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Towards *in-situ* TEM for Li-ion Battery Research

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Abstract

Due to recent developments in new battery materials for higher energy density applications there has been growing interest in new characterization techniques capable of time-resolved *in situ/in operando* analysis of dynamic Battery systems. This review provides an overview on recent development of liquid cell transmission electron microscopy (TEM) for Li-ion battery research and discusses the challenges, highlighting potential research areas. *In-situ* TEM offers the opportunity to study phenomena including solid electrolyte interphase (SEI) formation and phase changes during battery operation. There are two main challenging areas for *in-situ* TEM research (1) designing an *in-situ* TEM electrochemical cell that mimics a ‘real’ cell and (2) quantifying beam damage caused by electron irradiation of the electrolyte.

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1. Introduction

Recent interest in the development of electric vehicles and grid connected energy storage has led to higher demand for high energy density batteries and interest in developing them [1]. Higher energy densities can be achieved by increasing the cell capacity or the cell voltage [2]. Batteries are complex systems, consisting of a series of electrochemical cells containing two electrodes (an anode and cathode) separated by an electrolyte. Electrodes are subject to multiple processes during operation such as volume changes, solid electrolyte interphase (SEI) layer formation (potentials at the anode/ electrolyte interface cause the breakdown of electrolyte producing a passivating

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layer [2]) and phase transitions. Reaction complexity increases at higher capacities, and voltages as the materials are often operating at the limits of their properties. Electrolyte break-down is a major problem in high voltage (4–5 V vs. Li/Li+) Li-ion batteries [3]. Development of new materials requires detailed characterization of their structure, functionality, and integrity but battery processes are dynamic. Traditional post-mortem analysis involves characterisation of the electrode after removing an electrode from the cell and often result in issues such as sample contamination due to handling/sample preparation, and loss of information on transient processes [4]. Ideally characterization should be performed *in-situ/ in-operando* where characterization of battery processes is performed during operation (charge and discharge), avoiding the issues generated by post-mortem treatments [4] leading to growing interest in developing these techniques.

Transmission electron microscopy (TEM) is a technique where electrons are transmitted through a sub-micron sample. TEM provides high-resolution imaging and diffraction on features down to the atomic scale, and chemical analysis using electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDS). The spatial resolution of TEM microstructural analysis is ideal for studying battery processes such as charge/ discharge mechanisms and solid electrolyte interphase formation [5]. This review will provide an overview of the recent developments in *in-situ* liquid-cell TEM for batteries, discussing challenges and highlighting some future research perspectives.

2. *In-situ* TEM techniques for battery research

An ideal set-up for *in-situ* TEM for battery research would consist of an electrochemical cell inside the TEM- a technique which has been developed over the last 8 years. The first example of an Li-ion electrochemical cell in a TEM was in 2010 by Huang et al. SnO₂ nanowires were grown on an *in-situ* TEM electrical biasing holder. The SnO₂ nanowires were separated from bulk LiCoO₂ by an ionic liquid electrolyte and biased to induce charge and discharge, allowing the lithiation mechanisms to be observed [6]. There are limitations to this type of set-up- (1) the set-up is exposed to the 10⁻⁴-10⁻⁷ Pa vacuum, limiting electrolytes to low vapour pressure liquids excluding most standard battery electrolytes such as LiPF₆ in ethylene carbonate and dimethyl carbonate [7]. (2) there is only point contact between the SnO₂ anode, electrolyte and LiCoO₂ cathode as the SnO₂ anode is a nanowire. This could change the diffusion patterns present in a bulk Li-ion electrochemical coin cell as the electrode material should be submerged in electrolyte [7].

To circumvent the issues generated by the Huang et al.'s set-up, the electrical biasing technique was combined with *in-situ* liquid TEM, a technique first demonstrated by Ross and co-workers in 2003 who imaged the electrochemical deposition of copper from copper sulfate solution [8]. Similar xxx? studies have been performed using battery materials, where Low potentials at the electrolyte-electrode interface can also cause plating of metallic Li from the electrolyte [9]. Mehdi et al. employed an *in-situ* electrochemical liquid cell to observe the morphology of plated and stripped Li onto patterned Pt from LiPF₆ solutions [10].

Current research revolves around applying the Ross technique [9] to battery systems to mimic a 'real' battery system by depositing typical anode and cathode materials onto metal (typically Pt or Au) patterned electrodes on the manufactured cell, using an appropriate reference electrode, and submerging the material in electrolyte (see Fig. 1). Some of the first examples of depositing material onto the electrodes in an *in-situ* electrochemical liquid cell look at studying solid electrolyte interphase formation and lithiation mechanisms. SEI layers typically form on anodes from potential induced breakdown of the electrolyte and act as a passivating layer to prevent further consumption of the electrolyte due to the voltage [2]. Unocic and co-workers observed the SEI formation onto graphite [11]. Holtz et al. mimicked a full battery cell *in-situ* TEM to study the lithiation mechanisms of LiFePO₄. By depositing anode (activated carbon) and cathode (LiFePO₄) material on both electrodes Holtz and co-workers employed valence energy loss spectroscopy to observe phase contrast between LiFePO₄ and FePO₄ [12].

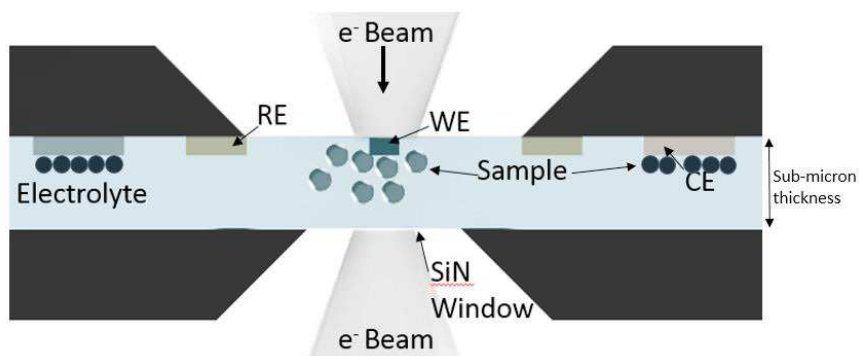


Fig. 1. (a) Schematic of an ideal *in-situ* electrochemical cell for Li-ion battery research. The electrodes (WE- working electrode, RE- reference electrode, CE- counter electrode) are connected to an external potentiostat.

To date initial applications of the *in-situ* electrochemical cell have included plating and solid electrolyte interphase formation studies with future possibilities of creating a Li-ion electrochemical cell within an *in-situ* TEM electrochemical holder.

3. *in-situ* TEM electrochemistry challenges

3.1. Linking *in-situ* testing to 'real' cell electrochemistry

The ideal *in-situ* battery TEM cell would mimic a bulk coin cell (Fig. 1) so that electrochemistry could be quantified and compared with the coin cell data whilst imaging the reactions. The set-up in Fig. 1 requires electrode material or Li to be loaded and adhered to the electrodes. This geometry is a significant challenge as *in-situ* electrochemical cell electrodes are $< 100 \mu\text{m}$ wide and many battery materials/ electrolytes are air sensitive. There are a number of methods to load electrode material onto the electrodes. Unocic et al. dropped suspended graphite onto electrodes but did not have control on the position of the graphite [11]. To counter this more controlled deposition processes have been used. Holtz et al. used an inkjet printer to print a suspension of LiFePO_4 (LFP) in isopropanol onto the working electrode [12]. Leenheer et al. deposited LFP onto electrodes using dielectrophoresis (DEP) where an AC voltage of 8 V was applied between electrodes submerged in a suspension of LFP and ethanol [13]. Li is required as a counter electrode for an electrochemical half-cell set-up. Unocic et al. attached metallic Li to a Ni wire submerged in electrolyte external to the *in-situ* cell, using tubing to allow flow of electrolyte between the *in-situ* TEM cell and the Li [11]. This increases cell resistances and is not comparable to a bulk coin cell. Mehdi et al. used a glassy carbon electrode as an electrode to study Li deposition as a result of applied voltage [14] implying Li could be directly plated onto a counter electrode from the electrolyte.

The limited *in-situ* TEM battery studies so far have used constant potentials potential sweeps or cyclic voltammetry using potentials of electrochemical processes to link the *in-operando* observations to bulk electrochemical cells [10,12]. The nature of the *in-situ* thin film liquid geometry used may change the electrochemistry as diffusion processes change. Unocic et al. used the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ system to study the impact of the thin film set-up on electrochemistry. They found that ? constant electrolyte flow was required to prevent complete electrolysis of the system, and that understanding the electrochemically active area is important for quantification [15]. Due to the difficulties applying electrode material to the patterned electrodes described above, quantitative electrochemistry is very difficult in most *in-situ* electrochemical systems. Overall for quantitative electrochemistry it is important that the set-up of the *in-situ* electrochemical cell is controlled so that the electrochemically active material's mass and area is known. More work is needed to standardise this.

3.2. Electron beam damage

Electron beam damage is a well-documented phenomenon in electron microscopy. It is important to understand the effects of the high energy electron beam, typically 200keV, on the sample in order to ascertain which effects are a result of the system and which result from the experimental set-up. There are three predominant electron beam damage mechanisms, radiolysis, knock-on damage and heating [16].

The dominant damage mechanism *in-situ* liquid TEM is radiolysis [17]. Radiolysis in salt solutions can cause nucleation and subsequent growth of solid from the salt. Electron beam induced nucleation of silver nanoparticles from silver salts [18] and the growth Pd on Au seeds to form Au-Pd [19] have been observed in water. In both instances, radiolysis of water induced by the electron beam resulted in the formation of solvated electrons which reduced metal ions in the solution, allowing them to nucleate as metal nano-particles.

Battery electrolytes are typically a lithium containing salt dissolved in a solvent (typically carbonates for commercial Li-ion batteries) and thus undergo a similar mechanism to that described above. One example of a commercial electrolyte is LiPF₆ salt dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) [2]. A systematic study on the electron beam interaction with different electrolyte solution was performed by Abellan et al. Initial electron irradiation at 200keV of LiAsF₆ in EC and DMC resulted in the instantaneous formation of LiF salt followed by subsequent polymerisation carbonates. Solvated electrons resulting from inelastic scattering of the solution with the electron beam, reduced LiAsF₆ to form the highly reactive lewis acid, AsF₆⁻. Subsequent recombination with Li⁺ and F⁻ resulted in the formation of LiF [17]. This is followed by polymerisation of the organics in the solvent leading to the growth of larger particles. Similar results were found with LiPF₆ although the rate was lower.

Beam damage can be avoided by decreasing the electron beam energy, total electron dose, dose rate and exposure time by varying the accelerating voltage, employing different imaging modes such as scanning transmission electron microscopy (STEM) to reduce the dwell time or ‘sneaking up’ to the area of interest [20][20]. The composition of the electrolyte will also determine the extent of beam damage [21]. The bimolecular rate constant [22] (rate constant of e⁻_{aq} + electron scavenger → product) can give an indication of how likely the electrolyte is to damage under the beam [17].

The electron beam damage phenomenon is potentially a useful tool for studying the formation of solid electrolyte interphase layers. Liquid-phase TEM offers the unique opportunity to apply a controlled dose of electrons to a solution and study the resulting reduction characteristics of the solution, providing a model system for SEI formation [23].

4. Conclusions

In-situ TEM electrochemistry shows significant promise for battery research. Currently, the limited studies to date have focused on understanding solid electrolyte interphase formation, Li plating, and few-cycle charge and discharge mechanisms of battery electrode materials.

There are a number of challenges associated with *in-situ* TEM for battery research which also open new research avenues. The set-up of the liquid cell needs to be perfected to create an *in-situ* cell which mimics a ‘real’ cell and the resistances quantified to aid quantification of electrochemistry. Electron beam damage is a major challenge for all *in-situ* TEM testing. Researchers must optimise beam conditions to minimise sample damage during operation. However, recently beam damage is being seen as a potential tool to understand breakdown of electrolytes, opening a new research avenue which is so far relatively unexplored.

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