



Short communication

Using electrochemical surface plasmon resonance for *in-situ* kinetic investigations of solid electrolyte interphase formation in lithium ion batterySylvia Ayu Pradanawati^a, Fu-Ming Wang^{a, b, *}, Chia-Hung Su^c^a Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei, Taiwan^b Sustainable Energy Center, National Taiwan University of Science and Technology, Taipei, Taiwan^c Graduate School of Biochemical Engineering, Ming-Chi University of Technology, Taipei, Taiwan

HIGHLIGHTS

- ECSPR is the first time in use to evaluate the kinetic processes of lithium ion battery.
- ECSPR studies the formation rate and mass of SEI in lithium ion battery.
- ECSPR studies the dissociation rate of EC-Li⁺ clusters and the thickness of SEI.
- ECSPR study avoids the destructiveness analysis.

ARTICLE INFO

Article history:

Received 31 May 2016

Received in revised form

1 September 2016

Accepted 3 September 2016

Keywords:

Lithium ion battery

Kinetic

Surface plasmon resonance

Solid electrolyte interphase

Dissociation

ABSTRACT

The solid electrolyte interphase (SEI) significantly affects the energy density and safety performance of lithium ion batteries. Previous studies have shown that conventional analyses cannot characterize the real-time molecule interactions of SEI formation on the surface of an electrode. In this study, a novel *in situ* electrochemical-surface plasmon resonance (EC-SPR) was developed for evaluating the kinetic changes of ionic dissociation, SEI formation, and Li-Au alloying reaction. The novel EC-SPR not only indicates the rates of each reaction stage but also reveals the characteristics of the passivated layers. This research demonstrates that the dissociation rates of ionic clusters are affected by several reactions on the surface of an electrode. The rate and mass of the SEI formation from the reduction of ethylene carbonate (EC) are calculated at 0.004 ngs⁻¹ and 5.858 ng, respectively. The EC-SPR is a powerful tool for further *in situ* kinetic investigations of different electrolyte and electrode systems.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The solid electrolyte interphase (SEI) plays a crucial rule in determining the performance of lithium ion batteries regarding its customized multiple functions, which are high ionic diffusivity [1], strong electrochemically ability [2], and safety [3]. SEI formation typically occurs during the first charge in accordance with the relation of the reduction reaction potential of the carbonate solvents and the active material infrastructure of the surface [4]. However, the kinetic growth mechanism, chemical composition, physical dimensions, and applications for enhancing battery

performance are still unclear in correlation to SEI formation.

Currently, numerous *in situ* evaluations and *in operando* analyses have been developed and employed to study the SEI. These include atomic force microscopy [5], X-ray photoelectron spectroscopy [6], Fourier transform infrared spectroscopy [7], scanning electrochemical microscopy [8], X-ray absorption [9], nuclear magnetic resonance [10], transmission electron microscopy (TEM) [11], scanning electron microscopy [12], Raman spectroscopy [10], positron annihilation life-time spectroscopy [13], and electrochemical quartz crystal microbalance (EQCM) [14]. However, few *in situ* studies have ascertained real-time kinetic information on SEI formation. Sacci et al. directly visualized initial SEI formation on an Au-coated electrode by using an *in situ* electrochemical TEM system. Several small Li crystalline particles were discovered within the SEI because of the irregular surface coverage of the SEI, causing

* Corresponding author. IB 606, 43 Keelung Road, Section 4, Taipei 106, Taiwan.
E-mail address: mccabe@mail.ntust.edu.tw (F.-M. Wang).

a non-uniform diffusivity of lithium ions on the surface of an electrode. The Li dendrite then grows through the SEI into a conduction pathway and interrupts the electrochemical reaction. Research has indicated that the electrolyte composition is responsible for the irregular infrastructure of the SEI [15]; however, the kinetic discussion concerning different electrolyte composition has yet to be investigated. Two studies have examined the fluoroethylene carbonate (FEC) effects on Sn [16] and Si [17] electrodes by using EQCM. The dissipation measurement results from above both studies have indicated that the FEC produces less SEI formation and a less rigid structure on the surface of an electrode. However, other literature holds an opposite view against above explanation [18]. It is necessary to analysis the true story in which the formation rate and precise *in operando* kinetic process of SEI formation must be revealed in a new observation. Wang et al. demonstrated a direct observation of the structure of charged ions and the consequence of their insertion by using *in situ* liquid secondary ion mass spectroscopy [19]. The result indicated a substantial concentration difference of Li^+ and PF_6^- around the surface of the anode, which reduces the ionic conductivity of the electrolytes and contributes a polarization effect.

To create a precise *in operando* kinetic process of SEI formation, a new device of *in situ* electrochemical-surface plasmon resonance (EC-SPR) was developed and employed. The results of previous studies that used surface plasmon resonance (SPR) were used to estimate the real-time binding kinetics of biomolecules such as the protein–aptamer interactions [20], molecule detection [21], and drug developments [22]. We used the EC-SPR to determine the reflection angle and reflection intensity changes of SEI formation as a function of charging potential. By interpreting the aforementioned data, the individual reaction rate, mass, thickness, and detailed reaction mechanism of the SEI were determined.

2. Experiment

2.1. Preparation of the electrolytes

The electrolyte mixture used in this research was 0.1 M lithium hexafluorophosphate (LiPF_6) in ethylene carbonate (EC):ethyl methyl carbonate (EMC) (1:2 in volume) and was prepared inside a glove box within an Ar gas atmosphere to avoid any moisture influence.

2.2. Instrumentation

A Navi™ 200 from BioNavis Ltd. was used in this study. Fig. 1a shows the configuration design of the *in situ* EC-SPR measurement. A gold chip (working electrode) was installed to detect the time-resolved SPR angle shifts and intensity variation during the SEI formation. The laser beam (wavelength 735 nm) was p-polarized by a polarizer before entering the prism. Attenuated total reflection (ATR) occurred once the light beam was propagating 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.

2.3. *In situ* EC-SPR cell

Fig. 1b depicts the *in situ* EC-SPR cell. Polyether ether kethone constituted the electrochemical cell, which was insulated with NBR-70/Kalrez type O-ring. A Pt pseudo-reference electrode ($\text{Pt}_{\text{pseudo}}$) and Pt counter electrode (CE) were used in this study [15,23]. Au working, Pt counter, and $\text{Pt}_{\text{pseudo}}$ reference electrode were each directly connected to a multichannel potentiostat (Biologic VMP3). Fig. 1c shows the infrastructure of the *in situ* EC-SPR cell. Before starting the experiment, the electrolyte mixture was injected into the cell (bottom left corner) until the space was filled.

2.4. Electrochemical operation and data analysis

In situ EC-SPR measurements were performed using the angular scanning mode to evaluate angle (θ) changes during the linear sweep voltammetry (LSV) process (scanning rate was 1 mV^{-1} ranging from 0–(-3) V). In order to analyze the refractive index, thin-film thickness, and angular scanning curves, commercial software Winspall was used to simulate the SPR curves required for calculating the mass and thickness changes. Winspall software is a simulation software package to facilitate the calculation regarding the surface plasmon resonance performance based on the Fresnel's equation. This software computes the reflectivity of optical multi-layer systems. The thickness and refractive index of the gold layer was determined by the Bionavis™, which was used as the reference

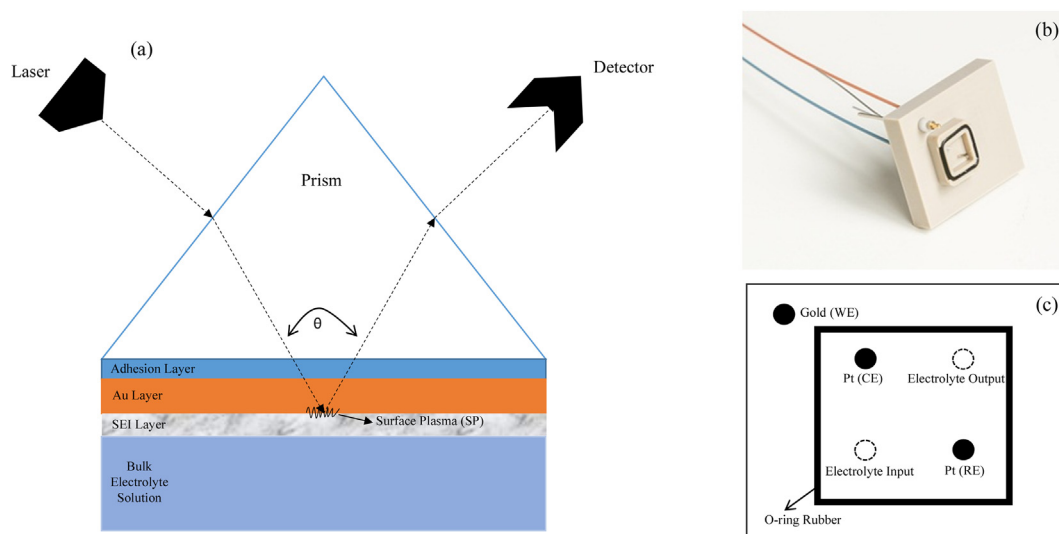


Fig. 1. (a) The configuration design of *In-situ* EC-SPR measurement. (b) The appearance device and (c) the infrastructure of *In-situ* EC-SPR cell.

Download English Version:

<https://daneshyari.com/en/article/5150246>

Download Persian Version:

<https://daneshyari.com/article/5150246>

[Daneshyari.com](https://daneshyari.com)