = x_1 e^{-\frac{u t}{\tau_{1/2}}} - x_1 e^{-\frac{u t}{\tau_{1/2}}} \Delta t \cdot \frac{u \Delta t}{A_0} \cdot e^{\frac{-u t}{\tau_{1/2}}} = 2e^{-2u} - 2e^{-u} - \frac{2u \Delta t}{A_0}
\]

\[
y_2 = y_1 + x_1 - x_1 \cdot e^{-\frac{u t}{\tau_{1/2}}} \Delta t
\]

(5)

At \( t = 3\Delta t \), we have:

\[
x_3 = x_2 e^{-u} - x_2 e^{-u} \cdot \frac{u \Delta t}{A_0} - 2u \Delta t = 2e^{-3u} - 2e^{-2u} - \frac{2u \Delta t}{A_0}
\]

\[
y_3 = y_2 + x_2 \cdot e^{-u}
\]

(6)

At \( t = 0 \), we have \( x_0 = 2 \), \( y_0 = 0 \), and at \( t = \Delta t \), equation (4) can be written as:

\[
x_1 = x_0 \left( e^{-u} - \frac{u \Delta t}{A_0} \right), \quad y_1 = x_0 \left( 1 - e^{-u} \right).
\]

(7)

At \( t = 2\Delta t \), equation (5) becomes:

\[
x_2 = x_0 \left( e^{-2u} - e^{-u} \cdot \frac{u \Delta t}{A_0} - \frac{u \Delta t}{A_0} \right)
\]

\[
y_2 = x_0 \left( 1 - e^{-2u} + e^{-u} \cdot \frac{u \Delta t}{A_0} - \frac{u \Delta t}{A_0} \right)
\]

(8)

and with the relationship \( x_2 + y_2 = x_0 \left( 1 - \frac{2u \Delta t}{A_0} \right) \). Similarly, at \( t = 3\Delta t \), equation (6) becomes:

\[
x_3 = x_0 \left( e^{-3u} - e^{-2u} \cdot \frac{u \Delta t}{A_0} - e^{-u} \cdot \frac{u \Delta t}{A_0} - \frac{u \Delta t}{A_0} \right)
\]

\[
y_3 = x_0 \left( 1 - e^{-3u} + e^{-2u} \cdot \frac{u \Delta t}{A_0} + e^{-u} \cdot \frac{u \Delta t}{A_0} - \frac{2u \Delta t}{A_0} \right)
\]

(9)

and also with the similar relationship \( x_3 + y_3 = x_0 \left( 1 - \frac{3u \Delta t}{A_0} \right) \).

It can be inferred that at \( t = n\Delta t \), there are similar relationships below:

\[
x_n = x_0 \left[ e^{-na} - \frac{u \Delta t}{A_0} \left( e^{-na} - e^{-(n-1)a} + \cdots + e^{-a} - e^0 \right) \right]
\]

\[
y_n = 2 \left( 1 - \frac{u \cdot n \Delta t}{A_0} \right).
\]

(10)

Using the formula \( e^0 + e^1 + e^2 + \cdots + e^\ell = e^{\ell+1} - 1 \), equation (10) becomes:

\[
x_n = 2 \left[ e^{-na} - \frac{u \Delta t}{A_0} \left( e^{-na} - 1 \right) \right]
\]

\[
y_n = 2 \left( 1 - e^{-na} - e^{-u} \cdot \frac{u \Delta t}{A_0} \cdot e^{-na} - 1 \right).
\]

(11)

Finally, suppose that \( \Delta t = 1 \) s, which is very short compared to the half-life of tritium, and is short enough to fulfill our premise. The density can be written as:

\[
\rho_0 = \frac{M_{\text{T}_1} + x_0 M_{\text{He}} + y_0 M_{\text{He}}}{N_A S_0 H_0 (1 + v)^2} \cdot \frac{T_{1/2}}{A_0} \cdot \frac{e^{\frac{-u \Delta t}{\gamma - 1}}}{\gamma x_0 \ln 2}
\]

(12)
The self-absorption effect is inevitable in solid beta sources, which causes temperature rise and degradation of the beta-voltaic battery [16]. As time goes by, the changes in density and source component may have an impact on the self-absorption and emission characteristics of the source. Therefore, in this kind of betavoltaic battery, it is necessary to figure out the relationship between the self-absorption rate and time. A 1 cm $\times$ 1 cm rectangular TiT$_2$ source with some specific thicknesses (h) is utilized in the simulation. The self-absorption rate at the initial time can be defined as:

$$\eta = 1 - \frac{A_{\text{surfaces}}}{A}$$  \hspace{1cm} (13)

where $A_{\text{surfaces}}$ is the radioactivity of all surfaces of the source, and $A$ is the absolute radioactivity at a specific time, respectively. Figure 1(a) shows the time-related self-absorption rate of chosen source. As time goes by, the self-absorption rates show a downward trend, and for a larger expansion rate, the trend is more obvious because both the matter density (shown in figure 1(b)) and the electron density become lower, and the reaction possibilities among $\beta$-ray and source atoms become lower. The time-related component changes are shown in figure 2. Because of leakage, the decrease of $^3$H shows a totally different pattern from the exponential decay law, and at about 10.7 a, all adsorbed tritium will leave the titanium material completely. However, the changing amount of $^3$He shows little influence on these trends, but the aged TiT$_2$ source may be delaminated from the semiconductor or fragmentated because of the released $^3$He, leading to the structure failure of the battery [10, 15].

The source decays and swells continuously as time goes by, which cause different energy deposition behaviors. In this work, a Si-based homojunction is utilized as the energy converter because of technical maturity. In order to avoid the edge effect, the size of the p–n junction is set as 2 cm $\times$ 2 cm $\times$ 0.5 cm, and the junction depth is set as 300 nm. The doping concentrations are selected by the following method: first, we obtain the energy deposition range in Si material and the deposition energy in the depletion region by using the Monte Carlo method. The depletion width is set as the difference between the energy deposition range and the junction depth because the electron-hole pairs can be completely collected only in the depletion region of the p–n junction. Finally, the doping concentrations can be derived from formulas. The energy deposition range in Si material is obtained as about 4.069 $\mu$m, and the depletion width is set as 3.769 $\mu$m. According to the formula

$$W = \sqrt{\frac{2e_{\text{e}}e_{\text{e}}}{q} \left( \frac{N_A + N_D}{N_A N_D} \right) V_{bi}}$$

the $N_A$ and $N_D$ can be selected as $3.79 \times 10^{15}$ and $5 \times 10^{13}$ cm$^{-3}$, respectively, and corresponding $V_{bi}$ is 0.53229 V according to formula $V_{bi} = \frac{kT}{q} \ln \left( \frac{N_A N_D}{n_i^2} \right)$ [17].

The simulating model is illustrated in figure 3 and this model is also utilized to calculate electrical properties of the battery. Figure 4 illustrates the relationship between normalized energy deposition and time. As time goes by, more energy can be deposited in the depletion region because...
of the decreasing self-absorption rate, and if the expansion rate is the larger one, this regular pattern will be more obvious.

In a betavoltaic battery, the short-circuit current \( I_{SC} \) is given by [17]:

\[
I_{SC} = \frac{Aq}{E_{c-h}} \sum_{n=1}^{N} CE(n) \times E(n)
\]

where \( N \) is the total number of layers, \( CE(n) \) is the collection rate of the electron–hole pair in layer \( n \) of the sample, within the depletion depth, \( CE(n) = 1 \). \( E(n) \) is the deposition energy in layer \( n \), and in this work, it is considered that the energy deposited in the depletion region \( A \) is the absolute radioactivity, \( q \) is the electron charge, and \( E_{c-h} \) is the average ionization threshold. The open-circuit voltage \( V_{OC} \) is given by [1]:

\[
V_{OC} = \frac{k_B T}{q} \ln \left( \frac{J_{SC}}{J_0} + 1 \right)
\]

where \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, and \( J_0 \) is the minimum value of ideal reverse saturation current density of the semiconductor energy converter, which can be estimated by \( J_0 = 1.5 \times 10^5 \exp \left( -E_g/k_BT \right) \) [8]. \( J_{SC} \) is the density of short-circuit current. The fill factor \( (FF) \) can be calculated by [17]:

\[
FF = \frac{v_{oc} - \ln(v_{oc} + 0.72)}{v_{oc} + 1}
\]

where \( v_{oc} = V_{oc}/(kT/q) \). The maximum output power is given by \( P_m = FF \times V_{OC} \times I_{SC} \) and the power conversion efficiency is given by \( \eta = P_m/ P_{source} \), where \( P_{source} \) indicates the surface power of the source.

The processes of leakage and decay cause a faster performance degradation of betavoltaic battery. As time goes by, \( V_{oc}, FF \) and \( \eta \) have accelerating downward trends, while \( I_{SC} \) and \( P_m \) have near-linear downward trends. Table 2 shows theoretical performances of the cell at 3.5 a and 10.5 a. At 10.5 a, the \( I_{SC} \) and \( P_m \) are very low, remaining only about 1% of the initial quantity, which means the battery has almost run out of power. Regarding all factors including decaying, swelling and gas releasing, the battery has its best performance period before 3.5 years.

In summary, simulations of a tritium silicon \( p-n \) junction betavoltaic battery are carried out in this work. Considering the tritium leaking, decaying, swelling and \( ^3He \) releasing processes, a method which can figure out the relationship among time, source component and density change of TIT\textsubscript{2} source is given, and the self-absorption rate is decreasing. The time has great impact on the performances of batteries with TIT\textsubscript{2} source. All electrical performances decrease as time goes by, especially \( I_{SC} \) and \( P_m \), but these decrease patterns no longer follow the exponential law. Within 3.5 a, the battery has its best performance. The expiry date of the battery is about 10.7 a, shorter than the half-life of tritium, indicating that the tritium leakage is an important factor that leads to the failure of the battery. Although Si is used as the semiconductor energy converter material of the betavoltaic batteries in this study, the research methods can also be used in other semiconductor materials.
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