



Short communication

A novel way to calculate energy efficiency for rechargeable batteries

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ABSTRACT

A new method to calculate energy efficiency for rechargeable batteries is proposed successfully and described in the study. The energy efficiency is divided into three categories, the energy efficiency under charge, the energy efficiency under discharge and the energy efficiency under charge–discharge. A key factor in calculating the energy efficiency is attributed to resolve the chemical energy stored in batteries (referred to as net energy hereafter). The net energy is stated with an equation of a function of the open circuit voltage (OCV) and the state of charge (SOC). Therefore, the relationship of OCV and SOC must be sought to solve the function. The OCV curve is computed by average of the charge curve and the discharge curve at a low rate. The quantitative relation of OCV to SOC is acquired by nonlinear fit. According to the method, LiFePO₄ power batteries' energy efficiencies are measured under the moderate current charging and discharging condition. The quantitative relations of the efficiencies are also analyzed for the batteries.

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1. Introduction

Rechargeable batteries play important roles in many applications, such as in power tools, portable power products, and, most especially, electric vehicles. The characteristics of batteries are harder to predict compared with other electric and mechanical devices due to the complexity of the chemical and physical processes involved. A battery is a device that converts chemical energy directly into electric energy; in the case of a rechargeable system, the battery is recharged by reversing the process [1]. Therefore, energy efficiency represents the utilization rate of energy, including the chemical energy and the electric energy, during processes. Unlike those of tiny-scale batteries, the parameters or characteristics of large-scale batteries, especially of power batteries used in transportation, require thorough analysis, not only with regard to basic properties such as voltage, capacity, and energy, but also properties concerning the vehicle's environment, such as temperature, power and energy efficiency. The current study on energy efficiency aims to (1) raise the utilization rate of energy to save energy by optimizing the working parameters; (2) predict the discharge time of batteries used in pure electric vehicles, assuming the energy efficiency given, by which the remaining mileage can be forecast; (3) judge whether the batteries are excellent by using measured energy efficiency as an evaluation measure; and (4) contribute to thermal management, because thermal energy is related

to the loss of electric or chemical energy, based on conservation of energy.

Owing to its importance, energy efficiency is a key parameter for evaluating the properties of batteries; therefore, it is studied in systems that consist of neptunium redox flow batteries [2,3], nickel/metal hydride batteries [4,5], fuel cells [5,6], sodium–sulfur batteries [7], photovoltaic batteries [8], and zinc–bromine batteries [9]. Moreover, the methods to calculate energy efficiency vary with the battery systems. The method of energy efficiency calculation for rechargeable batteries generally cited in the literature is from the US Department of Energy (DOE) [10], and only provides the method to be used to determine the energy efficiency under discharge. Briefly summarized, the abovementioned literature states that efficiency is the ratio of the discharged energy to the recharged energy with the given steps. The details of the method are introduced in Section 2. In spite of the merit of operability, the method has two disadvantages. First, it does not offer a way to determine energy efficiency under charged condition. Second, the recharged energy is not equal to the chemical energy stored in the batteries, i.e., the net energy, because the recharged electric energy cannot be totally converted to chemical energy. To our knowledge, in addition, the method of calculating energy efficiency for rechargeable batteries has never been found or published in a paper or book except in the abovementioned literature.

According to the above discussion, a method for calculating energy efficiency for rechargeable batteries would be highly desirable. In the current study, a novel method for calculating efficiency of rechargeable batteries based on electrochemistry theory is proposed. The proposed method is tested on LiFePO₄ power batteries, and the quantitative relations of the efficiencies are analyzed.

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2. Method

2.1. Definition of terms related to energy efficiency of batteries

The PNGV Battery Test Manual [10] prepared by the US DOE provides the formula to calculate round-trip efficiency as the ratio of discharge energy removed to regen energy returned during the profiles:

$$\text{Round-trip efficiency} = \frac{\text{watt} \times \text{hours (discharge)}}{\text{watt} \times \text{hours (regen)}} \times 100\% \quad (1)$$

Regen energy in Eq. (1) is the recharged energy inputted with given steps. Note that only discharging energy efficiency can be calculated from the equation, and that regen energy is not equal to the changed energy of the battery itself because of the occurrence of polarization in the charge process. The demerits of the method are discussed in Section 1.

In the current study, energy efficiency is divided into different categories: energy efficiency under charge (η_{charge}), energy efficiency under discharge (η_{disch}), and energy efficiency under charge–discharge (η_{battery}). Energy efficiency under charge is the ratio of the net energy (ΔQ_n) to the charged energy (Q_{in}) when the battery is charged.

$$\eta_{\text{charge}} = \frac{\Delta Q_n}{Q_{\text{in}}} \quad (2)$$

The way to calculate the net energy of batteries is discussed in Section 2.2. The value of Q_{in} is calculated using the following equation:

$$Q_{\text{in}} = \int_{\text{SOC}(0)}^{\text{SOC}(t)} U_{\text{charge}} C_n d\text{SOC} \quad (3)$$

In Eq. (3), $\text{SOC}(0)$ is the initial state of charge (SOC) when the battery is charged, $\text{SOC}(t)$ is the terminal SOC when the process is complete, U_{charge} is the voltage of the battery when it is charged, and C_n is the standard capacity of the battery. Note that C_n is not given by the factory or by others; instead, it is measured in a specific way (see Section 3).

Energy efficiency under discharge is the ratio of the discharged energy (Q_{out}) to ΔQ_n when the battery is discharged.

$$\eta_{\text{disch}} = \frac{Q_{\text{out}}}{\Delta Q_n} \quad (4)$$

The value of Q_{out} is calculated using the following equation:

$$Q_{\text{out}} = \int_{\text{SOC}(0)}^{\text{SOC}(t)} U_{\text{disch}} C_n d\text{SOC} \quad (5)$$

In Eq. (5), U_{disch} represents the voltage of the battery when it is discharged. Generally, data regarding the batteries, such as current, voltage and time, are recorded automatically by the facility when the batteries work. Therefore, Q_{in} and Q_{out} can be calculated from the recorded data. Ignoring the side reactions, $\text{SOC}(t)$ is calculated by Ref. [11] as follows:

$$\text{SOC}(t) = \text{SOC}(0) - \frac{\int I dt}{C_n} \quad (6)$$

In Eq. (6), the value of I is the positive when the battery is discharged.

Energy efficiency under charge–discharge is the ratio of Q_{out} to Q_{in} when the battery experiences a charge–discharge cycle in a certain conditions.

$$\eta_{\text{battery}} = \frac{Q_{\text{out}}}{Q_{\text{in}}} \quad (7)$$

The certain condition means that the temperature and the current are constant during the charge–discharge cycle.

2.2. Calculation of the net energy of batteries

The input or output energy should not be considered as the net energy attributed to the polarization resulting from the charge or discharge [12]. According to Ref. [12], the free energy ($|\Delta G|$) of batteries, which represents the stored chemical energy, is given by

$$|\Delta G| = \text{Charge passed} \times \text{Reversible potential difference} \quad (8)$$

In the present study, free energy is substituted with net energy because the former is a thermodynamic term. The reversible potential difference that is a constant for the given battery is replaced by the open circuit voltage (U_{OCV}). In fact, all activities are changed during the charge or discharge. Owing to the U_{OCV} varying with the SOC, the net energy, ΔQ_n , is given by

$$\Delta Q_n = \int_{\text{SOC}(0)}^{\text{SOC}(t)} U_{\text{OCV}} C_n d\text{SOC} \quad (9)$$

The value of U_{OCV} can be determined by two methods. One method involves artificially measuring the voltages of the batteries after these have rested for several hours after the SOC is set at a given value. This method is rather time consuming. The other method is offered by Plett [13]: for the LiFePO_4 battery, the cell is first fully charged (constant current 0.33 CA–3.6 V) and then discharged at a rate of 0.04 CA until fully discharged (2.5 V). The cell is then charged at a rate of 0.04 CA until voltage reaches 3.6 V. Cell voltages, as functions of SOC under discharge and under charge, are averaged to compute U_{OCV} . The quantitative relationship of U_{OCV} and solid Li-ion concentration was given in Refs. [14,15].

3. Experimental

3.1. Battery systems

The studied battery system consisted of a series of 30 LiFePO_4 batteries. The lithium-ion battery used in the investigation was VLP 50/62/100S-Fe (3.2 V/40 Ah) LiFePO_4 /graphite cells. The nominal cell capacity was 40 Ah, and the dimension (thickness \times width \times length) was 52 mm \times 64 mm \times 102 mm. Cathodes and anodes were coated in aluminum and copper foils, respectively. Polyvinylidene fluoride (PVDF) and N-methyl-2-pyrrolidone (NMP) were used as binders in manufacturing both electrodes. The separator was made of trilayers of polypropylene, polyethylene, and polypropylene (PP/PE/PP). The electrolyte consisted of 1 M LiPF_6 in ethylene carbonate (EC)–dimethyl carbonate (DMC)–ethyl methyl carbonate (EMC) (1:1:1, mass ratio) electrolyte.

3.2. Apparatus

A multichannel battery testing system (Arbin-EVTS, Arbin Limited) was used to charge and discharge the battery system and to record the voltage and the current. The battery testing system is able to measure the voltage and the current with an accuracy of $\pm 0.2\%$ and $\pm 0.1\%$, respectively. The battery system was inserted into the reference chamber equipped with an air conditioning system to balance the temperature at $25 \pm 2^\circ\text{C}$. A commercial batteries management system GTBMS005 (Haerbin Guantuo Power Corp., China) was used to monitor the voltage and the temperature at each cell, preventing the cell from overcharging, overdischarging, and overheating.

3.3. Charge and discharge conditions

The batteries discharged at 0.33 CA (20 A), the discharge was finished when the voltage reached 2.5 V per cell. After 1 h rest, the batteries charged at 0.33 CA (20 A) until the voltage reached 3.6 V

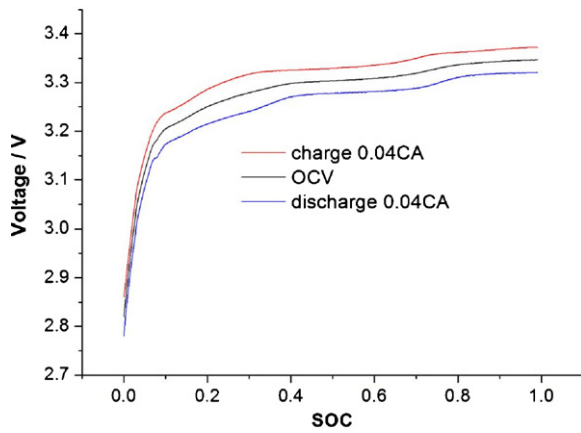


Fig. 1. The OCV curve obtained by the mean of 0.04 CA charge and 0.04 CA discharge curves.

per cell. Following another 1 h rest, the batteries then discharged at 0.33 CA (20 A) until the voltage reached 2.5 V per cell. Discharge capacity of 40.6 Ah was recorded, and was considered the standard capacity of the batteries. In the experiment, the batteries were at rest 1 h before next operation. The cut-off voltages of charge and discharge were set at 3.6 V and 2.5 V per cell, respectively. The remaining capacity was fully discharged at 0.33 CA (20 A). All steps were in accordance with the Chinese Standard QC/T 743-2006 [16].

4. Results and discussion

4.1. The function of OCV to SOC

OCV is the voltage of the cell when no current passes through; put simply, it is the potential difference between the positive electrode and the negative electrode when they are in the state of equilibrium. However, the measured voltage at the breaking of the current cannot be considered as OCV because the electrodes are not in the state of equilibrium, which is attributed to the relaxation of ions both in electrolyte and solid particles. In fact, in the present study, the voltage was found to have not changed after the cell was at rest for 1 h. Therefore, obtaining OCV using the method of artificial measurement would be too time consuming. According to the method described in Section 2.2, OCV as a function of SOC (Fig. 1) is computed by averaging the charge curve at a rate of 0.04 CA and the discharge curve at a rate of 0.04 CA. The low rate minimizes the dynamics excited in the cells, which eliminates the possible presence of hysteresis and ohmic resistance in the final function to the greatest extent [13]. For the purpose of computations involving OCV, the final curve is digitized at 1000 points and stored in a table.

To judge the accuracy of the OCV curve computed by the method, the artificially measured OCV was implemented at different SOC (see the blue solid triangle in Fig. 2). The implementation is as follows. First, the batteries are fully discharged, and then the voltage is measured after 1 h rest. Afterwards, the batteries are charged at different SOC (i.e., 0.2, 0.4, 0.5, 0.6, 0.7, 0.8, 1, respectively) and the voltages are also measured after 1 h rest. The red hollow circles in Fig. 2 are the OCV curves computed using the mean of the charge and the discharge value. As seen in the figure, the curves coincide well with the artificially measured values, proving the fine accuracy of the method.

Wang [14,15] stated that the equilibrium potential at the negative electrode (U_-) and the positive electrode (U_+) of a Li-ion battery, of which the active materials of the positive electrode are $\text{Li}_y\text{Mn}_2\text{O}_4$, Li_yCoO_2 , Li_yNiO_2 , or some combination of metal oxides, serve as a function of the solid Li-ion concentration in the negative

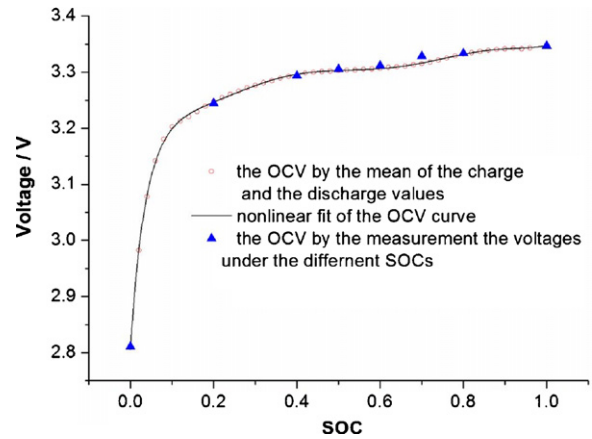


Fig. 2. Comparison of the OCV curve using nonlinear fit and the OCV dots by measured voltages. (For interpretation of the references to color in the text, the reader is referred to the web version of the article.)

(x) and positive (y). The relationships are described as follows:

$$U_-(x) = 8.00229 + 5.0647x - 12.578x^{1/2} - 8.6322 \times 10^{-4}x^{-1} + 2.1756 \times 10^{-5}x^{3/2} - 0.46016 \exp[15.0(0.06 - x)] - 0.55364 \exp[-2.432(x - 0.92)] \quad (10)$$

$$U_+(y) = 85.681y^6 - 357.70y^5 + 613.89y^4 - 555.65y^3 + 281.06y^2 - 76.648y - 0.30987 \exp(5.657y^{115.0}) + 13.1983 \quad (11)$$

However, no literature describes the function concern on LiFePO_4 battery. Note that, although relative, the solid Li-ion concentration and the SOC are not equivalent. In the present study, the quantitative relation (Eq. (12)) displays the function of OCV (y) to SOC (x) based on the theory above, but ignores U_- .

$$y = k_1x^6 + k_2x^5 + k_3x^4 + k_4x^3 + k_5x^2 + k_6x + k_7 + k_8e^{(k_9 - x^{k_{10}})} \quad (12)$$

The nonlinear fit of Eq. (12) to the computed SOC is shown in Fig. 2 (black line). The black line matches the hollow red circle, showing the accuracy of the fitted result. The values of k_1 to k_{10} are -14.194 , 114.943 , -181.199 , -219.605 , 626.090 , 13.461 , -533.413 , 3.204 , 5.120 , 1.883 , respectively, and the correlation coefficient of the fit is 0.9999. Thus, the quantitative relation of OCV to SOC can be obtained based on the above result.

4.2. The energy efficiency under charge

The charge curves of the LiFePO_4 batteries at different rates, as well as the OCV curve, are shown in Fig. 3a. As seen in the figure, the charge voltage plateaux rise greatly with the increment of the charge rate. Unsurprisingly, the SOC of the batteries at high charge rates cannot reach 1 when the charge is complete. A good example is the magenta line that represents the charge curve at a rate of 2 CA (Fig. 3a), displaying SOC of approximately 0.92 (represented by the dotted line) when the charge is complete. Note that the SOC interval of the OCV curve must be the same as that of the charge curve when energy efficiency under charge is calculated by ΔQ_n ratio to Q_{in} ; otherwise, a wrong outcome is obtained. The calculated η_{charge} as a function of SOC is shown in Fig. 3b. The red line in the figure is the polynomial fit of the efficiency, which describes the energy efficiency under charge (y) and current (x) with the equation $y = 0.99121 - 0.04221x + 0.0082x^2$ shown in the figure. The correlation coefficient of the fit is 0.9984, proving the validity of the outcome.

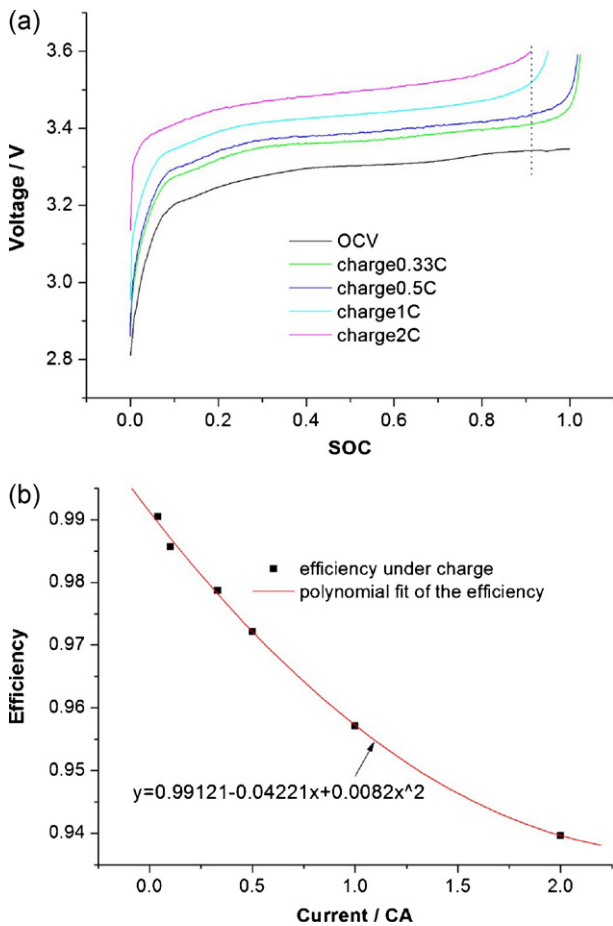


Fig. 3. The charge curves and the energy efficiencies, (a) the voltages (per cell) varied with SOC under different charge current rates, the dot line shows the SOC when the charge is complete for the 2 C curve, (b) the energy efficiencies under charge (η_{charge}) varied with the current rates and the corresponding fit results.

4.3. The energy efficiency under discharge and charge–discharge

Fig. 4a reveals the discharge curves of the LiFePO₄ batteries at different rates, as well as the OCV curve. Based on the figure, the discharge voltage plateaux decline considerably with the increment of the discharge rate. Similar to the charge curves, the SOC of the batteries at high discharge rates cannot reach 0 when the process is complete. For example, the blue line in Fig. 2a represents the discharge curve at the 3 C rate, demonstrating its SOC by the dot line when the discharge is complete. In the same way, the SOC interval of the OCV curve must be the same as that of the discharge curve when η_{disch} is calculated by Q_{out} ratio to ΔQ_n . The calculated η_{disch} as a function of SOC is shown in Fig. 4b. The blue line in Fig. 4b denotes the polynomial fit of the efficiency with the equation $y = 0.9972246 - 0.0413746x + 0.0034396x^2$ with a correlation coefficient of 0.9994.

The hollow magenta circle in Fig. 4b displays the efficiency calculated using the USA DOE method (round-trip efficiencies). By comparison, (1) the round-trip efficiencies are smaller than η_{disch} ; and (2) the difference between the efficiencies increases with the increment of the discharging current. According to the US DOE method, round-trip efficiency is the ratio of discharged energy removed to regen energy. The method to calculate the discharged energy removed is the same as that of Q_{out} , as described in Section 2.1. However, regen energy is different from ΔQ_n in two ways. First, regen energy is charging energy inputted with given steps, which is bigger than ΔQ_n . Second, regen energy is constant if the battery

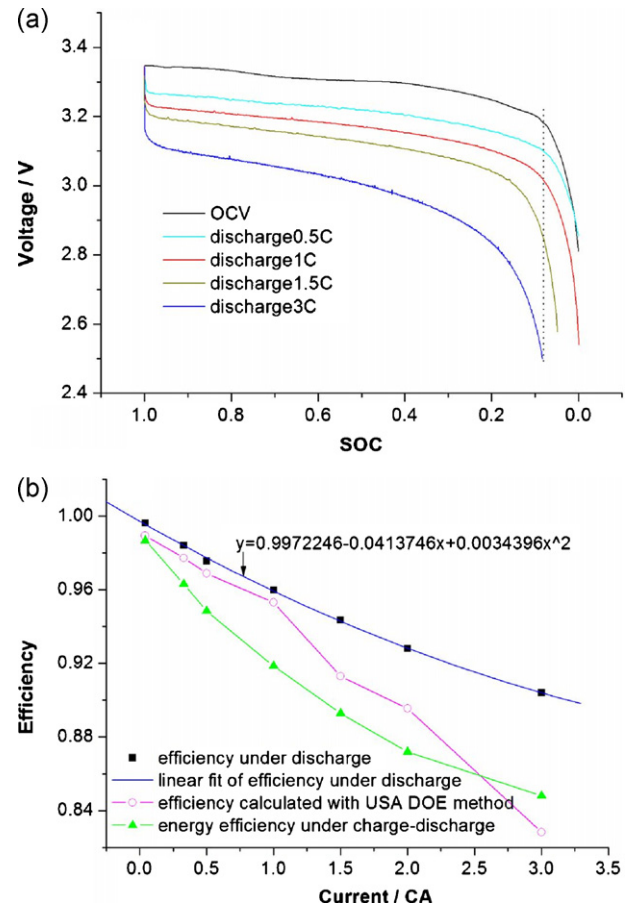


Fig. 4. The discharge curves and the energy efficiencies, (a) the voltages (per cell) varied with SOC under different discharge current rates, the dot line shows the SOC when the discharge is complete for the 3 C curve, (b) the energy efficiencies under discharge (η_{disch}) and charge–discharge (η_{battery}) varied with the current rates, the corresponding fit results of η_{disch} and efficiency calculated with USA DOE method. (For interpretation of the references to color in the text, the reader is referred to the web version of the article.)

system are given; however, ΔQ_n changes with the SOC interval. As discussed above, the electric charge in batteries cannot be completely exhausted, especially when the discharging current is large, thereby making round-trip efficiencies greatly smaller than η_{disch} .

The calculated η_{battery} (green solid triangle) is also plotted in Fig. 4b. In fact, η_{battery} is the product of η_{charge} and η_{disch} at the same passing current. As shown in the figure, η_{battery} decreases gradually with the increasing current.

5. Conclusion

A novel method to calculate the energy efficiency for batteries has been described in the present study. The energy efficiency of batteries consists of the energy efficiency under charge, the energy efficiency under discharge, and the energy efficiency under charge–discharge. A key factor in calculating energy efficiency is to seek a way or a function that represents the net energy of batteries. The equation of the function of OCV and SOC stated in the present study follows electrochemistry theory. Moreover, the quantitative relationship of OCV and SOC is computed using non-linear fit. Based on the result, in the present study, the energy efficiency of LiFePO₄ batteries is calculated under charge, discharge, and charge–discharge at different current rates. The relations of the energy efficiencies and currents are also analyzed using polynomial fit. The results indicate that the energy efficiency for LiFePO₄

batteries is high under charge or discharge, proving the good utilization rate of energy.

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