

< Abstract >

Analytical Study for Correlation of Materials / Interfaces Composed All-Solid-State Batteries Koji HIRAOKA

Purpose in this study is discussion about understanding the electrochemical / charge-discharge reactions in every component materials and electrode / electrolyte interfaces through the construction of the advanced-analysis techniques and their applying for the various battery systems under dynamic state, in addition to the material / cell designs in the solid electrolytes for the polymer, sulfide, and oxide-based all-solid-state batteries (ASSB), expecting high energy density, abundant resource, and safety. In particular, charge-discharge operation in the ASSB proceeds the ionic transport, redox, and interfacial reactions in the solid electrolyte, electrode layers and their interface with extremely wide spatial range, *i.e.* atomic to micrometer scales under intrinsic time scale. Therefore, since these complex / hierarchical reactions is one of the reason to be hard to development of the high-performance ASSBs, understanding charge-discharge reaction overall is strongly expected to obtain the guidelines materials / cell designs in practical use of the batteries. Herein, this study aimed to establish the new-type analysis method for development of the ASSBs with the high energy density, resource abundant, and safety by the directly and comprehensively capturing the various reaction steps inside the battery via combination with the electrochemical / spectroscopic / electron microscopic techniques, based on designing the high-performance solid electrolytes.

In chapter 1 was marshaled the demand / supply of the electric power in Japan undergo transforming to sustainable society through the decarbonization, discussed the battery systems to satisfy these demands, and summarized the analysis techniques enabled to direct observe the electrochemical reactions under charge-discharge operation. For long-term demand in the batteries, development is required the material / cell designs ensured the safety and resource abundantly, in addition to further improve the energy density. One of this candidate system, the ASSBs using carrier ion species with high resource abundantly have been desired. On the other hand, development of this ASSB system has merits and issues in every solid electrolyte material, additionally, charge-discharge operation also proceeds extremely complex reactions at component materials and their interfaces during charge-discharge. Therefore, research trends on the *in situ (operando)* observation techniques and analytical methods, enabling to capture each reactional field inside the battery under dynamic state, mainly Raman spectroscopy and electron microscopy are summarized.

In chapter 2, composite solid electrolyte (CSE) composed by the solid polymer electrolyte (SPE) with

high flexibility and inorganic solid electrolyte (NZSP) with high ionic conductivity (σ) was fabricated for utilizing both advantages, and evaluated these physicochemical / electrochemical properties. In addition, Na-based ASSBs was also prepared using sulfur-based and layered-oxide as the active materials of the positive electrodes for demonstration as a Na conductive solid electrolyte and extracting factors of the internal resistance. The σ as the bulk property increased / decreased in the low ($< 100\text{wt}\%$) and low ($> 100\%$) composite ratio, respectively, by NZSP addition, suggesting change of ionic conduction mechanism in the CSEs. From evaluations of the thermal property and intermolecular interaction, CSE with low NZSP ratio was promoted the salt dissociation and increased free volume in the SPE phase, which were factor to improve the σ . The interfacial resistance (R_{int}) with metallic Na electrode decreased the electric resistance and apparent activation energy (E_a) in the higher NZSP ration compared to that of lower, suggesting promotion of Na^+ transport, according to existence of the NZSP particles with higher σ value and Na^+ transport number than that of the SPE phase. The Na-based ASSBs applied these CSE film were obtained the reversible capacity at 333 K, in which lower operation temperature over 300 K compared to commercialized Na-S battery. from above, CSE design for Na-based ASSB is effective, however, internal resistance at charged state was in the order of electrolyte bulk \ll electrode / electrolyte interface. Therefore, optimization of the interface design and these essentially understanding are important factor for further improvement of capacity, cycle capability in the Na-based ASSB.

In chapter 3, various cation conductive SPEs (Li^+ , Na^+ , Ca^{2+} , and Mg^{2+}) were fabricated and systematically understanding for physicochemical / electrochemical / interfacial property every cation species. For ASSBs with resource abundantly, various cation conductive electrolytes are required. The polyether-based SPEs achieve ionic conduction by coordination between ether oxygen (ligand) and each cation dissolved from metal salts, and they exhibit highly repeatable solvation / desolvation reactions. Therefore, SPE play as Li^+ , Na^+ , Ca^{2+} , Mg^{2+} conductive solid electrolytes, in this chapter, thermal, electrochemical, anion diffusion, and electrode / electrolyte interfacial properties were exhaustive evaluated. The prepared SPEs containing each metal salt were confirmed the glass transition temperature related to free volume inside the polymer in order of $\text{Mg} < \text{Li} < \text{Na} < \text{Ca}$ systems. Because the ionic radii are larger in order of $\text{Mg}^{2+} < \text{Li}^+ < \text{Na}^+ < \text{Ca}^{2+}$, interaction between cation and ether oxygen were strong with high charge density of cation, suggesting contribution for order of the glass transition temperature. On the other hand, R_{int} at electrode / electrolyte in the [metallic Li or Na | SPE | metallic Li or Na] symmetric cells exhibited approximately 100 and 1,000 Ω in the Li and Na systems with same cationic valence, respectively. Moreover, E_a at the electrode / electrolyte interface also exhibited approximately 80 and 95 kJ mol^{-1} in the Li and Na systems, respectively. Therefore, σ , R_{int} , and E_a are significantly differed, revealed that understanding interfacial reactions under electrochemical reaction is necessary for construction of the non-Li-based ASSBs.

In chapter 4, *operando* Raman spectroscopy was constructed for directly evaluating ionic transport property based on the concentration change inside the Li- and Na-based SPEs under electrochemical reaction. From chapter 3, interfacial reaction at electrode / electrolyte was suggested the rate-determine step in the charge-discharge reaction. Therefore, *operando* Raman spectroscopy, enabled to observe the concentration change inside the electrolyte as the bonding state during the electrode reaction, was applied for cross-section of the [Li | SPE | Li] cell and [Li or Na | SPE | Li or Na] symmetrical cell. IN static condition, associated anion specie in the Na-based SPE were greater than that of Li-based SPE, and this trend was significant in the higher concentration region. In addition, Raman peak area derived from the solvated ether oxygen with a cation came close to constant at the lower concentration region in the Na-based SPE compared to those of Li-based SPE, suggesting easily saturation of ether oxygen by the large Na^+ radius. From the [Li | SPE | Cu] cell under potential sweep, anion concentration in the middle point of the electrolyte layer maintained constant, while this value clear changed at near the electrodes, and this analysis method was expected to evaluate the concentration change with the electrode reaction. For detail analysis of the concentration change, Raman spectra acquired from the symmetrical cells under applying constant voltage drastically increased / decreased near the electrodes, then became to constant values in the both Li- and Na-based SPEs. This trend corresponds to ionic transport step and steady-state inside the SPEs during the electrode reaction. Furthermore, time to reach steady-state in the Na-based SPE was longer than that of the Li-based SPE, suggesting that Na-based SPE proceed to slow Na^+ transport due to their stable and rugged solvation structure by the large cationic radius. Therefore, *operando* Raman spectroscopy was revealed to evaluate the concentration change based on the ionic transport under electrochemical reactions inside the SPEs.

In chapter 5, *operando* Raman spectroscopy was applied for the sulfide-based ASSBs with high σ , to extract the negative electrode reaction during the charge-discharge operation. Herein, anode-free type ASSB was used, which *in situ* formed negative electrode via metallic Li deposition during an initial charging, by introducing the Ag/C layer between the solid electrolyte layer and SUS current collector for leading high energy density. *Operando* Raman spectroscopy also applied for the Ag/C layer in cross-sectional ASSB, to clarify the carbon structural and bonding state changes with Li deposition / dissolution. Although the short-circuit was happened during the charging, peaks derive from the carbon became broader shapes, and then reversed those behaviors by the discharging. From the curve fitting, these peak shapes and positions were clear changed, suggesting partially intercalation / deintercalation of Li^+ by the Li deposition / dissolution reactions, despite use of the disordered carbon material. In addition, new appeared peaks were observed with the charging, and can attributed to the formed compounds and formation of activated vibrational mode, such as the Ag-Li alloy, Li-intercalated carbon and so on. The cross-section of ASSB after the charging was also observed the precipitates with luster located closely crack in the solid electrolyte layer. The Raman spectra acquired

from those precipitates agreed with appeared peak with the charging, and suggested that local short-circuit was occurred by the forming the percolated Ag-Li and others in the cross-section, which was lower pressure compared to the bulk. Therefore, *operando* Raman spectroscopy can estimate not only degree of the ionic transport inside the electrolyte, but also structural changes and short-circuit mechanism in the electrode layer.

In chapter 6, multi-scale analysis combined the *operando* scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) / Raman spectroscopy, and time-of-flight secondary mass spectrometry (TOF-SIMS) was constructed for the comprehensive understanding charge-discharge reactions in the oxide-type Na-based ASSBs. This multi-scale analysis was expected to extract the elemental distribution and structural changes with widely range atomic to micrometer scales every reaction field. In the same sample, complementary evaluation of the Na concentration and bonding state changes with micrometer and atomic scales, respectively, were performed by using *operando* SEM-EDS (1st cycle) and *operando* Raman spectroscopy (2nd and 3rd cycles). *Operando* SEM-EDS was clarified that Na amount decreased / increased in the positive and negative electrode layers, respectively, during the charging, and then increased / decreased during the discharging with micrometer scale. This trend implies to Na concentration changes with intercalation / deintercalation reaction in the active materials in the electrode layers. From the *operando* Raman spectroscopy, although the Raman spectra of the SE layer did not change, in contrast, that of the positive electrode layer reversible increased / decreased peak intensity during the charging and discharging, respectively. These calculated peak areas also clear increased / decreased, suggesting correspondence to crystal structural changes based on the Na intercalation / deintercalation with atomic scale. Therefore, combination of the *operando* SEM-EDS / Raman spectroscopy can expect to not only evaluate the Na concentration and structural changes, but also complementary estimate the state-of-charge inside the battery. In addition, TOF-SIMS measurement after 3 cycles observed precisely elemental distributions along the particle shapes of the component materials with nanometer scale. In particular, the solid electrolyte layer was confirmed the Na distribution in the grain boundary region differed to inside the particles, and estimated the Na conduction pathway during the charge-discharge operation. Therefore, this multi-scale analysis can fundamental / comprehensive evaluate for every reaction field under various electrochemical steps, and strongly contribute to understand for overall of the charge-discharge reactions in the ASSBs.

In chapter 7, as a summery, this study was concluded that *operando* measurement for the inside battery under dynamic state can direct observe the charge-discharge reactions in the component materials and interfaces, which are continually and hierarchical changing, such as the ionic transport, morphology / structure, and reaction speed. In other words, comprehensive extracting for every reaction step inside

the battery allows to constructure the theory for the realization of the all-solid-state batteries with the high energy density, resource abundantly, and safety via the materials / cell designs based on actually operation conditions.