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Short communication

Boostcharging Li-ion batteries: A challenging new charging concept

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Abstract

Boostcharging is proposed as a new, ultra-fast, recharging algorithm for Li-ion batteries. Characteristic for boostcharging is that close-to-fully discharged batteries can be recharged with very high currents for a short period of time. Cycle life of Li-ion batteries, boostcharged and additionally standard charged to full capacity do not introduce any negative degradation effects. Boostcharging is shown to be very rapid. For example, a fully discharged battery can be recharged within 5 min to one-third of its rated capacity.

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1. Introduction

Rechargeable Li-ion batteries are nowadays widely accepted as efficient energy storage devices in many lightweight electronic appliances, including portable telephones, laptop computers, PDA's and electrical shavers [1,2]. In particular, the gravimetric energy density is much more favourable compared to that of competing rechargeable battery systems, such as NiMH and NiCd [3].

Although all small rechargeable batteries can, in principle, be frequently recharged after operation, customers often consider the time needed to recharge these high-energy dense batteries as rather inconvenient. Evidently, ultra-fast recharging is under many circumstances not just a desire but sometimes even a necessity. For example, for employees working in many utility- and emergency services, this might play a crucial role in their daily-life activities. Based on hardware modifications, a new ultra-fast charging method was proposed by Rayovac for NiMH batteries. For Li-ion batteries this is, on the other hand, much more complicated.

Charging times up to 2 h for Li-ion batteries are not uncommon. These long charging times are mainly due to the dedicated charging algorithm, which have to be adopted in order to meet the strict safety and cycle-life requirements for Li-ion. It is generally accepted that deviation from conventional, standard, recharging conditions induces side-reactions to occur, having detrimental effects on the above-mentioned aspects [4,5]. It is more than likely that the magnitudes of these side-reactions are more pronounced under more extreme voltage conditions, suggesting that the rates are dependent on the battery state-of-charge (SoC).

Based on this observation we propose "boostcharging" as a new ultra-fast recharging algorithm for Li-ion batteries [6,7]. Characteristic for boostcharging is that close-to-empty batteries can be recharged with very high currents for a short period of time without introducing any detrimental effects. The aim of the present paper is to show the feasibility of this new charging concept. Boostcharging characteristics will be compared with those obtained with conventional charging methodologies. The feasibility study has been carried out with both cylindrical and prismatic commercial Li-ion batteries. Special attention has been paid to the impact of boostcharging on long-term effects. Extended cycle-life studies have therefore been performed.

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2. Experimental

Boostcharge experiments have been carried out with both cylindrical (US18500, Sony) and prismatic LP423048 (Philips) Li-ion batteries. The results are compared with conventionally, constant-current-constant-voltage (CCCV), charged batteries. Fresh and fully activated batteries were used for each condition to be investigated.

Since the employed commercial batteries do have a specified SoC upon delivery, the activation procedure started with constant-current discharging at a 0.5 C-rate followed by a 30 min resting period. Subsequently, the batteries were subjected to 3, as-denoted standard CCCV cycles, after which constant charge/discharge behaviour was attained. Standard (s) charging was carried out with a constant maximum current (I_s^{max}) at a 1 C-rate in the CC-mode until the maximum charge voltage V_s^{max} of 4.2 V was attained in the subsequent CV-mode [6,7]. Evidently, the charging currents dropped in the CV-mode and charging was terminated at a predefined minimum current (I_s^{min}) of a 0.05 C-rate, after which Li-ion is considered fully charged. After a resting period of 30 min, the batteries were discharged at 0.5 C. Discharging was terminated until the cut-off cell voltage of 3.0 V was reached. A single activation cycle was completed by a 30 min resting period.

The various applied boostcharge (b) regimes can be defined by $I_b^{\rm max}$, $V_b^{\rm max}$ and time (t_b). These more specific conditions will be described in the results section. The battery temperatures were measured in all cases by means of Pt-100 sensors, which were directly glued onto the metallic casings (mid-way positions). The experiments have been performed in temperature-controlled boxes at an ambient temperature of 25 °C.

3. Results and discussion

A standard CCCV charging plot for a cylindrical Li-ion battery is shown in Fig. 1. Clearly, the battery voltage rises (curve (a)) during the constant-current period ($I_s^{\rm max}=1\,{\rm C}$ in curve (b)) until the $V_s^{\rm max}$ value of 4.2 V is attained. As a consequence, the current decreases in the CV-region. Charging is terminated when the current cut-off value has reached a current of 0.05 C. Obviously, standard charging takes more than 100 min. In accordance with the nominal capacity approximately 1100 mAh is delivered by the battery during the subsequent discharging period (not shown).

In order to accelerate the charging process significantly the simplest strategy, which can be adopted is to immediately bring the battery in the CV mode, i.e. without any limitations with respect to the maximum charging current. Fig. 2 shows such CV-mode experiment for two distinct cases, at $V^{\text{max}} = 4.2$ and 4.3 V in curves (a) and (b), respectively. The corresponding current levels are also represented in the lower part of the figure. Initially, high charging currents up to 8 A are flowing through the batteries. This current, however, de-

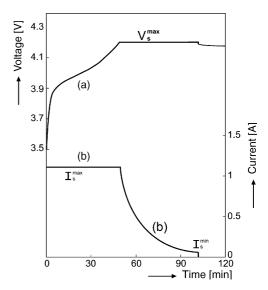


Fig. 1. Voltage (a) and current (b) characteristics of a cylindrical Li-ion cell (Sony US18500) under standard CCCV charge conditions ($I_s^{\max} = 1$ C-rate, $V_s^{\max} = 4.2$ V). CV-charging is terminated at $I_s^{\min} = 55$ mA (0.05 C-rate) after about 100 min.

creases rapidly as a result of the increasing impedance of the cells to level off after about 2 min when 0.04 Ah was included in the batteries. After the initial current peak the current decreases more slowly. For comparison the standard CCCV charging results are also plotted (see curves (c)). Remarkably, the current behaviour of both 4.2 V experiments is exactly the same in the CV-mode, as curves (a) and (c) reveal. Because the current and voltage profiles are generally considered to be dependent on the established concentration profiles [2], this suggests that diffusion limitations do not play a significant role in this region. As expected, the currents are

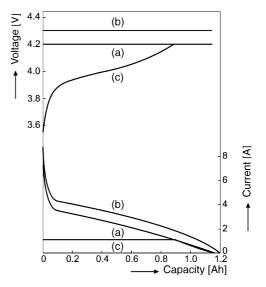


Fig. 2. Voltage and current characteristics of CV-charging cylindrical Li-ion at $V^{\max} = 4.2$ and 4.3 V (curves (a) and (b)), respectively. Standard CCCV charging is shown in curves (c) for comparison. $I^{\min} = 0.05$ C-rate in all cases.

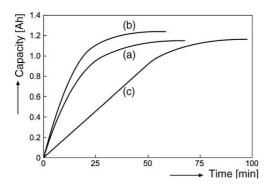


Fig. 3. Capacity build-up upon CV-charging cylindrical Li-ion batteries at 4.2 V (a) and 4.3 V (b). The capacity build-up during standard CCCV-charging is shown in curve (c) for comparison.

significantly higher at $V^{\text{max}} = 4.3 \text{ V}$ over the entire charging period.

Fig. 3 shows a comparison of the charge build-up as a function of time for the same CV- (curves (a) and (b)) and CCCVcharging (curve (c)) conditions, as described above (compare with Fig. 2). In the CCCV-charging mode the two distinct regions can clearly be recognised; during the constant-current mode the charge build-up is expectedly linear and it starts to deviate from this behaviour as soon as the CV-mode is entered after approximately 50 min (curve (c) in Fig. 3). Such linear behaviour is obviously not found in the CV-charged batteries, as constant currents are not applied in these cases. The most striking difference between the two CV-charged batteries with respect to the CCCV-charged battery is that the charging times are significantly reduced. For example, 1 Ah can easily be included within 20 min at $V^{\text{max}} = 4.3 \text{ V}$ (curve (b)) compared to the almost 60 min required under standard charging conditions.

Fig. 4 shows the impact of the maximum charging current on the total charging time of an empty cell towards different levels of state-of-charge at a moderate $V^{\rm max}$ of 4.2 V. The graph clearly shows that hardly any time profit is gained with maximum charging currents larger than 4 A for a battery of 1100 mAh. This is due to the fact that initially the currents very rapidly drop (see Fig. 2). Moreover, the minimal time needed to charge towards a desired SoC can easily be derived

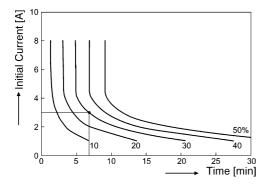


Fig. 4. Impact of initial current on the total charging time towards various indicated levels of SoC for cylindrical Li-ion batteries. Charging is commenced at 0% SoC in all cases.

from this figure. For example, it takes less than 7 min to charge an empty battery till 30% SoC, when I^{max} is limited to 3 A at a V^{max} of 4.2 V.

The impact of the more severe CV-charging conditions on the cycle life is shown in curves (a) and (b) of Fig. 5. A cycle life plot obtained under standard CCCV-charging is added for comparison (curve (c)). Even under the moderate CCCV-charging conditions the capacity loss is substantial, especially at higher cycle numbers. Two regions can be clearly distinguished for these cylindrical cells; during the initial 300 cycles only 15% of the original capacity is lost, whereas the degradation is enhanced after this cycle number. In our recent adaptive modelling work, we have attributed these two regions to two separate degradation processes, taking place at each individual electrode at a different rate; on the one hand, the slow degradation rate during the initial cycles has been attributed to Li consumption in the growing Solid-Electrolyte-Interface (SEI) layer while, on the other hand, the high degradation rate has been attributed to decomposition of the LiCoO₂ electrode [8]. Allowing the maximum current to increase during CV-charging at 4.2 V induces the high-rate degradation to become visible already after 160 cycles (see curve (a) of Fig. 5). Increasing V^{max} to 4.3 V has an even more dramatic and unacceptable effect on the cycle-life; degradation of both the graphite and the LiCoO₂ electrode are significantly enhanced, as curve (b) reveals. Recent reference electrode measurements performed under boostcharge conditions clearly revealed that metallic Lithium deposition does not take place, as will be reported shortly in a separate paper.

From the above experiments it is clear that simply adopting CV-charging is not a feasible route to ultra-fast charging of Li-ion batteries. Based on the insight gained by our recent modelling work it has been concluded that degradation is enhanced at the higher levels of SoC [8,9]. For example, the LiCoO_2 electrode is argued to be much more sensitive for decomposition into Co_3O_4 and oxygen gas at relatively low Li contents. In reverse, this suggests that it is to be expected that the detrimental effects of this and other side reactions can be well controlled by adopting a new strategy for which

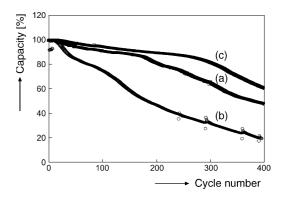


Fig. 5. Cycle life of cylindrical Li-ion batteries under high charging load conditions at $I^{\text{max}} = 4.5 \text{ C}$, $V^{\text{max}} = 4.2 \text{ V}$ (a) and $I^{\text{max}} = 4.5 \text{ C}$, $V^{\text{max}} = 4.3 \text{ V}$ (b). Cycle life upon standard CCCV-charging ($I^{\text{max}} = 1 \text{ C}$, $V^{\text{max}} = 4.2 \text{ V}$) is indicated in curve (c).

the severe charging conditions are maintained only during the initial stages of charging at low SoC. Therefore, a new charging algorithm is introduced in the present paper, which we denote as "Boostcharging".

The basic principles of boostcharging are schematically outlined in Fig. 6, revealing that a short boostcharge period (t_b) , during which a V_b^{max} voltage is applied to the battery in the initial CV-mode (curve (a)). Evidently, during the boostcharge period the currents (curve (b)) can be initially very high, for the batteries investigated in Fig. 2 up to 8 A. In order to eventually fully charge the battery the boostcharge period is, subsequently, followed by a standard CCCV-period for which the currents are much lower. The entire boostcharge cycle can then be characterised by CVCCCV-charging. V_i^{max} is not necessarily the same for both CV-periods as Fig. 6 schematically indicates. When the currents in the initial boostcharging period are, for some reasons, unacceptably high an alternative option can also be to apply a more moderate value for $I_{\rm b}^{\rm max}$ during the initial boostcharge CC-mode (not shown in Fig. 6). Also in this case boostcharging has to be followed by standard CCCVcharging. The whole charging sequence can then be denoted as CCCVCCCV or alternatively by $(CCCV)^2$.

Typical boostcharge experiments obtained with cylindrical cells are shown in Fig. 7. During the relatively short boostcharge period ($t_b = 5 \text{ min}$) either a V_b^{max} of 4.2 V (curve (a)) or 4.3 V (curve (b)) is applied to the batteries. After 5 min, the charging regime is switched to the standard CCCV-mode. Conventional CCCV-charging results are shown in curve (c) for comparison. The resulting currents are represented by the corresponding curves. It is obvious that higher currents indeed result from the higher values of V_i^{max} . Although the charging time during the boostcharge period is relatively short a significant amount of charge has been implemented during

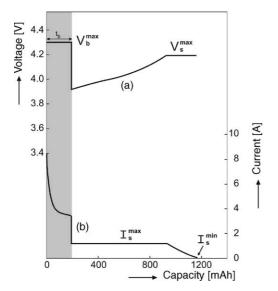


Fig. 6. Basic principles of boostcharging Li-ion batteries, consisting of a limited boostcharge period (shaded region) followed by standard CCCV-charging. The voltage (a) and current (b) responses are indicated.

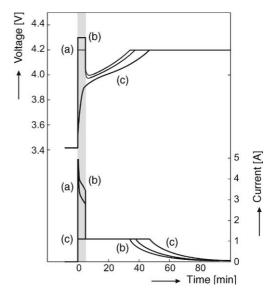


Fig. 7. Voltage and current transients for cylindrical Li-ion batteries under various boostcharging and (subsequent) standard-charging conditions. Boostcharging is performed at $0 < t_b < 5$ min, $I_b^{\rm max} = 4.5$ C, $V_b^{\rm max} = 4.2$ V followed by standard charging (a), $0 < t_b < 5$ min, $I_b^{\rm max} = 4.5$ C, $V_b^{\rm max} = 4.3$ V followed by standard charging (b). Standard charging conditions for t > 0 min (c) and for t > 5 min ((a) and (b)) are $I_s^{\rm max} = 1$ C, $V_s^{\rm max} = 4.2$ V.

this period. This becomes apparent when the same results, as shown in Fig. 7, are plotted versus the amount of charged capacity. Fig. 8 indeed shows that the boostcharge period is becoming much more dominating now. The lower part of Fig. 8 shows that the temperature rise is current-dependent but is under all boostcharge conditions rather moderate. Even

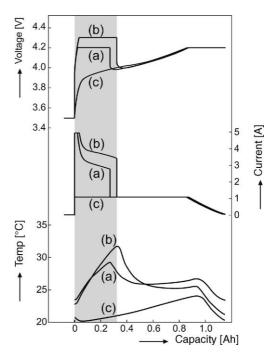


Fig. 8. Same results as shown in Fig. 7 now presented as a function of charged capacity. In addition, the temperature development has been included for the various boostcharge and standard conditions.

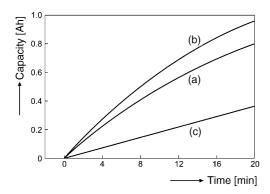


Fig. 9. Capacity build-up upon boostcharging cylindrical Li-ion batteries at 4.2 V (a) and 4.3 V (b). The capacity build-up during standard CCCV-charging is shown in curve (c) for comparison. The same boostcharging conditions are used as indicated in Fig. 7 except that the boostcharge time is not restricted to 5 min in this case.

charging with extremely high currents up to 5 C-rate, does not affect the temperature change more than $10\,^{\circ}$ C.

Fig. 9 reveals that recharging can be very quick under boostcharge conditions. For completely discharged batteries at 0% state-of-charge, about 60 and 33% of its nominal capacity can be charged within 10 and 5 min, respectively, at $V_{\rm b}^{\rm max}$ of 4.3 V (see curve (b)). These values decrease somewhat at a lower $V_{\rm b}^{\rm max}$ value (curve (a)) and become even very low under standard charging conditions, as expected (see curve (c) of Fig. 9).

The impact of the initial state-of-charge condition (SoC_i) of the battery on the boostcharge capacity is calculated in Fig. 10 for three different boostcharging times. The boostcharge conditions are $V_b^{\rm max} = 4.3 \, {\rm V}$ with $I_b^{\rm max} = 5 \, {\rm A}$. These results clearly show that boostcharging is most effective at lower initial States-of-Charge. Remarkably, more than 50% storage capacity can be recharged within 10 min whereas a 30% charge level is accomplished within 5 min under these boostcharge conditions.

Fig. 11 shows a comparison of the cycle-life behaviour upon standard charging (curve (a)) and boostcharging (curve (b)). In this latter case, the 5 min boostcharge period is again followed by standard charging up till 100% SoC. It is clear

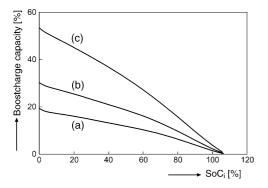


Fig. 10. Impact of the boostcharge time and state-of-charge (SoC_i) at which boostcharging is initiated on the boostcharge capacity: boostcharge times are 3 min (a), 5 min (b), and 10 min (c) with $I_{\rm b}^{\rm max}=4.5$ C, $V_{\rm b}^{\rm max}=4.3$ V.

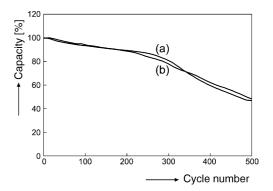


Fig. 11. Comparison of the cycle-life performance of cylindrical Li-ion batteries upon standard charging (a) and boostcharging (b). Standard charging conditions are $I_s^{\max} = 1 \text{ C}$, $V_s^{\max} = 4.2 \text{ V}$; boostcharge conditions are $0 < t_b < 5 \text{ min}$, $I_b^{\max} = 4.5 \text{ C}$, $V_b^{\max} = 4.3 \text{ V}$ followed by standard charging.

that boostcharging with additional standard CCCV-charging does not have any negative impact on the cycle-life compared to standard charging, indicating that degradation is initiated at higher levels of states-of-charge. More detailed cycle-life experiments, revealing the dependence of the various boost-charge conditions are in progress.

Similar boostcharge experiments have been performed with prismatic cells. Typical examples are shown in Fig. 12. Curves (a) correspond to $V_b^{\rm max} = 4.3 \, {\rm V}$ and $I_b^{\rm max}$ is limited to 2.4 A (4 C-rate). The boostcharge period is characterised by a constant-current and a constant-voltage part and charging is completed under standard CCCV-charging conditions. As such, this example relates to the, as-denoted, (CCCV)² algorithm. Curves (b) shows the results obtained under even more extreme boostcharge conditions. $V_b^{\rm max}$ has been raised to 4.4 V while $I_b^{\rm max}$ remains at the same high value. As a consequence, the boostcharge period consists only of a CC

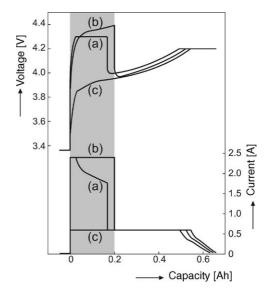


Fig. 12. Voltage and current characteristics of boostcharging prismatic Liion at $V_{\rm b}^{\rm max} = 4.3$ and 4.4 V (curves (a) and (b), respectively); $I_{\rm b}^{\rm max} = 4$ C. Standard CCCV charging is shown in curves (c) for comparison. $I_{\rm min} = 0.05$ C in all cases.

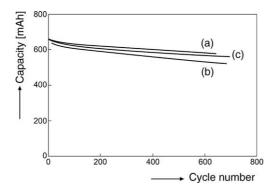


Fig. 13. Comparison of the cycle-life performance of prismatic Li-ion batteries upon standard charging (a) and boostcharging ((b) and (c)). Standard charging conditions are $I_s^{\max} = 1$ C, $V_s^{\max} = 4.2$ V; boostcharge conditions are $0 < t_b < 5$ min, $I_b^{\max} = 4$ C, $V_b^{\max} = 4.3$ V (b) and 4.4 V (c) followed by standard charging.

part and the entire charging algorithm can be characterised by CCCCCV. The charge capacity under these latter conditions is somewhat higher, as expected. It should be noted that the battery packs are generally equipped with safety electronics, generating a significantly higher internal resistance, allowing to safely recharge at these "compensated" high voltage levels.

Some cycle-life results of the prismatic cells are shown in Fig. 13. The results show that boostcharging does not have a significant impact on cycle life. It is likely that the differences are due to statistical variations as the more severe boostcharge conditions reveal a somewhat better performance than the more moderate boostcharge conditions. Furthermore, it is worthwhile to note that up till cycle number 700 no second degradation effect is observed, which was so characteristic for the cylindrical cells (compare Figs. 11 and 13). More detailed boostcharge experiments are in progress, including cycle-life and reference electrode measurements to determine the impact of boostcharging on the individual electrodes.

4. Conclusions

Boostcharging is proposed as a new, ultra-fast, recharging algorithm for Li-ion batteries [6,7]. Characteristic for boostcharging is that close-to-fully discharged batteries can be recharged with very high currents for a short period of time without introducing any detrimental effects. For example, a fully discharged battery can be recharged within 5 min to one-third of its rated capacity without inducing any extra degradation effects. Boostcharging has been shown feasible for both cylindrical and prismatic Li-ion batteries.

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