



A MODELLING APPROACH TO UNDERSTAND CHARGE DISCHARGE DIFFERENCES IN THERMAL BEHAVIOUR IN LITHIUM IRON PHOSPHATE – GRAPHITE BATTERY



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ABSTRACT

Lithium iron phosphate is a promising positive electrode material. It shows apparent asymmetry between charge and discharge affecting not only the electrochemical but also the thermal behaviour. Physics based models for batteries are usually parameterized for discharge behaviour, which can lead to inaccuracies in prediction of battery behaviour during charging or dynamic conditions, especially in the case of this battery chemistry. This has consequences for battery modelling and safety. A pseudo 2D electrochemical – 3D thermal model is parameterized for charging using experimental data. Substantial differences in parameters between charge and discharge are seen in the validated model. The model is used to quantify the thermal differences during charging and discharging and separate the contribution of the different battery layers. Reversible heat losses are seen to be the main cause for the difference between charge and discharge while graphite electrode are seen to have a much higher heat contribution compared to lithium iron phosphate electrode.

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1. Introduction

The global market for lithium ion batteries continues to grow as their power densities and energy densities keep on increasing. Moreover, manufacturing abilities for large format cells and decreasing costs of production have widened the application areas for this battery chemistry. Lithium ion batteries are now used not only in consumer goods such as mobile phones and laptops but also for vehicles and stationary storage applications.

Lithium iron phosphate (LiFePO₄) was shown as a potential positive electrode material in 1997 [1]. LiFePO₄ has interesting characteristics for use in batteries such as low cost since it contains iron and not expensive metals Co or Ni, it has low toxicity, flat charge–discharge potential, good cycle life and high structural stability [2]. However, it differs from other known positive electrode materials due to its olivine structure and the phase change that it undergoes. Asymmetry between charge and discharge in LiFePO₄ electrode has been well studied [3–7]. Path

dependence and hysteresis phenomena in LiFePO₄ are now generally accepted to have a thermodynamic origin; however, disagreements in the form of different theories to explain it exist. The theories that satisfactorily explain it include core-shell model [3,8] and the many particle system model [5]. Experimental evidence that validates both these theories is also found [6,9]. Hysteresis is also reported in graphite electrodes [10–12]. A constant value of 20 mV of hysteresis for LiFePO₄ is reported by Dreyer et al. [5] while for graphite a value of 10 mV is reported by Ohzuku et al. [10]. Other upcoming chemistries such as Li₂FeSiO₄ and TiO₂ are also known to have large hysteresis behaviour, of the order of tens of millivolts [5].

In LiFePO₄, apart from the known hysteresis phenomenon that leads to different voltages during charge and discharge, the thermal behaviour is also dissimilar between charge and discharge suggesting a difference in internal resistance in the charging and discharging processes. In Fig. 1, experimental results of temperature increase in similar environmental and operating conditions for charge and discharge for the LiFePO₄ cells used in this work (see Section 2) are shown. Unequal temperature increases are seen during charge and discharge and the differences are more at higher C rates.

Ignoring such differences in modelling can have potentially big consequences for battery performance prediction and safety.

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Nomenclatures

List of terms

i	current density
i_0	exchange current density
a	C rate = i/i_{1C}
σ	electrical conductivity
σ_T	Stephan Boltzmann constant
φ	potential
D	diffusivity
t	time
r	radius dimension
r_p	radius of the particle
R	universal gas constant
T	Temperature
a_v	specific surface area
η	over potential
ε	volume fraction
ε_T	emissivity
c	concentration
k	rate constant
K	thermal conductivity
F	Faraday's constant
φ	potential
c	heat capacity
ρ	density
SOC	the local concentration of lithium = c_{Li}/c_{ref}
T	Temperature
L	thickness of battery component layer
η	over potential
c	concentration
E_{eq}	Equilibrium potential
f	activity coefficient
t	transport number
EC	ethylene carbonate
DEC	diethyl carbonate
w/w	weight ratio
PSD	particle size distribution
CC-CV	constant current constant voltage

Subscript

s	solid phase
l	electrolyte phase
ref	reference state
r	reversible
irr	irreversible
NC	negative current collector
NE	negative electrode
S	separator
PC	positive current collector
PE	positive electrode
c	cathode
a	anode
n	negative
p	positive

module/pack and thus low performance and lifetime but in the worst case can potentially be even a safety hazard. Unfortunately models being developed for battery management systems are usually parametrized for only discharge for lithium ion batteries [13–28]. Charge models have received much less attention. The same set of parameters is assumed to be valid for both charging and discharging [29–34]. In some papers, a charge model is developed by changing some parameters of the discharge model but either validation results are not presented [35,36] or this model is only validated electrochemically and not thermally [37,38].

Thus, in this work, charge model has been separately parameterized for a pouch cell whose physics based discharge model has been previously developed [28]. The representative battery parameters have been found out using inverse parameterization approach described in detail for the discharge model for different parameters [28]. The charge and discharge parameters are compared with each other. Then, with the aid of this physics based model the thermal behaviour is investigated and the contribution of different cell components which leads to differences in thermal behaviour such as in Fig. 1 is quantitatively determined.

2. Experimental

B5 format prototype lithium-ion pouch cells with a nominal capacity of 6 Ah manufactured by Lithops S.r.l (Fig. 2) were tested during this work and used to collect experimental data. Prototype Lithium ion cells were prepared using artificial graphite (IMERYS[®], D50 about 6 μm) as anodic active material and Lithium iron phosphate (LiFePO₄) (BASF[®], D50 about 11 μm) as cathodic active material. The electrodes were obtained by a comma bar roll coating over common commercial Cu (Schlenk[®], 16 μm thickness) and Al (Showa Denko[®], 20 μm thickness) metal foils. A 25 μm thick polypropylene membrane was used as separator (Celgard[®]). For these cells 1 M LiPF₆ in ethylene carbonate: diethyl carbonate (2:3 w/w) + 1% vinylene carbonate liquid electrolyte was used. The resultant pouch cells (B5 format, external dimension 250 mm x 164 mm, thickness around 4 mm) have an operational voltage between 2.50–4 V and 6 Ah rated capacity. After a proper activation process, cells were delivered at 30% SOC (~3.1 V). The cell nominal capacity was verified via galvanostatic cycling at 0.1C with respect to the nominal value (the current needed to discharge the cell completely in 10 h), the current applied was therefore 0.6 A. In these conditions the measured capacity was around 6 Ah, corresponding to the nominal one given by Lithops S.r.l.

Starting with a discharged cell (2.5 V cut-off), the cell was then charged repeatedly using CC-CV procedure till 4.0 V and current cut-off of 10 mA at 0.1C, 0.2C, 1C, 2C, 5C and 10C rate. After each charge, it was discharged again with the same conditions. Moreover, after every charge and discharge step a 5' rest period was adopted in order to let the cell stabilize, preventing safety problems due to high current switches and ensuring that the cell is near the ambient temperature. The minor differences in temperatures and SOC at the beginning of different charge rates were not ignored in the model. The temperature was monitored during the whole charge-discharge test by means of a thermocouple placed in contact to the surface of the cell case near the anodic tab while the front surface was monitored through a thermal camera.

3. Modelling

Choosing a particular modelling approach is based on the trade-off between computing costs, the scale of the model and the accuracy needed. Computing costs depend on the computing resources at disposal and thus are directly correlated to the economic costs of modelling, while the scale of the model and the

Wrong voltage prediction can lead to a non-optimized use of the battery, leading to faster degradation, higher lifetime costs and a poor prediction of the performance, for example, of the remaining available charge in a device or a vehicle battery pack. While wrong thermal performance prediction by a thermal management system can lead to not only non-optimum temperature levels for a battery

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