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A review of lithium deposition in lithium-ion and lithium metal secondary batteries

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HIGHLIGHTS

- A review of major aspects on lithium deposition in lithium-ion and lithium metal batteries.
- Review of the deposition criteria and models that predict the occurrence of Li deposition in Li-ion batteries.
- The universality of critical potential and concentration criteria for Li deposition in Li-ion batteries is discussed.
- The morphology control is key to suppress the initiation and propagation of Li dendrites in Li metal batteries.
- Uniform, elastic and resistive SEI layers may induce favorable morphology for Li deposition.

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ABSTRACT

Major aspects related to lithium deposition in lithium-ion and lithium metal secondary batteries are reviewed. For lithium-ion batteries with carbonaceous anode, lithium deposition may occur under harsh charging conditions such as overcharging or charging at low temperatures. The major technical solutions include: (1) applying electrochemical models to predict the critical conditions for deposition initiation; (2) preventions by improved battery design and material modification; (3) applying adequate charging protocols to inhibit lithium deposition. For lithium metal secondary batteries, the lithium deposition is the inherent reaction during charging. The major technical solutions include: (1) the use of mechanistic models to elucidate and control dendrite initiation and growth; (2) engineering surface morphology of the lithium deposition to avoid dendrite formation via adjusting the composition and concentration of the electrolyte; (3) controlling battery working conditions. From a survey of the literature, the areas that require further study are proposed; e.g., refining the lithium deposition criteria, developing an effective AC self pre-heating method for low-temperature charging of lithium-ion batteries, and clarifying the role the solid electrolyte interphase (SEI) plays in determining the deposition morphology; to facilitate a refined control of the lithium deposition.

1. Introduction

The lithium (Li metal) secondary battery was proposed as a high energy-density power source for high energy-demand applications in 1970s, but this battery system has remained in controversy for decades due to its vulnerability to safety and short cycle life. Continuous efforts have been made to address the most detrimental problem: the Li dendrite growth during the Li deposition in this system, which could cause capacity loss and even trigger short circuit. In recent years, although the safety and cycling efficiency have been significantly improved, this battery system has not been commercialized for large-scale applications. In contrast, the Li-ion batteries, usually having graphite as the anode in a rocking-chair configuration to facilitate the Li ions in electrode reactions, has embraced successful commercialization for portable electronic devices in the 1990s and recently for electric vehicle applications. While sacrificing the benefits of higher cell voltage and energy density of the Li metal kin, the Li-ion battery has the evident advantages in its lower risk of Li dendrite formation [1].

Fig. 1 shows two images of Li depositions on (a) a graphite negative electrode after overcharging [2] and (b) a Li metal electrode after charging [3]. In both cases, the deposited Li could grow into dendrites and cause irreversible capacity fade or even internal

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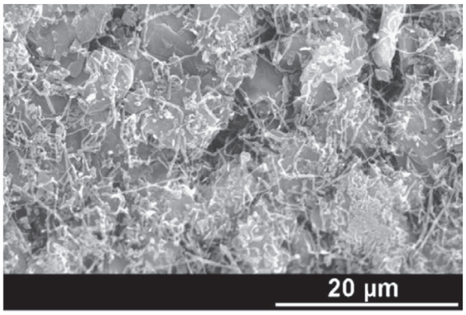
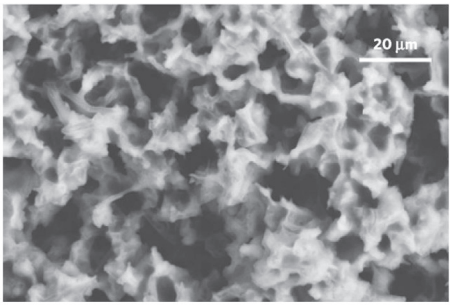


(a) An SEM image shows the Li deposition on a graphite negative electrode after overcharging [2].



(b) An SEM image exhibits the Li deposition on a Li metal electrode after charging [3].

Fig. 1. Images of Li deposited at the negative electrodes (graphite and Li metal respectively).

short. However, despite the similarity of such detrimental effects, the Li deposition phenomena are essentially different in secondary Li metal and Li-ion batteries since the depositions occur under different working conditions.

For the Li-ion battery with the graphite anode, under normal working conditions (i.e. the cycling rates, temperature and cut-off voltage in the nominal range), Li ions intercalate into or deintercalate from the active materials reversibly between the two electrodes. Only under harsh charging conditions such as overcharging or charging at low temperatures, the Li ions could be reduced to metallic Li and deposit as an interphase. Therefore, to study the Li deposition phenomenon in Li-ion batteries, the electrochemical models, which are based on the mechanism and electrochemical kinetics of Li deposition with specific criteria, should be helpful in providing quantitative understanding of this phenomenon. The application of these electrochemical models would allow us to quantify the criteria to prevent or mitigate the occurrence of Li deposition during cycling. The model could provide solutions in two aspects: (1) improvements in battery design, electrode architecture and material property and (2) developments of appropriate charging protocols for commercial chargers.

For the Li metal secondary battery, Li deposition/dissolution is an inherent process at the interface of Li metal/electrolyte during normal cycling. The deposited Li could form several types of surface morphology: including moss-like, particulate (granular), or dendritic (needle-like) deposits. The dendritic aggregation is the most detrimental to the cycling efficiency and battery safety since dendrites could accelerate the capacity fade due to the formation of electrically isolated Li ('dead Li'), or even trigger the internal short when piercing through the battery separator. Therefore, unlike aiming at the inhibition of Li deposition in the Li-ion battery, the morphology control of the Li-deposited surface is key to successful development of the Li metal secondary battery. The formation of dendrites should be minimized or eliminated, and the deposited Li should be confined to less harmful, smoother microstructure with mossy or particulate morphologies. The key aspects of Li deposition in the Li-ion and Li metal secondary battery systems are compared in Table 1.

The Li deposition in both battery systems is reviewed in this paper. For the Li-ion battery, the electrochemical kinetic models are investigated, and the threshold condition control and measures, including novel charging protocols, are evaluated. For the Li metal secondary battery, the dendrite propagation models elucidating the dendrite initiation and simulating the growth are discussed, and the attempts to suppress dendrite propensity are presented, mainly on the electrolyte modification and the working condition control. In the end, resulting from the survey of the literature, emerging research areas for further studies are suggested.

2. The Li deposition in Li-ion batteries

The mechanistic models of Li deposition in Li-ion batteries are summarized in Table 2. Subsequently, several optimization theories for ideal charging protocols are reviewed. Since most of the theoretically optimal charging methods are difficult to implement in practice, we shall focus on practical charging methods, which may be good approximations to the theoretical optimal methods for easy adoption by commercial chargers.

2.1. The mechanistic models and criteria of Li deposition in graphite electrodes

The mechanistic models describing the ion concentration and current distribution based on diffusion laws and conservation equations can predict the timing of deposition occurrence with the proposed criteria. From the perspective of the deposition criteria, the models of Li deposition in Li-ion batteries are listed in Table 2.

Purushothaman and Landau [4] predicted that Li would accumulate at the interface of the negative electrode and the electrolyte during charging when the Li flux of charge transfer reaction at the graphite/SEI interface was higher than the Li diffusion flux into the graphite particles. This interfacial accumulation would eventually lead to the dendritic growth when the Li ion concentration at the interface exceeded the saturation level of 0.077 mol cm^{-3}. Based on

Table 1
Comparisons of the Li deposition in Li-ion and Li metal batteries.

Item	Li-ion battery	Li metal battery
Normal reaction at negative electrode during charging	$xLi^{+}+6C+xe^{-} \rightarrow Li_xC_6$	$Li^{+}+e^{-} \rightarrow Li$
Li deposition circumstances	Overcharging or charging at low temperatures	Normal charging
Focus	Threshold condition control	Surface morphology control
Description model	Electrochemical kinetic model	Dendrite propagation model
Controlling factors	(1) Battery design (2) Electrode architecture and material property (3) Charge protocol	(1) Battery components (2) Current density (3) Temperature, pressure and external interference