ANALYSIS OF THE CAPACITY OF LiFePO$_4$ BATTERIES BASED ON THE RELEASED ELECTRONS

ANALIZA KAPACITETE LiFePO$_4$ BATERIJ V ODVISNOSTI OD SPROŠČENIH ELEKTRONOV

Matic Krašovic[1][ℛ], **Peter Virtič**[1]

Abstract

The lithium iron phosphate battery, or LiFePO$_4$, has been analysed in this article. Initially, a comprehensive overview was provided concerning the properties and chemistry of batteries. Subsequently, the core focus of the research was addressed, which centred on quantifying the number of electrons released per 1 cm^2 in 1 second in one cell in the battery during charging. Additionally, comparisons were made, to ascertain whether batteries with capacities lower than the one selected for this study impact the number of electrons released during charging, assuming constant battery voltage, cell surface area and current, or whether the number of released electrons remains unaffected by the capacity variations. The analysis was conducted analytically, and demonstrated transparently using the MATLAB software package.

Povzetek

V tem članku je bila analizirana litij-železno-fosfatna baterija oziroma LiFePO4. Na začetku je bil podan celovit pregled lastnosti in kemije baterij. Nato je bilo obravnavano osrednje področje raziskave, ki se je osredotočalo na kvantifikacijo števila elektronov, sproščenih na 1 cm2 v 1 sekundi v 1 celici baterije med polnjenjem. Poleg tega je bila opravljena primerjava, da bi bilo ugotovljeno, ali baterije z manjšimi kapacitetami kot tista, izbrana za to študijo, vplivajo na število

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ℛ   Corresponding author: Matic Krašovic, E-mail address: matic.krasovic@student.um.si

1   University of Maribor, Faculty of Energy Technology, Krško, Slovenia

sproščenih elektronov med polnjenjem, ob predpostavki konstantne napetosti baterije, površine posamezne celice in toka, ali pa število sproščenih elektronov ostaja nespremenjeno ne glede na variacije kapacitete. Analiza je bila izvedena analitično in bolj pregledno v programskem paketu MATLAB.

1   INTRODUCTION

Nowadays, batteries have become used widely all over the world, and this leads to battery technology developing at a fast-paced rate. Batteries are now key elements in the development of electric vehicles, renewable energy sources, uninterruptible power supplies and portable systems *[1]*.

Lithium batteries are used for energy storage, due to their high-power densities and long lifespan compared to other battery types. Lithium iron phosphate, $LiFePO_4$ delivers good electrochemical performance alongside a low internal resistance of the battery. The $LiFePO_4$ cell is more tolerant to maximal charging conditions, and less stressed than Li-ion based cells when kept under high voltage for long periods. Low temperatures reduce performance, whereas high temperatures shorten the lifespan. $LiFePO_4$ cells have good thermal stability, high abuse tolerance and are safer than Li-ion based chemistries, but also have a higher self-discharging rate *[1]*.

Many things and terminology get mixed up in the field of batteries and their chemistry. That is why this article has been created: to give the readers an overall view of the batteries, cells, terminology such as oxidation, reduction, redox reaction, and, briefly, about the chemistry of the batteries and what is happening inside them, and to make that clear. Furthermore, research has been conducted on the number of electrons released in a chemical reaction. Because this is a redox reaction and the oxidation number of elements changes through the process, many electrons are released through the reaction.

2   LITHIUM IRON PHOSPHATE BATTERY

A battery is a device that converts chemical energy to electrical energy with the help of an electrochemical redox reaction (oxidation-reduction). Since this article talks about the $LiFePO_4$, which can be re-charged, there are two processes that can occur, and these are charging and discharging, so the redox reaction flows in a different way when charging or discharging. A redox reaction includes the flow of electrons from one material to other over the outside electric circuit *[2]*.

2.1   Battery building blocks

A cell is a basic electrochemical unit that converts electrical energy directly from chemical energy. A battery consists of one or more electrochemical cells that are connected electrically in appropriate series or parallel arrangements. A cell is made of four main components *[3]*:

1. <u>An anode,</u> or negative electrode, is an electrode where oxidation is always happening. The anode transmits electrons outside the circuit *[3]*.

2. <u>A cathode,</u> or positive electrode, is an electrode where reduction is always happening. The cathode gathers the electrons which the anode released *[3]*.

3. <u>An electrolyte</u> is an ion conductor, and provides a medium for charge transfer (ions) inside the cell between the anode and cathode. The electrolyte is typically water, or some other form of liquid where different kinds of salts or acids are dissolved *[3]*.

4. <u>A separator</u> is a material that is used for a mechanical separation of the anode and cathode. It is conductive for electrolyte *[3]*.

In this article, the focus will be on the $LiFePO_4$ battery. This type of battery is a secondary battery that can be charged again.

This battery is more tolerant to full charge conditions, and is less stressed than other lithium-ion systems if kept at high voltage for a prolonged time. The cathode is made of lithium iron phosphate ($LiFePO_4$) material, and the anode out of graphitic carbon. Its materials can be seen nicely in the chemical reaction equation, which will be presented further in the article. They are very safe (from damage, shock and fire does not occur spontaneously) *[4]*.

The parameters of the $LiFePO_4$ battery can be seen in Table 1.

Table 1: *Parameters of the $LiFePO_4$ battery [4]*

Lithium iron phosphate	$LiFePO_4$; lithium iron phosphate cathode; graphite anode; short form: LFP
Voltages	12,8 V rated voltage; 3,2 V nominal voltage (one cell); typical operating range: 2,5-3,65V (one cell)
Specific energy	90-120 Wh/kg
Cycle life	2000 and higher (related to the depth of discharge and the temperature)
Thermal runaway	270°C…. very safe battery, even if fully charged
Currents	They vary, and are related to capacitance (Ah)

3 BATTERY OPERATIONS OF AN $LiFePO_4$

3.1 Discharging process of an $LiFePO_4$

When the battery/cell relates to outside load, electrons flow from the negative anode (which is oxidised) over the load on the positive cathode, which collects the electrons (and is reduced). As the battery is used and the reactions at both electrodes chug along, new chemical products are produced *[5]*. The discharging process can be seen in Fig. 1.
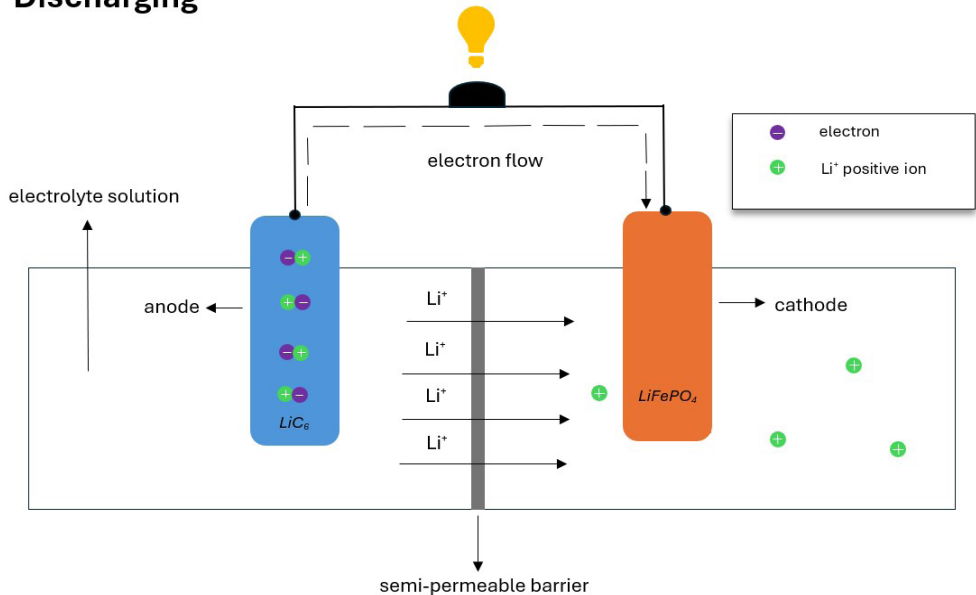
Discharging

Figure 1: LiFePo$_4$ discharging *[own source]*

3.2   Charging process of an LiFePO$_4$

In the charging process the flow of electrons is in the other direction than before. Now, let us clarify some definitions, as it was said in the Abstract. Before, the anode was a negative electrode and the cathode positive. Now, when the process flows in other direction, it can be said that, on the positive electrode, there is an oxidation, and on the negative a reduction. By definition, an anode is an electrode where oxidation happens and a cathode where reduction happens. In this case, a positive electrode is an anode and a negative one is a cathode. However, when charging of the battery occurs, the anode and cathode replace their positions and + and − stay in their positions *[5]. The c*harging process can be seen in Fig. 2.
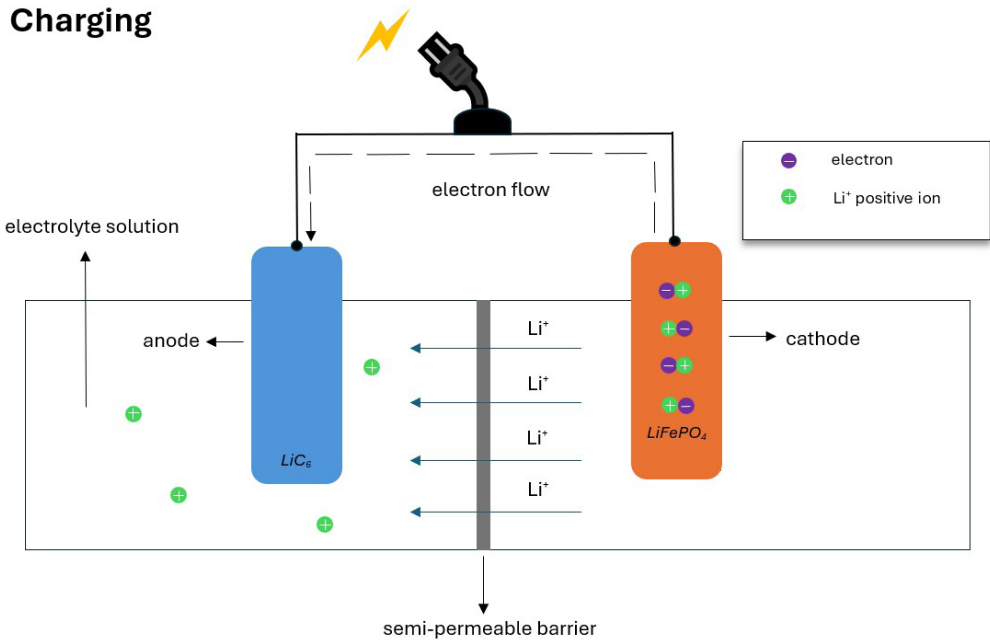
Charging

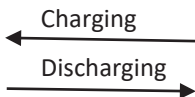**Figure 2:** LiFePo4 charging *[own source]*

3.3 Reactions in discharging and charging of an LiFePO$_4$

The charging and discharging of an LiFePO$_4$ can be shown as an electrochemical reaction which works in both ways *[6]*.

Anode:
$$LiC_6 \leftrightarrow Li^+ + 6C + e^-$$ (3.1)

Cathode:
$$FePO_4 + Li^+ + e^- \leftrightarrow LiFePO_4$$ (3.2)

Charging

Discharging

The arrows represent in which way the chemical reaction is happening, due to whether it is discharging or charging.

When the battery is discharging, the anode is negatively charged and the cathode positively, and, when it is charging, the anode is positively charged and the cathode negatively.

4   METHODS OF RESEARCH

An LiFePO$_4$ battery and its chemistry at a more advanced level have been analysed in this article.

A LiFePO$_4$ battery with *Q*=280 Ah and *V*=12,8 V has been taken *[7]*.

This battery is comprised of four cells arranged in a series configuration. Given that the battery's nominal voltage is 12.8 V, the voltage of each individual cell is 3.2 V. Furthermore, with a total capacity of 280 Ah, each cell possesses a capacity of 70 Ah *[7]*.

4.1   Area for calculation

Calculating the surface area is a crucial aspect of this article, as the research seeks to determine the number of electrons released per square centimetre (and per second), assuming that the material is structured such that the chemical reaction occurs solely on the electrode surface. One alternative method will be presented, called the BET method, but I have opted not to pursue it. The decision against this method was made because this method is experimental and requires laboratory execution. Since the calculations are primarily analytical and my focus was not on laboratory work, I chose to compute the surface area using equation (4.5). The method I employed will be detailed after the BET method chapter.

4.1.1   BET method

The BET method is a classic method for the determination of a specific area of some substance, and is carried out around relative pressures between 0,5 and 0,3 bars. In this process, one layer is adsorbed, which helps us determine a specific area by the BET method equation (4.1) *[8]*.

The BET equation can be seen in (4.1):

$$\frac{P_n}{V_a(P_0 - P_n)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \times \frac{P_n}{P_0}$$

(4.1)

where $\frac{P_n}{P_0}$ is the relative pressure in %, V_a is the adsorbed volume in *cm³,* and V_m is the volume of one layer in *cm³*. C is a constant, which tells the intensity of the reaction between gas and area, and can vary; a higher value means a stronger interaction. *[8]*

The whole area S$_t$ and specific area S are determined by calculating the following two equations (4.2) and (4.3):

$$S_t = \frac{V_m N_A A}{M}$$

(4.2)

$$S = \frac{S_t}{W}$$

(4.3)

where N_A is Avogadro's constant (6,023*20²³ mol⁻¹), M is a molecule's mass of the gas in *g/mol*, A is a cross-section area of the gas molecule in *cm²* and W is the mass of a substance in *g [8]*.

4.1.2   Proposed method

In this research, the area of the battery has been calculated a little bit differently than the previous alternative – the BET method.

The length of this battery is 533 mm and width 241 mm [7].

That is why the area of one side is calculated as seen in equation (4.4):

$$S = 533mm \times 241mm = 1284{,}53 \; cm^2 \tag{4.4}$$

The area of the battery's lower layer has been determined by calculating the equation (4.4). To calculate the area of one cell, equation (4.5) needs to be used:

$$S_c = S \times 0{,}75 \tag{4.5}$$

where S_c is the area of one battery cell and S is the whole area of the battery.

When everything is calculated, the area of one cell equals S_c=963,3975 cm².

The battery's maximum capacitance, denoted as Q', is specified at 280 Ah (ampere-hours). However, capacitance can also be quantified in C (Coulombs), which should not be confused with the C-rate associated commonly with battery charge and discharge rates. Battery capacity is defined as the total amount of electricity generated by the electrochemical reactions in the battery [9].

Given that one Coulomb equates to the flow of one ampere for one second (1C=1A*1s), the conversion of capacitance from ampere-hours to Coulombs can be accomplished using the formula (4.6). This calculation will provide the capacitance in terms of Coulombs, offering an alternative and scientifically equivalent measurement of the battery's storage capacity.

$$Q = Q' \times t = 280Ah \times \frac{3600s}{h} \tag{4.6}$$

where Q is the new capacitance in C, Q' is the old capacitance in Ah and t is the time.

By calculating the new capacitance in equation (4.6), the result equals Q=1008000 C.

The new capacitance is now measured in Coulombs, and this value encompasses the combined capacity of all four cells. However, the research focuses on just a single cell. Therefore, to align the measurements with the study's scope, it was necessary to adjust the starting capacitance, expressed in ampere-hours, to reflect only one cell. The result provides the following equation (4.7):

$$Q'_c = \frac{Q'}{4} = \frac{280Ah}{4} \tag{4.7}$$

where Q'_c is the capacitance of only one cell in Ah.

When Q'_c in equation (4.7) is calculated, the result is $Q'_c = 70$ Ah

We require the capacitance of a single cell to be expressed in the units of ampere-seconds or, equivalently, in Coulombs.

A similar equation as (4.6) has been used in (4.8):

$$Q_c = Q'_c \times t = 70Ah \times \frac{3600s}{h} \tag{4.8}$$

where Q_c in equation (4.8) is now the capacitance of only one cell in unit C and is equal to Q_c .=252000 C.

After previous calculations of the area of one cell in equation (4.5) and capacitance of one cell in equation (4.8), the results were: S_c=963,3975 cm² and Q_c=252000 C.

Everything was prepared to commence the analysis and calculations of the number of released electrons per square centimetre per second in a single cell of an LiFePO$_4$ battery.

To initiate the analysis, it is essential to determine the molar quantity, denoted as n [mol]. According to Faraday's law, the total electric charge Q required to oxidise/reduce the reactant in the redox reaction is proportional to the number of oxidised/reduced substances *[10]*. To do that, the equation (4.9) is needed:

$$Q_c = nFz \tag{4.9}$$

where n is the molar number in mol, and F is a Faraday constant which equals 96485 C/mol.

In this context, the variable *z* quantifies the number of electrons participating in a single chemical reaction within an exceedingly brief timeframe, which differs from the number of electrons central to the objective of this study. As elucidated in equations (3.1) and (3.2), only a single electron is involved in the reaction mechanism; therefore, for the purposes of analysis, *z* was set to 1.

After a modification of equation (4.9), the new equation (4.10) looks like this:

$$n = \frac{Q_c}{Fz} = \frac{252000 C}{96485 \frac{C}{mol} \times 1} \tag{4.10}$$

Upon calculating the molar number *n*, the result obtained ws 2,612 mol.

The final step was to calculate what this article has been about, so, electrons released per square centimetre per one second.

Now there are different calculated parameters: S_c=963,3975 cm², Q_c=252000 C and n=2,612 mol.

Having determined all the necessary parameters, the calculation of the number of electrons N released can now be proceeded with. Because we know *n*, the equation (4.11) can be used:

$$N = n \times N_A \tag{4.11}$$

where N represents number of electrons [e⁻] and N_A is the Avogadro's constant; N_A=6,023*20²³ particles (e⁻)/mol.

$$N = 2,612 mol \times (6,023 \times 10^{23} \frac{e^-}{mol}) \tag{4.12}$$

When *N* is calculated, the result is: $N = 1,573 \cdot 10^{24} e^-$.

The number of electrons released per square centimetre must now be determined, as N in equations (4.12) and (4.13) is calculated over the entire area of one cell. The calculation over one second will be addressed later in the article.

The equations that will determine the result are addressed in (4.13) and (4.14):

$$N_{cm^2} = \frac{N}{S_c} \tag{4.13}$$

$$N_{cm^2} = \frac{1{,}573 \times 10^{24} e^-}{963{,}3975 cm^2} \tag{4.14}$$

For the ith calculation of N over one squared centimetre in equations (4.13) and (4.14) the result is $N_{cm^2} = 1{,}6328 \cdot 10^{21} \frac{e^-}{cm^2}$.

where N_{cm^2} now represents how many electrons are released in one cell on 1 cm².

It is understood that, for a battery cell with a capacitance of 70 Ah, as specified in this research, the current over a period of one hour would be 70 A, assuming the presence of a resistance that would discharge the battery within this timeframe. However, this definition may vary, as this number is not always exact. In this method, the current will be calculated with the help of its losses through the circuit itself.

The maximum charge rate for a LiFePO$_4$ cell is approximately 26-30 % of the amp-hour rating, as reported in reference [11]. The authors in the cited article [11] provided an example with a lead acid battery, where they utilised 10 % of the amp-hour rating to determine their charging current. For the specific type of battery discussed in this research, the suggested charge rate falls within the range of 26-30 %. Consequently, a median value of 28 % has been adopted for this study.

To calculate the current for a battery with a capacitance of 280 Ah, the following equations (4.15) and (4.16) can be used:

$$I' = Q' \times 0{,}28 \tag{4.15}$$

$$I' = 280Ah \times 0{,}28 = 78{,}4\ A \tag{4.16}$$

The discrepancy in units between the left and right sides of the equation (4.16) arises directly from the earlier discussion regarding the percentage of the amp-hour rating, as detailed in reference [11]. After current calculation, this is the result: $I' = 78{,}4\ A$

In practical terms, it has been observed that losses, while charging, range between 20-40 %, as documented in reference [11]. The authors of article [11] provided an example with a lead acid battery, noting that this type of battery experiences a similar percentage of losses as the battery type discussed in this article. Previously, a median value of amp-hour was selected for the current calculation; similarly, a median value of 30 % will be adopted here, to account for the losses for the charging time calculation.

It can be seen in equation (4.16) that the charging current is 78,4 A.

This allows us to advance to the next stage of the article, which involves determining the charging time, considering the losses.

The calculation for quantifying the losses will be performed in equation (4.17):

$$Q'' = Q' \times 0,3 = 280Ah \times 0,3 = 84\ Ah \tag{4.17}$$

$$Q''' = Q' + Q'' = 280Ah + 84Ah = 364\ Ah \tag{4.18}$$

where Q''' in equation (4.18) is the new capacitance including the original capacitance Q' (280 Ah) of the battery and the battery's losses Q'' (84 Ah).

To proceed with the charging time calculation, equation (4.19) is needed in the most basic form:

$$Q = I \times t \tag{4.19}$$

With rearranging the equation (4.19) and implementing new values inside, the equation (4.20) is needed for the charging time calculation:

$$t = \frac{Q'''}{I_c} = \frac{364Ah}{78,4A} = 4,64\ h \tag{4.20}$$

When the calculation from equation (4.20) is done, the charging time equals t=16704 s.

Now that the charging time has been determined using equation (4.20), all the necessary data are available to calculate the main goal of this article

The number of released electrons per square centimetre has been calculated in equation (4.14). The calculation can now be extended to determine also the number of released electrons per second. All that needs to be done is to divide the results from equation (4.14) with the charging time that has been calculated in equation (4.20). The result will provide equation (4.21):

$$N_{cm^2 s} = \frac{N_{cm^2}}{t} = \frac{1,6328 \times 10^{21}\ \frac{e^-}{cm^2}}{16704\ s} \tag{4.21}$$

When the number of electrons from equation (4.21) are calculated, the result is:

$$N_{cm^2 s} = 9,78 \cdot 10^{16}\ \frac{e^-}{cm^2 s}.$$