



In operando measurements of kinetics of solid electrolyte interphase formation in lithium-ion batteries



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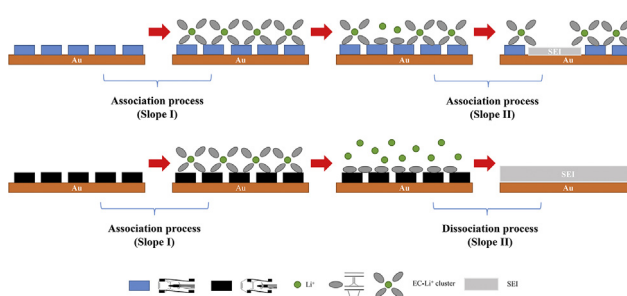
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HIGHLIGHTS

- In operando SPR and EQCM reveal the in-time kinetic reaction of electrolyte.
- In operando SPR and EQCM predicts SEI formation for graphite and Si anodes.
- LiMB is a good salt additive for Si anode to inhibit the SEI formation.
- LiTFB is a good salt additive for graphite anode to reinforce the SEI formation.

GRAPHICAL ABSTRACT



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ABSTRACT

This study applied two in operando techniques to reveal the reaction kinetics of solid electrolyte interphase formation on electrolyte and benzimidazole salt additives. The results obtained from studying interface effects reveal changes in solid electrolyte interphase mass, reflection angle, and reflection intensity within the electrolyte additives in accordance with electron-withdrawing and electron-donating substitutions. Surface plasma resonance results reveal that the electrolyte containing the electron-withdrawing salt additive exhibited the highest rate constant (774 s^{-1}) of the binding reaction between the benzimidazole additive and Au surface, indicating the strong reaction effects on Au. The electrolyte containing the electron-withdrawing salt additive accelerates and facilitates the dissociation reaction of the ethylene carbonate–lithium ion (EC-Li^+) ionic cluster. From the quartz crystal microbalance results, the electrolyte containing the electron-withdrawing salt additive shows the greatest solid electrolyte interphase mass ($14.84 \mu\text{g cm}^{-2}$), representing the intense dissociation reactions of the EC-Li^+ ionic cluster as well as solid electrolyte interphase formation and recombination. In this study, selecting a high rate constant and high binding strength of the EC-Li^+ ionic cluster on the electrode surface enhance solid electrolyte interphase formation and battery performance.

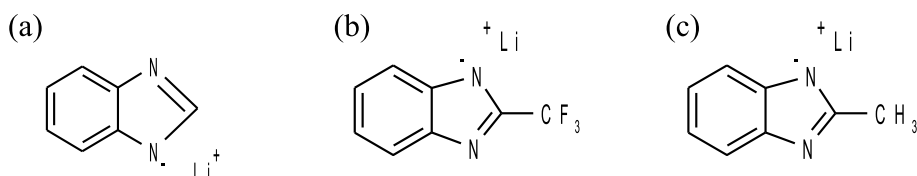
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Scheme 1. The chemical structures of (a) Lithium Benzimidazole (LiB), (b) lithium trifluoromethyl benzimidazole (LiTFB), (c) Lithium methyl benzimidazole (LiMB).

1. Introduction

A solid electrolyte interphase (SEI) is a layer created on the surface of active materials during the initial electrochemical reaction in lithium-ion batteries (LIBs). It is a key component that dominates battery performance in terms of tailored functions such as ionic diffusivity [1], electrochemical stability [2], and safety [3]. Notably, a stable SEI composed of organic materials such as R-OCO₂Li protects active materials from electrolyte side reactions in anode and cathode materials [4]. In LIBs, LiPF₆ is the most widely used salt, and this is due to its excellent SEI formation [5], excellent solubility in carbonate solvents [6], wide electrochemical operating window [7], and high ionic conductivity [7,8]. However, it may sustain thermal stability problems [9–11] and additional side reactions [8]. The side product PF₅ (a Lewis acid) usually reacts with the SEI in the presence of moisture to form HF, POF₃, CO₂, and LiF [8,12].

A study reported that a benzimidazole (BZ)-based Li salt additive plays a critical role in forming a new SEI film while maintaining the chemical stability of Li salt because of a Lewis acid–base reaction [12]. The study revealed a pentafluorophosphate BZ anion synthesized through a Lewis acid–base reaction between the BZ anion and PF₅. The new compound, pentafluorophosphate BZ anion, was reported to inhibit the decomposition of LiPF₆ by inhibiting PF₅ side reactions, leading to a well-maintained battery performance. Additionally, the electrochemical behaviors of LiPF₆, lithium BZ, lithium methyl BZ (LiMB; electron-donating), and lithium trifluoro methyl BZ (electron-withdrawing) salt additives were investigated. According to the report, the fluoromethyl (-CF₃) substitution facilitates the realization of a high electron cloud density on the structure to resist the electron releases from benzimidazole in oxidation (anodic) reactions and further neutralize PF₅ to form a stable SEI layer. It can also cause two adjacent (C–N) bond elongations because of the steric repulsion. This repulsion effect produces a lower ion-pair dissociation in accordance with weaker coordination because of extensive charge delocalization [13,14]. The electro-donating functional group (-CH₃) substitution engenders less electron negativity on the imidazole ring compared with -CF₃, which is ineligible for accepting PF₅. Therefore, PF₅ can continuously react with other Lewis bases in the electrolyte [8].

Conventional techniques such as transmission electron microscopy (TEM) [15,16], spectroscopic ellipsometry [17], and X-ray reflectivity analysis [18] can detect SEI behavior. There are some publications describing the in situ or in operando observations for the evaluations of battery materials such as Micro-Raman [19], interferometry [20], neutron scattering [21], and synchrotron radiation with thermal imaging [22], respectively. However, an SEI can be decomposed under ultra-high vacuum conditions to a nanometer size, which makes it difficult to perform a detailed exploration [17,23]. The aforementioned techniques have been extensively applied to study the mentioned parameters, because of the emergence of convenient modern in situ evaluations and in operando analyses. However, few in situ or in operando studies have ascertained real-time kinetic information on SEI formation. To realize precise in operando measurements of the kinetics of SEI formation, we developed two in operando measurement processes, namely surface plasmon resonance (SPR) and quartz crystal microbalance (QCM). These techniques were used to investigate the interface properties of salt dissociation, ionic diffusion, SEI formation, and binding reaction mechanisms on electrodes by using data regarding changes in mass, reflection angle, and intensity on the electrode

surface. In this study, in operando SPR and QCM were adopted to determine the reaction sequences during SEI formation in a case without a salt additive (the control sample) and in that with Li BZ salt additives (electron-donating and electron-withdrawing effects). By interpreting the data regarding the changes in mass, reflection angle, and reflection intensity, we determined the individual reaction rate constant, film thickness, mass change, and detailed reaction mechanisms of SEI formation on the Au electrode surface. In addition, the battery measurements on impedance analysis and rate testing are also investigated.

2. Experimental section

2.1. Electrolyte preparation

Four electrolytes were prepared for the in operando SPR and QCM experiments. Sample A was 0.1 M lithium hexafluorophosphate (LiPF₆) in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:2 v/v%, battery grade, water < 20 ppm), which was purchased from Unionward Company in Taiwan. The remaining samples were identical to Sample A, except for the addition of 0.1 wt % LiB to Sample B, 0.1 wt % LiMB to Sample C, and 0.1 wt % lithium trifluoromethyl BZ (LiTFB) to Sample D. All electrolytes were prepared in a glove box in an Ar gas atmosphere to avoid the influence of moisture. The chemical structures of all BZ additives are shown in Scheme 1.

2.2. Instrumentation

A Navi™ 200 from BioNavis Ltd. was used in the current study, which is the same as the method demonstrated Wang et al. [3]. As presented in the paper, a Kretschmann configuration design is used for in operando EC-SPR measurement. A gold chip (working electrode) was installed to detect the time-resolved SPR angle shifts and intensity variations during SEI formation. The laser beam (wavelength 670 nm) was p-polarized before entering the prism. Attenuated total reflection (ATR) occurred once the light beam propagated into the prism and struck a higher refractive index within the gold. The intensity changes of the incidence angle during ATR were then monitored. A slight change at the interface (a change in the refractive index or a formation of a nanoscale film thickness) would cause a change in the SPR signal, enabling precise measurements of thin-film properties as well as surface molecular interactions in real-time.

A three-electrode electrochemical cell setup for QCM measurements (QCA922, Seiko) was used.

Electrochemical impedance spectroscopy (EIS) was performed through a Biologic VMP3 in a frequency range of 100 M to 0.01 Hz along with an AC amplitude of 5 mV at 25 °C. All EIS measurements were performed using a half-cell (CR2032) comprising carbon and Li metal electrodes (area = 1.0 cm²) in a 100% depth of discharge.

The graphite anode consisted of 93 wt % mesocarbon microbeads ΣMCMB-2528, Osaka GasII, 3 wt % KS4 as a conductive additive, and 4 wt % PVDF as a binder. The Si anode consisted of 85 wt % silicon ΣAldrich, particle diameter 10–30 μmII, 7 wt % KS6 as a conductive additive, and 8 wt % CMC as a binder. The electrolyte was 1.1 M lithium hexafluorophosphate ΣLiPF₆II in EC:EMC Σ1:2 in volumeII mixed solvents.

A charge-discharge test was conducted in a constant current-constant voltage mode with a voltage range of 0.005–3.000 V at 0.1C/0.1C, measured using a U-bic battery tester at room temperature.

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