

## On the Question of Energy and Power Potentials of the Electrode Materials in the Rechargeable Cells

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The paper considers galvanostatic discharge of different rechargeable cells. In the first part of the paper, the useful mathematical equations for the calculation of voltage, capacity, capacitance, energy, and power is given. In the second part of the paper, the proposal for the determinations of energy and power potentials of the electrode materials introducing the reference electrode as a reference point is discussed for different charge storage cells. The proposed analysis is applied on the polyaniline and lead-lead sulfate electrode discharge, and procedure how from the single electrode measurements, capacity, energy, and power of the hypothetical lead sulfate - polyaniline cell could be estimated.

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**Keywords:** Battery; Supercapacitors; Supercapattery; Galvanostatic Discharge.

### 1. INTRODUCTION

The storage of electric energy in electrochemically rechargeable systems is today of great importance [1, 2, 3]. Many different storage systems that differ in the mechanism of the charge storage nature have been investigated, and many different names are used like, batteries, accumulators, energy storage systems, power sources, supercapacitors, hybrid supercapacitors, battery-supercapacitor hybrid devices, supercapatteries, Li-supercapacitors, pseudocapacitors, *etc.* [4-7]. In recent times, the discussion about the nature of the charge storage mechanisms of the electrode materials is in progress [8, 9]. For example, the previously described pseudocapacitive materials like  $\text{Co}_2\text{O}_3$ ,  $\text{NiOOH}$ , polyaniline, polypyrrole, *etc.* [10, 11] that show well-defined peaks in the cyclic voltammograms, and nonlinear galvanostatic charge-discharge characteristics, should not be considered as pseudocapacitive [9]. Also, there is a lot of confusions in the literature in reporting data, for examples, the nonlinear discharge curve is treated as triangular, the capacitance of the battery electrodes is reported, many approaches for the reporting of the electrochemical/electrical parameters of the charge storage systems are used, which complicate comparisons of the different systems [5].

Among voltage, capacity, or capacitance, the energy and power are crucial parameters to define the quality of rechargeable charge storage cells [12-21]. The main difference between rechargeable charge storage cells is that batteries store higher energy content than supercapacitors that mostly store power with limited energy content. In addition, the cyclization performances highly differ. Combining the battery electrode materials (high energy) and supercapacitor electrode materials (high power and long cycling life) in a hybrid device showing battery like behavior with increased power content, the device generically called “supercapattery” are recently introduced [4, 22, 23]. Therefore, it should be advised that the general term for all rechargeable systems (battery, supercapacitors, and supercapattery) should be rechargeable (electrochemical) *charge storage cells*. Hence, the battery combines the electrode materials that are characterized by the existence of the well-defined peaks in cyclic voltammograms and nonlinear charge-discharge curves, supercapacitive materials are characterized by rectangular cyclic voltammograms and triangular charge-discharge curves, and devices with combinations of those two electrode materials supercapattery, with increased energy in comparisons with supercapacitors and increased power in comparisons with battery materials. The usual way of representing the dependence of energy on power is the presentation of the values as Ragone plots [24-26].

Many researchers investigated single electrode materials, and as suggested by some authors, the energy and power are characteristics of a cell not of the single electrode. For example, Balducci et al. [27], Wang et al. [28] Chen [29] suggested that energy and power can only be released from two electrode cell - device, but not from a single electrode materials.

Investigation and determination of energy and power of the cell, even extremely important, in some manner is very complex, due to the electrode mass balancing, both electrodes must be in charged or discharged states, different utilization factors of electrode materials, etc. Also, from the behavior of the cell, the behavior of electrode materials could not be evaluated. Energy and power can indeed be obtained only from the device during the current flow, not from the single electrode. But, the energy and power of the cell originated from the hypothetical “*energy and power potential content*” of both electrodes, so finding the method to estimate the energy and power potential content of electrode materials will facilitate researches in the field of charge storage.

Hereafter, in this paper considering galvanostatic discharge of the different cells and electrode materials, as the most common method in the literature, will be treated. In the first part of the paper, as a reminder, useful mathematical equations for the cell voltages, capacity, capacitance, energy, and power will be presented. The main focus of the paper will be to show that under proper mathematical treatment, by introducing a reference point (selected reference electrode) for discharge, the energy and power potential content of the electrode materials could be evaluated.

## 2. THEORETICAL CONSIDERATION

In this section, the basic electric/electrochemical parameters will be considered for the discharge of charge storage cells.

### 2.1. The voltage of the charge storage cells

The voltage,  $U$ , of the battery during galvanostatic discharge is dependent on the behavior of the separate electrodes and can be given as:

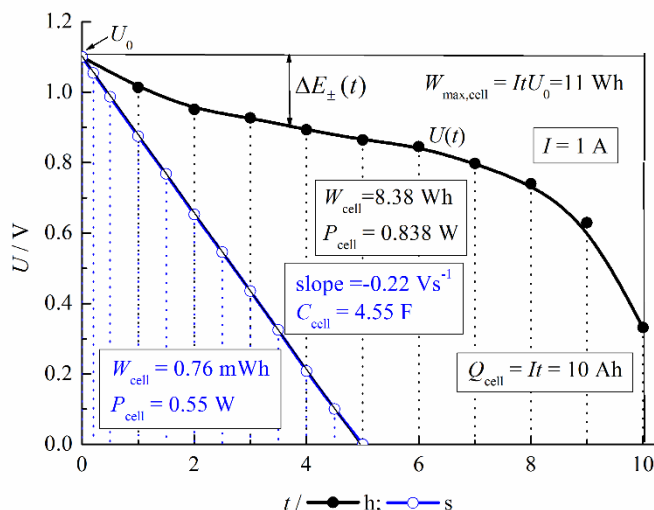
$$U(t) = U_0 - \Sigma \Delta E_{\pm}(t) - I \Sigma R_{\Omega}(t) \quad (1)$$

where  $U_0$  is the open-circuit voltage (or as recommended by IUPAC “potential difference” [30] of the cell at zero current and can be calculated as a difference of the electrode potentials at zero current of the positive and negative electrode,  $U_0 = E_+ - E_-$ . The terms “*positive*” and “*negative*” electrode, or “*positrode*” and “*negatrode*” as suggested by Chen [31], should be preferred for rechargeable cells, rather than anode and cathode, because during charge positive electrode is the anode and during discharge cathode and *vice versa*. The reversible potential of an electrode could be in some cases calculated using the Nernst equation. One example is the zinc electrode in for example 1 mol kg<sup>-1</sup> of ZnCl<sub>2</sub>:

$$E_r = E_r^{\theta}(\text{Zn}^{2+} | \text{Zn}) + \frac{2.3RT}{nF} \log a(\text{ZnCl}_2)$$

where the activity of zinc chloride is  $a(\text{ZnCl}_2) = 4m^3 \gamma^3$ , and knowing the value of the activity coefficient of  $\gamma = 0.337$ , reversible potentials of  $-0.814$  V vs. SHE can be calculated. In many cases, authors neglect the activity coefficient, and instead use the concentrations, which will give the potentials of  $-0.76$  V vs. SHE. For many electrode materials where solid-state reactions occur, the real reversible electrode potentials usually cannot be calculated and should be experimentally determined. The  $\Delta E_{\pm}(t) = \Delta E_+ + |\Delta E_-|$  represents the loss of the voltage due to the system irreversibility, caused by the transformations of the electrode active to inactive materials, and existences of the different polarizations or overpotentials of the positive and negative electrodes, by slow electron transports, bulk or solid-state diffusion, *etc.* Part  $I \Sigma R_{\Omega}(t)$  is connected with all the voltage drops caused by the different resistances of the systems, electrolytes, separators, contacts, active mass, *etc.*  $R_{\Omega}(t)$  is in some cases time-dependent, due to the change of the electrolyte concentration, increase or decrease of the active mass resistance, and will be neglected in the presented paper.

In Fig. 1, as an example, typical galvanostatic,  $I = 1$  A, discharge curve of a hypothetical battery and supercapacitor is shown. Open circuit voltage,  $U_0$ , is assumed to be 1.1 V. During the time, the voltage of the battery,  $U(t)$ , nonlinearly decrease, due to the conversion of the electrode active to inactive materials, and the existence of the polarization.



**Figure 1.** The galvanostatic discharge curves for the hypothetical battery cell (●) and a supercapacitor (○). Energy and power are calculated using Eq. 17 and Eq. 21.

The voltage of the supercapacitor linearly depend on time, due to the decrease of the available charge of the supercapacitors:

$$U(t) = \frac{dQ_{\text{cell}}}{C_{\text{cell}}} = \frac{\int_t^{t_{\text{max}}} I \times dt}{C_{\text{cell}}} = \frac{I \times (t_{\text{max}} - t)}{C_{\text{cell}}}$$

where  $t_{\text{max}}$  is the time when  $U(t)$  reaches 0 V, and  $t$  is between 0 s and  $t_{\text{max}}$ . Knowing the  $t_{\text{max}}$ , it is possible to calculate the voltage at any time,  $t$ . For example, for  $t = 2$  s, the voltage is 0.659 V. But it is questionable do useful power could be obtained when  $U(t) < \sim 0.2\text{-}0.3$  V even with DC-DC voltage convertor.

### 2.2. The capacity and capacitance of the charge storage materials

The main differences between supercapacitors and the other types of charge storage cells are in the nature of charge storage [4, 5]. Hence, the capacitance of the cell,  $C$ , F, can be only used for the cells, which shows a triangular charge-discharge galvanostatic curve. In other cases when discharge curves have a plateau or nonlinearly depend on time, the capacity,  $Q$ , Ah, must be used and reported [5, 9, 31].

The delivered capacity ( $Q$ ) of the cell or electrode materials during discharge could be easily calculated by multiplying the current with discharge time, and is usually given as a specific capacity,  $q_s$ , mAh g<sup>-1</sup> (or Ah kg<sup>-1</sup>), volumetric capacity,  $q_V$ , mAh cm<sup>3</sup> and areal capacity,  $q_A$ , mAh cm<sup>-2</sup>. The capacity of the battery cell, Fig. 1, is then  $I \times t = 10$  Ah.

The theoretical values of specific, areal, and volumetric capacity of the electrode materials can be calculated, knowing the molar mass ( $M_B$ ), the number of exchanged electrons,  $n$ , and  $\rho_B$  density, g

$\text{cm}^{-3}$  of the active mass. For 1 g of active material, surface area,  $A_B$ ,  $\text{cm}^2$  or volume,  $V_B$ ,  $\text{cm}^3$  can be written as:

$$q_s = \frac{I \times t}{m_B} = \frac{nF}{M_B}; \quad q_A = \frac{I \times t}{A_B} = \frac{m_B nF}{A_B M_B}; \quad q_V = \frac{I \times t}{V_B} = \frac{\rho_B nF}{M_B} \quad (2)$$

where  $F$  is usually taken as  $26.8 \text{ Ah mol}^{-1}$ , because discharge time is in order of hours. In the following text, the focus will be on specific values.

The specific capacity of the battery cell,  $q_{s,\text{cell}}$ ,  $\text{Ah g}^{-1}$ , depends on the specific capacities of the positive (+) and negative (-) electrode, and can be calculated as:

$$\frac{1}{q_{s,\text{cell}}} = \frac{1}{q_{s,+}} + \frac{1}{q_{s,-}} \quad (3)$$

or after rearmament:

$$q_{s,\text{cell}} = \frac{n_+ n_+ F}{n_+ M_+ + n_+ M_-} \quad (3a)$$

Certainly, the theoretical mass balance (supposing that utilization of the active mass is  $\sim 1$ ) should be considered, thus that  $Q_{\text{cell}} = Q_+ = Q_-$ :

$$Q_+ = Q_- = \frac{m_+ n_+ F}{M_+} = \frac{m_- n_- F}{M_-} = m_+ q_{s,+} = m_- q_{s,-} \quad (4)$$

or

$$\frac{m_+}{m_-} = \frac{q_{s,-}}{q_{s,+}} \quad (5)$$

After the mass balancing, the theoretical capacity of the battery can be given as:

$$Q_{\text{cell}} = \frac{m_+ q_{s,+} + m_- q_{s,-}}{2} = \frac{(m_+ n_+ M_- + m_- n_- M_+) F}{2} \quad (6)$$

and specific capacity as:

$$q_{s,\text{cell}} = \frac{Q_{\text{cell}}}{m_+ + m_-} \quad (7)$$

More details about the practical mass balance can be obtained following the procedure given by Kasnatscheew et al. [32].

The capacitance of the supercapacitor cell is given as:

$$\frac{1}{C_{\text{cell}}} = \frac{1}{m_+ C_{s,+}} + \frac{1}{m_- C_{s,-}} \quad \text{or} \quad C_{\text{cell}} = \frac{m_+ m_- C_{s,+} C_{s,-}}{m_+ C_{s,+} + m_- C_{s,-}} \quad (8)$$

and the specific capacitance as:

$$C_{s,\text{cell}} = \frac{C_{\text{cell}}}{m_+ + m_-} \quad (9)$$

To achieve the charge balance, the mass balance of the electrode materials has to be done, according to [31, 33]:

$$\frac{m_+}{m_-} = \frac{C_{s,-} \times \Delta E_{w,-}}{C_{s,+} \times \Delta E_{w,+}} \quad (10)$$

where  $\Delta E_w$  is the potential window of the single electrode.

In the special case of the symmetrical cell, in which  $C_+ = C_- = C$  and  $m_+ = m_- = m$ , and  $\Delta E_{w,+} = \Delta E_{w,-}$ , specific capacitance of the cell is:

$$C_{s,\text{cell}} = \frac{C}{4m}$$

The specific capacitance,  $C_s$ , of the supercapacitor electrode materials during galvanostatic discharge can be calculated from the determined values of the slope ( $\Delta E_{\pm}/\Delta t$ ) of the linear dependences of the potential over time [5]

$$C_{s,\pm} = \mp \frac{I}{(\Delta E_{\pm} / \Delta t) m_{\pm}} \quad (11)$$

where  $\Delta E_{\pm}$  is the change of the potential of the positive or negative electrode for a given time, or slope of  $E(t)$  vs,  $t$ , while for the supercapacitors cell is:

$$C_{s,\text{cell}} = - \frac{I}{(\Delta U / \Delta t)(m_+ + m_-)} \quad (12)$$

where  $(\Delta U/\Delta t)$  is a slope of the voltage over time.

It should be noted that Eq. 12 is derived from the following formulas [4]:

$$Q = C \times U$$

by the total differentiation with  $dt$ ,

$$\frac{dQ}{dt} = C \frac{dU}{dt} + U \frac{dC}{dt} \approx C \frac{dU}{dt}$$

and for the  $dQ = I \times dt$ , one can obtain only for the ideal slope of the straight line of  $U$  over  $t$ :

$$C = \frac{I}{(dU/dt)} \approx \frac{I}{(\Delta U/\Delta t)}$$

so this equation is valid only in the case when  $C$  is a constant across the entire discharge region. In many papers, the curvature line is treated as an ideally straight line, giving incorrect values of capacitance, and consequently for the energy and power. For the lengthy approaches of treating supercapacitors see [4, 31, 34].

For the case shown in Fig. 1 the slope of the supercapacitor discharge curve is  $-0.22 \text{ V s}^{-1}$ , and for the current of 1 A, the capacitance is 4.55 F.

For the supercapaciteery cell, all the above mentioned equation could be used, and charge balance must be achieved, for example for the positive battery and negative supercapacitor electrode materials are [31]:

$$Q_+ = Q_- = m_+ q_{s,+} = m_- C_{s,-} \Delta E_{w,-} \quad (13)$$

with mass balance given as:

$$\frac{m_+}{m_-} = \frac{C_{s,-} \times \Delta E_{w,-}}{q_{s,+}} \quad (13a)$$

### 2.3 The energy and power of the charge storage cells

The energy,  $W$ , of an electrochemically rechargeable cell during discharge can be obtained by multiplying the voltage of the cell with capacity. *Note:* correct term for the transferred energy is  $\Delta E$ , and is a sum of the work,  $W$ , done by the system and heat flow into the system,  $Q$  which can be in the first approximation neglected, so  $\Delta E = W + Q \approx W$ . In this paper,  $W$  is adopted for energy to avoid confusion with electrode potential. In an ideal case, without overpotentials and Ohmic drops, the maximum energy of the cell is given as:

$$W_{\max} = I \times t \times U_0 \quad (14)$$

and in Fig. 1 for some hypothetical case of the battery cell has a value of 11 Wh. The theoretical maximum energy of the battery cell can be calculated by:

$$W_{\max} = Q_{\text{cell}} U_0 = \frac{(m_+ n_+ M_- + m_- n_- M_+) F}{2} U_0 \quad (15)$$

and maximum theoretical specific energy, for the capacity balanced electrodes, by:

$$W_{s,\max} = \frac{W_{\max}}{m_+ + m_-} \quad (16)$$

Due to the irreversibility of the systems, the real discharge curve always has a voltage lower than the open-circuit voltage, so the available energy should be given as an integral form:

$$W_{\text{cell}} = I \int_0^t U(t) dt \quad (17)$$

where integral is the area under the discharge curve. The specific energy is:

$$W_{s,\text{cell}} = \frac{I \int_0^t U(t) dt}{(m_+ + m_-)} \quad (17a)$$

In Fig. 1 the real energy of the battery cell is 8.38 Wh. One important parameter is discharging energy efficiency that can be calculated by the ratio of the actual and maximum energy:

$$\eta_{d,w} = \frac{W_{\text{cell}}}{W_{\max}} = \frac{I \int_0^t U(t) dt}{I \times t \times U_0} \quad (18)$$

which is for the example shown in Fig. 1, 0.76, or 76%. Consequently, the discharge energy efficiency is an indication of the system's reversibility, and it should be reported in the papers.

The maximum energy of supercapacitor cell, in Wh, can be obtained using the equation:

$$W_{\max} = \frac{1}{2} \times \frac{C_{\text{cell}} \times U_0^2}{3600} \quad (19)$$

or the specific energy, in Wh g<sup>-1</sup>:

$$W_{s,\max} = \frac{1}{2} \times \frac{C_{\text{cell}} \times U_0^2}{3600 \times (m_+ + m_-)} \quad (19a)$$

because most of the supercapacitor cells deliver energy at the time scale of seconds. For the supercapacitor cell, shown in Fig. 1, the maximum energy calculated by Eq. 19 for the cell capacitance of 4.55 F is 0.76 mWh, which is an identical value obtained by the integration method, Eq. 17. Nevertheless, for the real systems, the cell will never be discharged to zero volts, and the available energy content should be calculated using the following equation:



$$W_{s,cell} = \frac{1}{2} \times \frac{C_{cell} \times (U_0^2 - U_{min}^2)}{3600 \times (m_+ + m_-)} \quad (20)$$

where  $U_{min}$  is the acceptable end-discharge voltage.

The power of the charge storage cells,  $P$ ,  $W$ , cannot be theoretically considered, because it is dependent on the discharge time. Practically, during discharge, power can be considered as the energy delivered over unit time. Therefore, for the case of the battery and supercapattery cell, the power is:

$$P_{cell} = \frac{W_{cell}}{\Delta t} = \frac{I \int_0^t U(t) dt}{\Delta t} \quad (21)$$

and specific power,  $W \text{ g}^{-1}$ :

$$P_{s,cell} = \frac{W_{cell}}{\Delta t(m_+ + m_-)} = \frac{I \int_0^t U(t) dt}{\Delta t(m_+ + m_-)} \quad (21a)$$

In Fig. 1, for the discharge time of a battery cell of 10 h, the power is 0.84 W.

For the supercapacitor cell, the maximum power is:

$$P_{cell} = \frac{1}{2} \times \frac{3600 \times C_{cell} \times U_0^2}{\Delta t} \quad (22)$$

and specific power:

$$P_{s,cell} = \frac{1}{2} \times \frac{3600 \times C_{cell} \times U_0^2}{\Delta t \times (m_+ + m_-)} \quad (22a)$$

where  $\Delta t$  is in seconds. In Fig. 1, the power of the supercapacitor cell using the value of capacitance 4.55 F and  $U_0 = 1.1$  V, is 0.55 W, and is identical to the values obtained using the integral form, Eq. 21. It should be noted that the maximum power of the cells can be estimated knowing the internal resistance of the cell,  $R_{int}$ .

### 3. ESTIMATION OF THE ENERGY AND POWER POTENTIALS OF THE ELECTRODE MATERIALS

The energy and power could be extracted only from the electrochemical cells during the current flow. But, for this purpose, it will be hypothesized that the energy and power of the cell, originated from the energy and power potentials of the positive and negative electrode materials.

In Fig. 2, the considered discharge curve of the battery cell shown in Fig 1. is further derived by representing  $E_{\pm}(t)$  for the mass balanced positive and negative electrode versus the standard hydrogen electrode (SHE). Therefore, the voltage of the cell can be treated as a sum of the potentials of two hypothetical cells  $U(t) = \Delta E_+ + \Delta E_-$ . For the positive cell,  $\Delta E_+ = E_+(t) - E_R(\text{SHE})$  and for the negative cell  $\Delta E_- = E_R(\text{SHE}) - E_-(t)$ . Theoretically, one can consider that SHE is an ideally polarizable electrode, which potential does not depend on current. The open-circuit potential of the positive electrode is arbitrarily set to 0.8 V vs. SHE and of the negative to -0.3 V vs. SHE. Hence, the open-circuit voltage of the cell is  $U_0 = E_+ - E_- = 1.1$  V. The maximum energy potential of the positive electrode is  $W_{\max,+} = I \times t \times E_+ = 1 \text{ A} \times 10 \text{ h} \times 0.8 \text{ V} = 8 \text{ Wh}$ , and for the negative electrode  $|W_{\max,-}| = |I \times t \times E_-| = 1 \text{ A} \times 10 \text{ h} \times |-0.3 \text{ V}| = 3 \text{ Wh}$ . The sum of the energy potentials of the positive and negative electrode gave 11 Wh which corresponds to the maximum energy of the battery cell. To obtain the energy potential of the positive and negative electrode materials, modified Eq. 17. is used

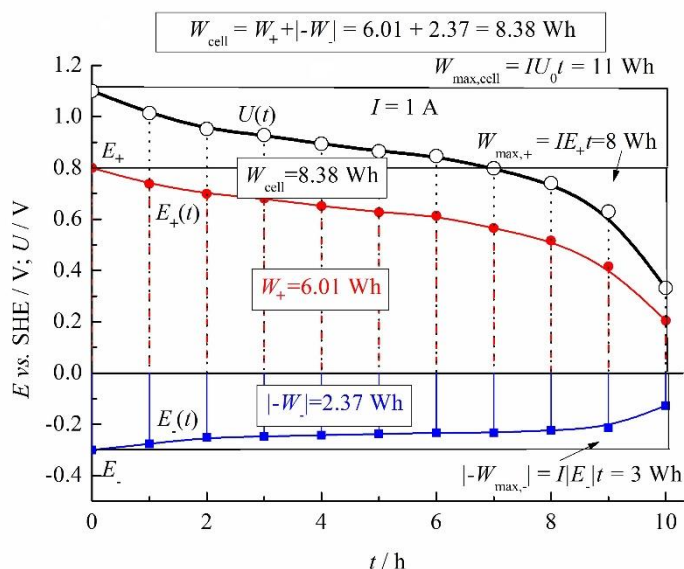
$$W_+ = I \int_0^t E_+(t) dt \quad (23)$$

and:

$$W_- = -I \int_0^t E_-(t) dt \quad (23a)$$

The potential energy of a positive electrode is 6.01 Wh with respect to the standard hydrogen electrode, as shown in Fig. 2. Using the softer for the integration, the integral of the negative electrode discharge curve would have a negative sign. Because negative area or energy does not exist, it is recommended that calculated energy potentials should be reported as absolute value  $|-W_-|$ . Sign “-“ indicate that electrode is negative against SHE, and “-“ in the subscript that the electrode is negative in the hypothetical cell. The calculated energy potential of the negative electrode against SHE is 2.37 Wh. The sum of energy potentials of the positive and negative electrode is  $W_+ + |-W_-| = 8.38 \text{ Wh}$  that is an identical value obtained for the integration of the battery cell voltage over time.

The reported energy potentials of the electrode materials should be given in analogy to the electrode potentials as  $W_+$  vs. SHE and  $|-W_-|$  vs. SHE or some other reference electrode, to avoid confusion (see section 4).

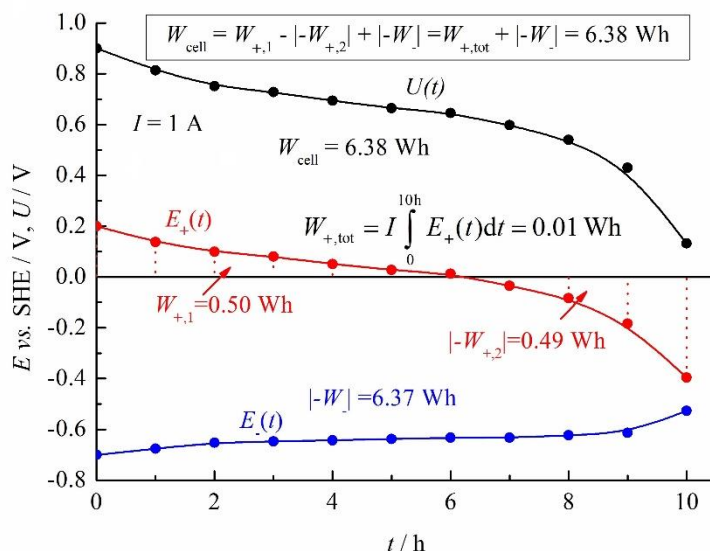


**Figure 2.** Estimations of the energy potentials of the electrode materials (vs. SHE) of the rechargeable battery cell.

The power of the cell is  $P_{\text{cell}} = W_{\text{cell}}/t = 0.838 \text{ W}$ . The power potentials of the positive electrode are  $P_+ = 0.601 \text{ W vs. SHE}$ , and of the negative electrode  $|-P_-| = 0.237 \text{ W vs. SHE}$ . So, the sum of the power potentials of the positive and negative electrode,  $P_+ + |-P_-| = 0.838 \text{ W}$  is identical to the power of the cell.

Adopting this method, one problem could arise. Namely, one of the electrodes could cross the 0 V vs. SHE. In Fig. 3, the positive electrode is at the beginning of the discharge positive against SHE, and after ~6 h is below the potentials of SHE. The discharge of hypothetical cell when the electrode potential is positive against SHE, has a value of  $\Delta G < 0$ , so the reaction is spontaneous. When a hypothetical cell change sign, the electrode potential becomes negative with the respect to the SHE, a value of  $\Delta G > 0$ , and the reaction is not spontaneous. Thus the total energy potential hypothetically delivered by the electrode is  $W_{+,1} - |-W_{+,2}| = 0.50 - 0.49 = 0.01 \text{ Wh vs. SHE}$ . The same value,  $W_{+, \text{tot}}$ , is obtained by the integration of the whole curve, from 0 to 10 h. The energy potential of the negative electrode obtained by applying Eq. 23a is  $|-W_-| = 6.37 \text{ Wh vs. SHE}$ . The sum of those two energy potentials gave 6.38 Wh, which is an identical value obtained by the integration of the whole discharge curve of the battery cell.

The power of the battery cell for 10 h of discharge is  $P_{\text{cell}} = W_{\text{cell}}/t = 0.638 \text{ W}$ . Also,  $P_{\text{cell}} = P_+ + |-P_-| = 0.637 + 0.001 = 0.638 \text{ W}$  that is again identical to the power of battery cell.



**Figure 3.** Estimations of the energy potentials (vs. SHE) of the electrodes of the rechargeable cell in the case when the positive electrode is discharged above and below 0 V vs. SHE.

To verify the above considerations, the experimental results for the rechargeable cell consisted of galvanostatically polymerized polyaniline (PANI) positive electrode, and zinc negative electrode in 0.5 M ZnCl<sub>2</sub>, 1 M NH<sub>4</sub>Cl, and 0.8 M sodium citrate, at pH = 4 are analyzed [35]. The potentials of the positive and negative electrodes and the voltage of the cell are given in Fig. 4. The measured voltage of the cell, during galvanostatic discharge with the current of 18 mA, is given with the line, and the sum of the electrode potentials over time is given with the open cycles. It is obvious, that  $U_0$  and  $U(t)$  correspond to the sum of the  $E_+ - E_-$  and  $E_+(t) - E_-(t)$ , respectively. The energy of the cell is obtained by the integration of the cell voltage over time, and because discharge is at the time scale of seconds, using the equation:

$$W_{\text{cell}} = \frac{I}{3600} \int_0^t U_{\text{cell}}(t) dt$$

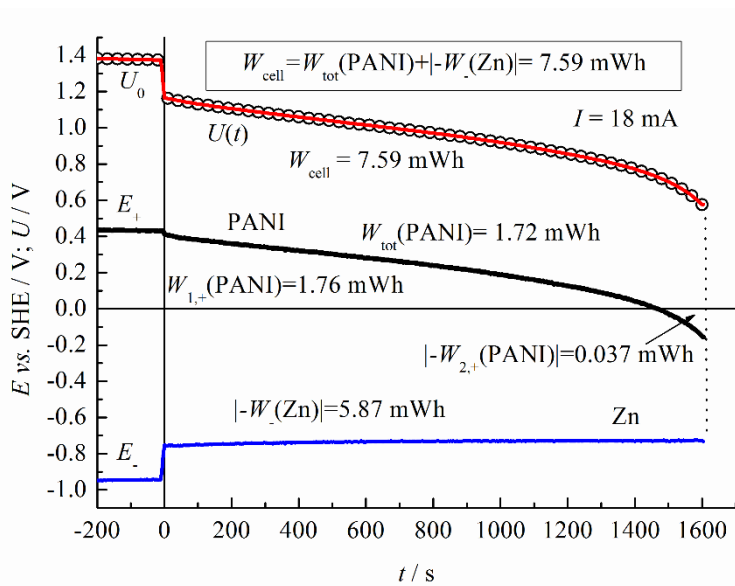
and has a value of 7.59 mWh. The energy potentials of the PANI and zinc electrode against standard hydrogen electrode are  $W_{\text{tot}}(\text{PANI}) = 1.72 \text{ mWh vs. SHE}$ , and  $|-W_-(\text{Zn})| = 5.87 \text{ mWh vs. SHE}$ , respectively. The sum of those two energy potentials is 7.59 mWh, and is identical to the value obtained by the integration of the cell voltage over time. The power of the cell is:

$$P_{\text{cell}} = \frac{3600 \times W_{\text{cell}}}{t} = 17.08 \text{ mW}$$

where  $t$  is in seconds. The identical result of 17.08 mW is obtained using the equation:

$$P_{\text{cell}} = \frac{3600 \times W_{+, \text{tot}}(\text{PANI})}{t} + \frac{3600 \times |-W_-(\text{Zn})|}{t}$$

Therefore, from this example, it can be seen that with a properly adopted reference point (in this case standard hydrogen electrode) the energy and power potentials of the electrode can be calculated.



**Figure 4.** The galvanostatic discharge curve of Zn| 0.5 M ZnCl<sub>2</sub>; 1 M NH<sub>4</sub>Cl, 0.6 Na-citrate| PANI cell, and discharge of the positive and negative electrode of the cell. The determination of the cell energy and energy potentials of the electrodes are explained in the text.

For the supercapattery cell, Fig. 5, combined with the battery positive electrode and supercapacitive negative electrode materials, a similar method could be applied. By the total integration of the discharge curve of the supercapattery cell, the energy is  $W_{cell} = 38.2$  mWh. The energy potentials of the positive electrode are  $W_{+} = 33.38$  mWh vs. SHE, and for the negative electrode is  $|-W_{-}| = 4.82$  mWh vs. SHE, which sum is again 38.2 mWh.

If one, try to calculate the energy potentials of an ideal negative supecapacitive electrode using a determined capacitance of 452.5 F and potential window of 0.43 V, the hypothetical energy potentials will be:

$$\begin{aligned}
 |-W_{-}| &= \frac{1}{2} \times \frac{C_{-} \times (\Delta E_{w,-})^2}{3600} = \\
 &= \frac{0.5 \times 452.5 \times 0.43^2}{3600} = 11.6 \text{ mWh}
 \end{aligned}$$

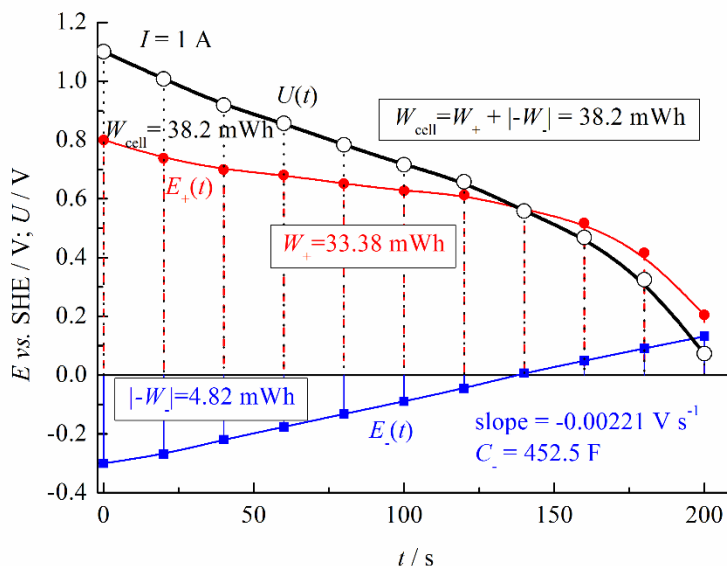
which highly differs, for 114%, from the values obtained by the integral method. Therefore, obviously, without a reference point, the obtained energy does not have a sense.

The power of the supercapattee cell is  $3600 \times W_{cell} / t = 0.688$  W. The sum of the power potentials of the electrodes are:

$$P_+ + |-P_-| = \frac{3600 \times W_+}{t} + \frac{3600 \times |-W_-|}{t} =$$

$$= \frac{3600 \times 33.38 \times 10^{-3}}{200} + \frac{3600 \times 4.82 \times 10^{-3}}{200} = 0.688 \text{ W}$$

which is identical to the value obtained for the supercapattery cell.



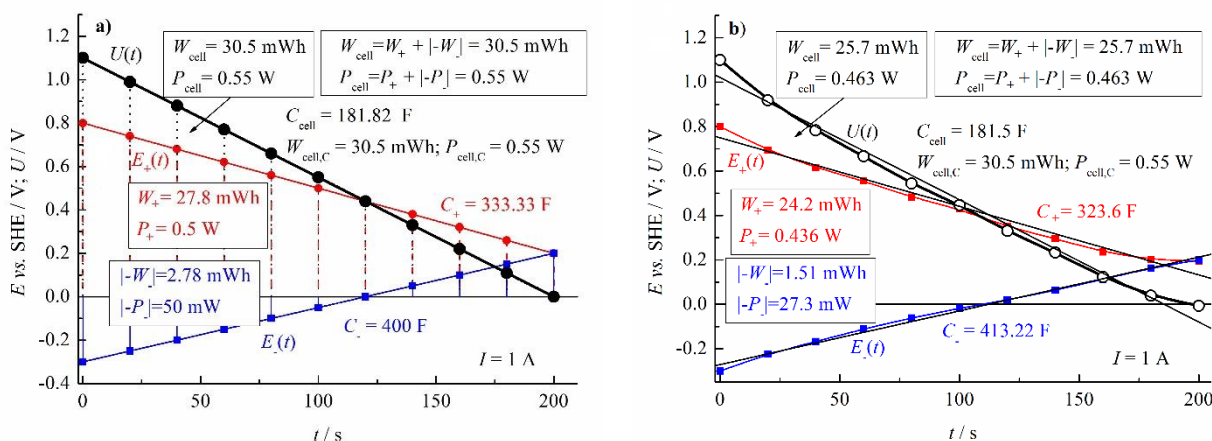
**Figure 5.** Estimations of the energy potentials of the electrodes (vs. SHE) of the rechargeable supercapattery cell.

Figure 6 shows the structure of the voltage and potentials during discharge of the mass balanced asymmetric supercapacitors. In Fig. 6a the ideal discharge behavior of the electrodes is shown. The energy and the power of the supercapacitor cell are  $W_{\text{cell}} = 30.5 \text{ mWh}$  and  $P_{\text{cell}} = 0.55 \text{ W}$  obtained using the integral form, Eq 17 and Eq. 21, are identical to the values obtained using the linear form with the determined capacitance of the cell of 182 F, Eq. 19 and 22. The energy and power of the cell obtained as a sum of the energy and power potentials of the positive and negative electrode (obtained only by integral method) are also identical. Because from the determined capacitance the energy and power potentials of electrode materials cannot be determined, as shown above, the linear method is not recommended. For the nonideal supercapacitor electrode discharge, Fig. 6b, points are deliberately slightly moved from the straight line. Using the integral method for the energy and power potentials determination, the values obtained by the sum of positive and negative electrode energy and power potentials are identical to the energy and power of the supercapacitor cell. On the contrary, applying the simplified linear form of energy and power determination for the cell using the Eqs. 19 and 22, much higher values ( $W_{\text{cell,C}}$  and  $P_{\text{cell,C}}$ ) are obtained. Unfortunately, most of the literature reported values used this approach, even for the nonlinear discharge of the supercapacitive cell. This problem arises because capacitance is not constant over the entire range of discharge. So, every point has the differential

capacitance, which can be estimated from the slope of the tangent at any point. To estimate the average integral capacitance of the cell, the energy of the cell should be obtained by the integration of the discharge curve, using Eq. 17, and then using the rearranged Eq. 19:

$$C_{av,cell} = \frac{2 \times 3600 \times W_{max}}{U_0^2}$$

to obtain the average cell capacitance. From Fig. 6b, the integral energy of the cell is 25.7 mWh and  $U_0 = 1.1$  V, so the average capacitance is 153 F, which is much smaller than the value of 185.1 F obtained by the linearization of the nonlinear discharge curve. For the details about the determination of integral capacitance from the differential capacitance see [36].



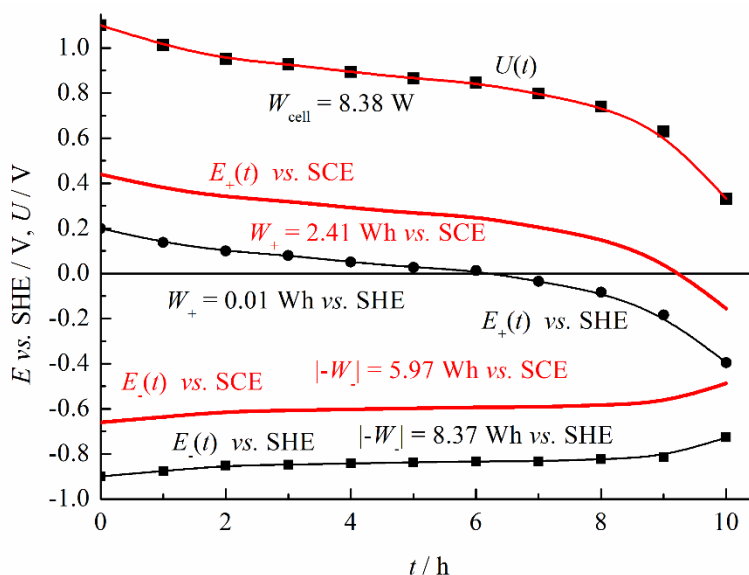
**Figure 6.** a) Estimations of the energy and power potentials of the ideal electrodes (vs. SHE) of the supercapacitor cell. b) Estimations of the energy and power potentials of the nonideal electrodes (vs. SHE) of the supercapacitor cell.

#### 4. THE PROBLEM OF THE REFERENCE ELECTRODE

Establishing the reference point for the calculations of the energy and power potentials of electrode material has a crucial significance. The most common reference electrodes are saturated calomel, SCE, silver-silver chloride, AgCl|Ag, electrode, while mercury sulfate and hydroxide electrodes are used occasionally. By choosing the reference point, the energy and power potentials of electrode materials will be changed. As an example, the discharge curves of the battery cell, together with discharge curves of the positive and negative electrode, measured against the saturated calomel electrode and converted to standard hydrogen electrode are shown in Fig. 7. In both cases, the cell voltage obtained as a difference of the single electrode potential  $U(t) = E_+(t) - E_-(t)$  is identical for the same reference electrode. Also, the energy and the power of the cell obtained as a sum of energy and power potentials of the positive and negative electrode have the same value:  $W_{cell} = 8.38$  Wh and  $P_{cell} = 0.84$

W. However, depending on used reference electrodes the energy and power potentials of the electrodes differ significantly:  $W_+ = 2.41 \text{ Wh vs. SCE}$ ;  $W_+ = 10 \text{ mWh vs. SHE}$ , and  $P_+ = 0.241 \text{ W vs. SCE}$ ;  $P_+ = 1 \text{ mW vs. SHE}$ ;  $|-W_-| = 5.97 \text{ Wh vs. SCE}$ ;  $|-W_-| = 8.37 \text{ Wh vs. SHE}$ , and  $|-P_-| = 0.597 \text{ W vs. SCE}$  and  $|-P_-| = 0.837 \text{ mW vs. SHE}$ . For the same reference electrodes, the sum of the energy and the power potentials are identical to the cell.

Therefore, it is of crucial importance to refer to which reference electrode the values are obtained and/or reported. It is advised that all single electrode charge-discharge curves measured against any reference electrode should be converted and presented to the scale of the standard hydrogen electrode (SHE).



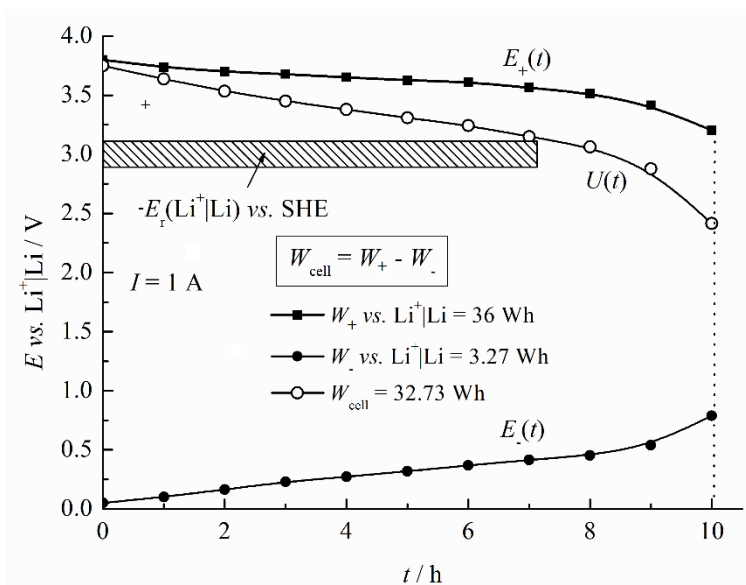
**Figure 7.** The structure of the cell voltage using the saturated calomel (SCE) and standard hydrogen electrodes (SHE) for the discharge of positive and negative electrode.

For the lithium-based systems in which the Li-foil is usually used as a reference electrode, the conversion to the standard hydrogen electrode potentials is not an option. The standard potentials of  $\text{Li}^+|\text{Li}$  of  $-3.04 \text{ V}$ , is a special case for aqueous solutions determined using the Li-amalgam. In aprotic, organic solvents, the standard potentials could vary significantly, the activity of the lithium-ions is also questionable, so the referred potentials should remain against  $\text{Li}|\text{Li}^+$  reference electrode [37]. In that case, as is shown in Fig. 8, most of the energy potentials are accumulated in the positive electrode, thus the variation of the  $\text{Li}^+|\text{Li}$  reference potentials in different solvents and  $\text{Li}^+$  ion concentrations could be neglected. Consequently, the energy of the cell obtained by the integration of  $U(t)$  curve is  $32.27 \text{ Wh}$ , and can be obtained as a difference of the energy potentials of positive and negative electrodes, and also for the power of the cell, it is also valid that represent the differences of the power potentials of the positive and negative electrode, *e.g.*:

$$W_{\text{cell}} = W_+ - W_-$$



$$P_{\text{cell}} = P_+ - P_-$$



**Figure 8.** The structure of the voltage for the lithium-based rechargeable cell using the lithium metal reference electrode.

One interesting observation can be evaluated for the systems where both electrode possess positive potentials in respect to the reference electrode. For example for the systems with the same positive electrode, increasing the potential of negative electrode, the energy and power potentials of negative electrode will increase, but the energy and power of the cell will decrease, because the voltage of the cell, responsible for the energy and power content of the cell, will decrease as well.

### 5. POSSIBLE USES AND PROPOSAL FOR THE DATA PRESENTATIONS

The possible uses of the proposed methods for the determination of the energy and power potentials of the electrode material and estimation of the possible characteristics of the cell will be explained for the system of polyaniline and lead-lead sulfate electrode in 2 M H<sub>2</sub>SO<sub>4</sub> [35]. The experimental procedures, which are not important for this purpose, of polyaniline and lead sulfate synthesis, can be found in [36, 38].

If two authors report the measurements of different electrode materials, from the discharge curves, which is shown in combined Fig. 9, first the specific current (mA g<sup>-1</sup> or A g<sup>-1</sup>) and specific capacity (mAh g<sup>-1</sup> or Ah g<sup>-1</sup>) of the possible positive and negative electrode can be calculated using the equations:

$$I_{s,\pm} = \frac{I}{m_{\pm}}$$

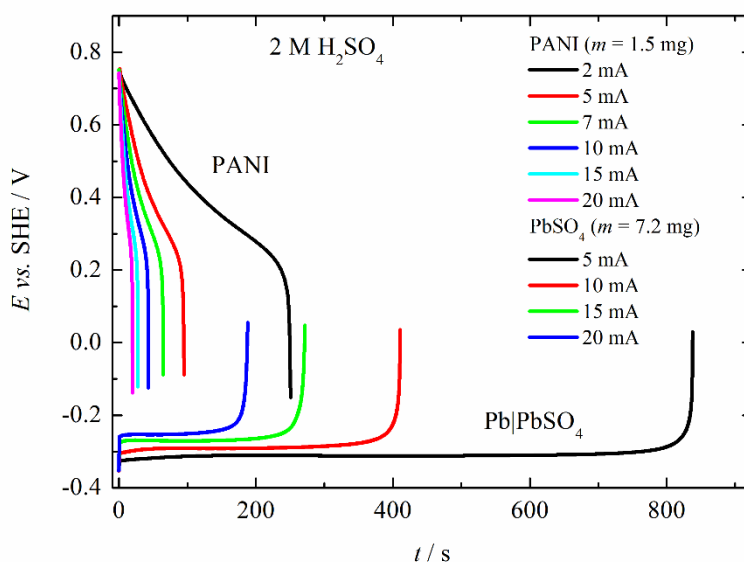
$$q_{s,\pm} = \frac{I_{s,\pm} \times t}{3600}$$

factor 3600 is introduced, because most of the research report data at the time scale of seconds. In the case of supercapacitors, the specific capacitance of the electrode over a specific current should be reported. Also, from the open circuit potentials, the open-circuit voltage of the possible cell can be estimated, which is in the case shown in Fig. 9, 1.1 V. By the integration of the discharge curves, the specific energy and power potentials using the reference electrode as zero can be calculated using the set of the equations:

$$w_+ = \frac{I_{s,+}}{3600} \int_0^t E_+(t) dt \quad \text{and} \quad |-w_-| = \frac{I_{s,-}}{3600} \int_0^t E_-(t) dt$$

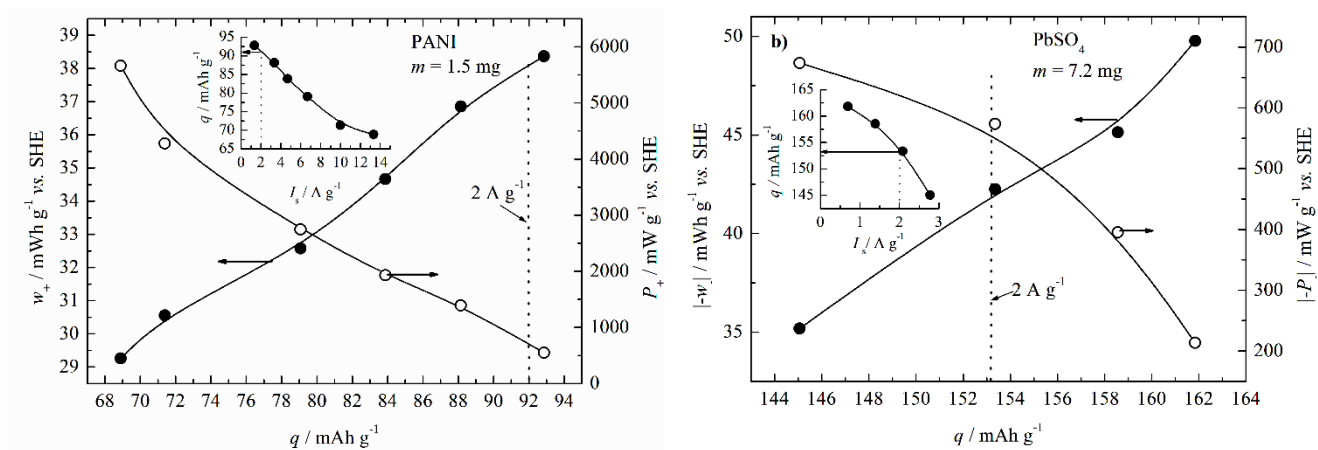
$$P_+ = \frac{I_{s,+}}{3600 \times t} \int_0^t E_+(t) dt \quad \text{and} \quad |-P_-| = \frac{I_{s,-}}{3600 \times t} \int_0^t E_-(t) dt$$

which always must be denoted against which reference electrode (*vs. SHE; vs. SCE, etc.*) are reported. Again, it should be noted that energy and power potentials for the capacitive electrode cannot be obtained from the determined electrode capacitance and potential windows.



**Figure 9.** The galvanostatic discharge of the polyaniline (PANI) and lead-lead sulfate electrodes in 2 M H<sub>2</sub>SO<sub>4</sub> with different currents.

Even the Ragone plot is the most widely used [24-26], to estimate characteristics of the possible cell consisted of two separately investigated electrode materials, the following presentation of the data could be suggested. First, the dependence of the specific capacity or capacitance over the specific current should be presented. In this paper, the dependence of specific capacity on specific current is shown as insets in Figs. 10a and b. Second, the specific energy and power potentials are shown in the same graph but as dependence on specific capacity, or in the case of supercapacitors specific capacitance.



**Figure 10.** Proposal for the possible presentation of the data a) for the positive (PANI) electrode b) for the negative (Pb|PbSO<sub>4</sub>) electrode.

Therefore, if one would like to estimate the performance of the possible PbSO<sub>4</sub>|PANI cell at some specific current, the following procedure should be performed. It should be noted that for the rough estimations, the composition of the used electrolyte could vary, but certainly, the acidic and alkaline electrolytes cannot be considered for comparisons.

For example, if we use 1 g of PbSO<sub>4</sub>, the corresponding specific capacity for a specific current of 2 A g<sup>-1</sup> is 153 mAh g<sup>-1</sup>, inset in Fig.10b. At the same conditions for 1 g of PANI electrode, the specific capacity is 92 mAh g<sup>-1</sup>, inset in Fig.10a. Therefore, from the mass balance it can be obtained that the mass of the PANI electrode should be:

$$m_+ = \frac{m_- q_-}{q_+} = \frac{1 \text{ g} \times 153 \text{ mAh g}^{-1}}{92 \text{ mAh g}^{-1}} = 1.66 \text{ g PANI}$$

Consequently, the capacity of the cell at 2 A g<sup>-1</sup> will be:

$$Q_{\text{cell}} = \frac{m_+ q_{s,+} + m_- q_{s,-}}{2} = \frac{1.66 \times 92 + 1 \times 153}{2} = 153 \text{ mAh}$$

and specific capacity:

$$q_{s,\text{cell}} = \frac{Q_{\text{cell}}}{m_+ + m_-} = 57.5 \text{ mAh g}^{-1}$$

The energy potentials of 1 g PbSO<sub>4</sub> is 42 mWh vs. SHE, Fig. 10b, while for the PANI is than  $m_+ w_+$  or 1.66 g × 38 mWh g<sup>-1</sup> = 63.1 mWh vs. SHE. So, the energy of the cell will be  $W_+ + |-W_-| = 63.1 + 42 = 105.1 \text{ Wh}$  or specific energy 39.5 Wh g<sup>-1</sup>. Finally, the power of the cell at the current of 2 A g<sup>-1</sup> could be written as:

$$P = m_+ P_+ + m_- |-P_-| = 1.66 \text{ g} \times 677 \text{ mW g}^{-1} + 1 \text{ g} \times 560 \text{ mW g}^{-1}$$

so the power of the cell will be 1684 mW or 633 mW g<sup>-1</sup>

## 6. CONCLUSIONS

The paper is treating the determination of energy and power potentials of the electrode materials for different charge storage cells. It is shown that by introducing the reference electrode as a reference point, the energy and power potentials of the electrode could be evaluated. Applying the graphical and mathematical treatment for the battery, supercapattery, and supercapacitors, it is shown that under the conditions of the same reference point, the sum of the energy and power potentials of the electrodes corresponds to the values of full cell. It is also suggested that energy and power potentials should be reported, with the analogies with electrode potentials, against used reference electrode, for example,  $w$  vs. SHE / Wh g<sup>-1</sup> or  $P$  vs. SHE / W g<sup>-1</sup>. The problem of the used reference electrode is also treated. The proposed analysis is applied on two separate electrode materials, and procedure how from the electrode measurements, capacity, energy, and power of the hypothetical cell could be estimated.

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