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Semi-empirical master curve concept describing the rate capability of lithium insertion electrodes

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HIGHLIGHTS

- Semi-empirical model describing the rate capability of insertion electrodes.
- Experimental verification using various active materials and design parameters.
- Rate capability of all investigated electrodes follows a single master curve.
- Rate capability is related to the time constant of the limiting transport process.
- Model-based optimization of design parameters regarding gravimetric capacity.

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ABSTRACT

A simple semi-empirical master curve concept, describing the rate capability of porous insertion electrodes for lithium-ion batteries, is proposed. The model is based on the evaluation of the time constants of lithium diffusion in the liquid electrolyte and the solid active material. This theoretical approach is successfully verified by comprehensive experimental investigations of the rate capability of a large number of porous insertion electrodes with various active materials and design parameters. It turns out, that the rate capability of all investigated electrodes follows a simple master curve governed by the time constant of the rate limiting process. We demonstrate that the master curve concept can be used to determine optimum design criteria meeting specific requirements in terms of maximum gravimetric capacity for a desired rate capability. The model further reveals practical limits of the electrode design, attesting the empirically well-known and inevitable tradeoff between energy and power density.

1. Introduction

Lithium-ion batteries are widely applied to serve portable electronic devices and their applications expand rapidly, e.g. towards hybrid and all-electric vehicles [1–3]. Typical electrodes for lithium-ion batteries are porous composites consisting of active material particles, binder and conductive additives coated on a current collector foil. The energy density of the electrode can be increased by reducing the proportion of electrochemically inactive compounds to a minimum. This can be achieved by changing the composition of the slurry, e.g. reducing the proportion of binder and conductive additives. Another opportunity is to vary the electrode design (thickness, porosity, morphology, etc.) with the objective to increase the mass ratio of active material to the inactive components (current collector, separator) [4]. Particularly, increasing the electrode thickness is a promising approach to design electrodes with a high energy density [5–7]. However, for high electrode thicknesses, mass transport limitations of lithium ions in the electrolyte phase and the resistance for electrons in the solid phase become dominating [8,9]. This reduces the capacity of the cell due to larger overvoltage, especially at high C-rates. However, fast charging and discharging of the electrode is obligatory in numerous applications, e.g. hybrid and all-electric vehicles [10]. Therefore, it is necessary to identify and quantify the manifold relationships between the electrode design and the electrochemical performance. Particularly, the importance of understanding the rate limiting processes inside the porous intercalation electrode is crucial to optimize electrodes for high-power as well as high-energy applications. The experimental evaluation of optimum design parameters is a sophisticated and very time consuming challenge due to the large number of mutual dependent factors (electrode thickness, porosity, tortuosity, nature of active material, particle size (distribution), particle shape, etc.) influencing the different

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performance parameters (gravimetric, volumetric, and area specific energy as well as power density, cycle and calendar life, etc.).

Modeling and simulation are a promising and potentially more time efficient alternative to identify optimum design parameters and electrode architectures [11–13]. Particularly, detailed 3D microstructure resolved simulations provide valuable insights into the local charge, mass and heat transport inside porous insertion electrodes [14–16]. However, such detailed simulations require a huge amount of input variables, describing the morphology, kinetics and thermodynamics of each component, that are usually not completely available. Besides the fundamental complexity of the underlying models, this may additionally complicate the straightforward identification of optimum design parameters. Therefore, the development of reduced order models and easy to handle design tools, in order to support targeted engineering of lithium insertion electrodes, is a major issue in battery research.

Herein, we propose a simple semi-empirical “master curve” concept describing the rate capability of lithium insertion electrodes based on the evaluation of the time constants of lithium diffusion in the liquid electrolyte and the solid active material. The model predictions are compared to the rate capability of a number of custom built and commercially available lithium insertion electrodes with different active materials and varying design parameters. The results are discussed regarding the limits and practical applicability of the proposed master curve concept including the tradeoff between energy and power density. Finally, a straightforward approach to optimize the gravimetric capacity of porous lithium insertion electrodes with specified rate capability is demonstrated.

Nomenclature and physical properties used in this work

D_e	Lithium diffusion coefficient (electrolyte)	$2{\cdot}10^{-10}$ [$m^2\ s^{-1}$] [17,18]
D_{LTO}	Lithium diffusion coefficient ($Li_4Ti_5O_{12}$)	$1{\cdot}10^{-15}$ [$m^2\ s^{-1}$] [19,20]
D_{NCM}	Lithium diffusion coefficient ($LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$)	$1{\cdot}10^{-14}$ [$m^2\ s^{-1}$] [21,22]
D_{LCO}	Lithium diffusion coefficient ($LiCoO_2$)	$5{\cdot}10^{-16}$ [$m^2\ s^{-1}$] [23,24]
D_{LMO}	Lithium diffusion coefficient ($LiMn_2O_4$)	$1{\cdot}10^{-15}$ [$m^2\ s^{-1}$] [25,26]
D_{LFP}	Lithium diffusion coefficient ($LiFePO_4$)	$3{\cdot}10^{-17}$ [$m^2\ s^{-1}$] [25,27]
F	Faraday's constant	96487 [$As\ mol^{-1}$]
I	C-rate (charge-discharge rate)	[h^{-1}]
L_e	Electrode thickness	[m]
L_s	Particle radius	[m]
L_{CC}	Thickness of Al-current collector	$15{\cdot}10^{-6}$ [m]
c	Concentration	[$mol\ L^{-1}$]
C	Capacity	[Ah]
C_m	Gravimetric capacity	[$Ah\ kg^{-1}$]
C_n	Nominal capacity	[Ah]
t	Time	[s]
m_S	Mass loading	[$kg\ m^{-2}$]
Greek letters		
β	Empirical power law constant	2 [−]
ε	Porosity	[−]
γ	Bruggeman coefficient	2.5 [−] [28]
ρ_{NCM}	Mass density of NCM	4500 [$kg\ m^{-3}$]
ρ_{CC}	Mass density of aluminum	2700 [$kg\ m^{-3}$]
ρ_{el}	Mass density of electrolyte	1500 [$kg\ m^{-3}$]
τ	Time constant	[s]
Subscripts		
CC	Current collector	
NCM	$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	
LTO	$Li_4Ti_5O_{12}$	
LCO	$LiCoO_2$	
LMO	$LiMn_2O_4$	
LFP	$LiFePO_4$	
s	Solid	
S	Refers to surface	
E	Electrolyte	
eff	Effective parameter	
0	Indicates initial conditions	
∞	Indicates final conditions	
m	Refers to mass	
fit	Refers to values obtained from fitting	

2. Theoretical considerations

We are interested in the rate capability of an arbitrary lithium insertion electrode. The fastest way to charge and discharge an insertion electrode, in compliance with a certain voltage range (e.g. 3.0–4.2 V), is the chronoamperometric method. For instance, assuming an electrode