Unveiling the SEI Formation in a Potassium Ion Battery Using Distribution of Relaxation Time

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Abstract

Understanding of solid electrolyte interphase (SEI) formation process in novel battery systems is of primary importance. Alongside increasing powerful in-situ techniques, searching for readily-accessible, non-invasive, and low-cost tools to probe battery chemistry is highly demanded. Here, we applied distribution of relaxation time (DRT) analysis to interpret in-situ electrochemical impedance spectroscopy results during cycling, which is able to distinguish various electrochemical processes based on their time constants. By building direct link between SEI layer and the cell performances, it allows us track the formation and evolution process of SEI layer, diagnose the failure of cell, and unveil the reaction mechanism. For instance, in a K-ion cell using SnS2/N-doped reduced graphene oxide (N-rGO) composite electrode, we found that the ion-transport in the electrolyte phase is the main reason of cell deterioration. In the electrolyte with potassium bis(uorosulfonyl)imide (KFSI), the porous structure of the composite electrode was reinforced by rapid formation of a robust SEI layer at SnS2/electrolyte interface and thus the KFSI-based cell delivers a high capacity and good cycleability. This method lowers the barrier of in-situ EIS analysis, and helps public researchers to explore high-performance electrode materials.

Introduction

Energy storage enables deeper penetration of renewable resources\(^1,2\). Recently, many novel battery systems, such as Li-S batteries\(^3\), Na-ion batteries (SIBs)\(^4\), K-ion batteries (PIBs)\(^5\), Mg-ion batteries\(^6\), etc, appear as appealing solutions. For these novel systems, the solid electrolyte interphase (SEI) layer plays an important role on the cell performance\(^7,8\). In the case of PIBs, conversion-type electrodes possess faster reaction kinetics than intercalation-type electrodes, and have been spotlighted as interesting candidates for PIBs\(^9,10\). However, conversion reactions present significant volume changes during discharge and charge processes, resulting in the breakdown and reconstruction of SEI layer and further leading to massive side-reactions between electrolyte and electrode, depletion of electrolytes, and electrode passivation\(^11,12\). Therefore, a robust and high-quality SEI layer is crucial to endow conversion-type materials good electrochemical performance in PIBs. While SEI in Li-ion batteries has been intensitively investigated, studies of SEI in PIBs remain sparse\(^13\). It has been suggested that good SEI additives for LIBs or SIBs do not necessarily provide promising results for PIBs\(^14\). One of the examples is fluoroethylene carbonate (FEC), which is an effective additive promoting SEI formation in LIBs, however delivers disappointing performance in PIBs\(^15,16,17\). This result could be partially explained by the difference of the redox potential between anode materials in K-ion and Li-ion batteries. Moreover, it is also worth noting that the mechanism of SEI formation on the electrode/electrolyte interface in PIBs might be remarkably different from that in LIBs.

In-situ and operando techniques enable greater understanding of formation process and properties of SEI. Therefore, there are intensive demands for readily-accessible, non-invasive, and low-cost in-situ tools without using a specific home-made cell and comprising the electrochemical performance, such as discharge capacity, coulombic efficiency, overpotentials, cycleability, etc\(^18,19\). In-situ electrochemical
Impedance spectroscopy (EIS) is a facile method that perfectly fits all these criteria. In the EIS measurement, the overall impedance ($Z$) is recorded and it is contributed by many factors and processes, including the contact resistance, ionic conductivity, charge transfer at the interface, impedance of mass transport, etc, due to the complexity of the reactions.$^{20, 21}$ Unfortunately, it is hard to separate these contributions without knowing all details of the reactions at the electrode-electrolyte interface. Typically, interpretation of the EIS results requires some details of the reactions at the interface and an accurate physics-based model, which brings into much ambiguity and controversy, particularly for unknown reactions.$^{22, 23}$

To circumvent the dilemma, herein, the distribution of relaxation time (DRT) analysis is carried out as a major tool to interpret EIS results. It can straightforwardly distinguish and separate various electrochemical processes by their different time constants ($\tau$), which represent the intrinsic properties of each process in a wide frequency range.$^{24, 25, 26}$ Previous studies used DRT to study the effect of temperature on the SEI layer and to find out the number of underlying process in SEI in order to make a good data fitting for the semi-circles in the EIS results.$^{27, 28}$ The EIS analysis is still based on the conventional data fitting of semicircles which is only suitable for an electrochemical system owning an accurate physical model of interface, such as Li-ion batteries. This drawback limits its wide application in novel batteries and hurdle its use by most researchers without electrochemistry background.

In this contribution, we show that DRT can do more than just counting the number of underlying processes as an assistant. It allows us establish the direct connection between SEI layer and the cell performance and thus track the formation and evolution of SEI layer in real time, diagnose the failure of cell, and unveil the reaction mechanism. Different from previously reported work, it no longer needs prerequisite of the reaction details or accurate physical model and trivial data-fitting of semi-circles. By lowering the barrier of in-situ EIS analysis, this DRT is friendly to wide community of researchers without specific electrochemistry knowledge, particularly to those who focus on material science and engineering. It provides a simple and powerful tool to researchers in the community and could accelerate the research and development of electrochemical energy storage.

Here, we show an example of tin sulfide/N-doped reduced graphene oxide (SnS$_2$/N-rGO) composite in KIBs, which has been studied in our previous work but not yet well understood even though in-situ XRD was applied.$^{29}$ In this study, in-situ EIS and DRT analysis on SnS$_2$/N-rGO were carried out during the cycling with electrolytes containing various K-salts, namely potassium bis(fluorosulfonyl)imide (KFSI), potassium bis(trifluoromethane-sulfonyl)imide (KTFSI), and potassium hexafluorophosphate (KPF$_6$). DRT results demonstrate that the poor cycleability of the cell is resulted from the deterioration of the ion-transport in the electrolyte phase, in which electrolyte salt plays an important role. The salt dominates the formation kinetics and the mechanical properties of the SEI layer. The robust SEI layer inhibits the loss of active materials during cycling leading to reinforced porous structure of the electrode, thus further facilitates the ion-transport in the electrolyte-filled porous electrode structure.
Results And Discussion

The SnS$_2$/N-rGO composite was prepared as described previously. The experimental details are described as well as the characterization of the SnS$_2$/N-rGO is shown in the Supporting Information. The XRD pattern (Figure S1a) of the composite confirms the formation and nano-size of SnS$_2$. Scanning electron microscopy (SEM) and TEM images (Figure S1b&e) show that the composite owns a sandwich structure with SnS$_2$ nanoparticles (ca. 5 nm) covering on N-rGO sheets homogeneously. Although SnS$_2$ has a low electronic conductivity, the special structure retains a good electrical contact between SnS$_2$ and N-rGO, providing channels for fast electron and ion transfers.

The electrochemical studies were carried out in Swagelok-type three-electrode cells to focus on the reactions at the SnS$_2$/N-rGO composite, as a working electrode, and to avoid the influence of the metallic K counter electrode. Another piece of K metal serves as the reference electrode. The electrolyte in such cell containing ethylene carbonate/diethyl carbonate (EC/DEC, 50/50, v/v) with 1 M of various K salts respectively (i.e. KFSI, KTFSI, and KPF$_6$).

The discharge and charge load curves for the 1$^{st}$, 2$^{nd}$, and 20$^{th}$ cycles are shown in Figure S2. For the first two cycles, the load curves are similar for cases of all three electrolytes, indicating that the main reactions of SnS$_2$ are the same in three electrolytes. On the discharging process, the reaction is divided into two stages. The first stage is from 1 V to 0.5 V (vs. K$^+$/K), where SnS$_2$ is transformed into SnS and K$_2$S$_5$. The second stage is from 0.5 V to 0.01 V (vs. K$^+$/K), which corresponds to the complete conversion reaction of SnS to KSn and K$_2$S. On the charging process, the reactions are reversed and two stages are observed as well, which are consistent with two oxidation peaks in the CV curves and the Q/V plot as shown in Figure S3.

Despite the same main redox-reactions taking place in the cells with three electrolytes, the cycleability of these cells exhibits significant differences. Figure 1a shows a similar behavior of all cells at current density of 200 mA g$^{-1}$ with high initial capacity and rapid capacity drop in the first couple of cycles, which is due to activation processes such as the side-reactions at N-rGO as we discussed previously. After the activation process, the discharge/charge capacity remains stable at ca. 600 mAh g$^{-1}$ for 30 cycles. After 30 cycles, the capacity of the cell using KPF$_6$ starts to decrease rapidly and it further decays to 86 mAh g$^{-1}$ after 100 cycles. A similar trend of capacity decay is observed with the cell using KTFSI but the rate of decay is slightly lower. The capacity starts to drop sharply after 60 cycles and the cell fails after 120 cycles. In a sharp contrast, the cell using KFSI retains a high capacity of 560 mAh g$^{-1}$ for over 200 cycles. As shown in Figure 1b, even at a high current density of 1 A g$^{-1}$, the capacity of the KFSI-based cell retains as high as 400 mAh g$^{-1}$, about two-fold higher than the cells with KTFSI and KPF$_6$, which are 200 mAh g$^{-1}$ and 180 mAh g$^{-1}$, respectively. To study their high-rate performance, cells using three salts were tested at a high rate of 1 A g$^{-1}$ and the result is shown in Figure S4. The capacity of the cell using KPF$_6$ decreased to below 100 mAh g$^{-1}$ after 10 cycles. The cell using KTFSI is slightly better. It
remains a capacity of 110 mAh g\(^{-1}\) after 200 cycles. In comparison, a cell using KFSI delivers capacities of 400 mAh g\(^{-1}\) and 331 mAh g\(^{-1}\) after 10 and 200 cycles, respectively, exhibiting a high capacity retention of 83%. Overall, cells with KFSI exhibit better performance than KTFSI and KPF\(_6\) both at high and low current densities.

As mentioned above, the electrode reactions on discharge and charge are the same in the cells with different salts, hence the reason leading to the remarkable difference in cycling performance could be related to the SEI formation on SnS\(_2\). Figure 2 shows the load curves for the 1\(^{st}\), 10\(^{th}\), 20\(^{th}\), and 50\(^{th}\) cycle for the cells using various K salts. As guided by the arrows in Figure 2b&c, the overpotentials during discharge and charge in the cells with KTFSI and KPF\(_6\) continuously increase upon cycling as expected. On the contrary, in the KFSI-based cells, the overpotentials are mitigated during cycling, which suggests a different formation process and quality of SEI layers in these three electrolytes.

To further understand the influence of the salts on the cell cycleability, in-situ EIS spectra were recorded during cycling, as seen in Figure 3. For the cell with KFSI electrolyte, the overall impedance (Z) increases during the first 10 cycles, gradually decreases after 10 cycles and then remains constant beyond 30 cycles (Figure 3a). In comparison, Z keeps increasing slowly upon cycling for both cells with KTFSI and KPF\(_6\) electrolytes. Unfortunately, it is hard to separate the contributions of each process at the electrode-electrolyte interface without knowing more details of the reactions. In most cases, a physics-based model is required to fit the EIS data, which is not used here. In its stead, DRT analysis of the EIS results was carried out to probe the change at the interface and the results are plotted in Figure 3 d-f. The x-axis is the time constant (), equaling to resistance (R) times capacitance (C), which is independent of the surface area and represents the intrinsic properties of each process. The peak area represents the impedance of the corresponding process. Therefore, various processes owning different can be separated and identified in the DRT plots. More importantly, the change of each process upon cycling can be tracked and associated with the cell performance, such as capacity decay and overpotentials. In this case, three main contributions are identified and marked as 1, 2, and 3 in Figure 3 d-f. Typically, the slow processes (> 10 s) are assigned to the ion transports in the bulk electrolyte phase such as diffusion resistance in the porous electrode structure. The intermediate processes (0.01 s < < 10 s) are assigned to the charge transfer reactions and the fast processes (< 0.01 s) are due to the ion transport across SEI layer.\(^{34}\)

In all three cells, overall Z values are mainly contributed by three types of processes, which are ion transport in the electrolyte phase (1), the charge transfer reactions (2), and the ion transport across the SEI layer (3), as briefly described in Figure 4. Other factors such as contact resistance, electrolyte resistance, etc, are negligible in this study. Among 1, 2, and 3, Z is dominated by ion transport in the electrolyte phase (1), which is unusual and suggests the porous electrode structure changes significantly during cycling. In the case of the KFSI-based cell, 1 peaks increase during the first 10 cycles and reach the maximum after 10 cycles. In the following tens of cycles, 1 peaks decrease sharply to the minimum, ca. a quarter of the maximum, and they stay at the minimum after 30 cycles. This result is consistent with the change of overpotentials on discharging and charging processes, which increase initially but decrease gradually.
upon cycling, as shown in Figure 2a. However, the results are opposite in KTFSI and KPF₆ electrolytes. Peaks increased by several-fold slowly and steadily, indicating a continuous deterioration of the ion transport in the electrolyte-filled pores during cycling (Figure 3e&f). This is likely caused by the collapse of the porous electrode structure, and thus the ions are blocked out and cannot access the active materials, as shown in Figure 4b.

During discharging and charging processes of SnS₂, soluble polysulfide species are formed as intermediate, which is soluble in the electrolyte and might escape from the electrode structure irreversibly. Combining with the large volume change of SnS₂ during cycling, the porous structure of SnS₂ composite electrode loses its support gradually and collapses. To confirm that, the cells were dissembled after 40 cycles and the separators and electrodes were collected for further characterizations. As shown in Figure S5, the separator in the KFSI cell is still as white as pristine but both separators in KTFSI and KPF₆ cells are yellowish. The residual electrolytes after cycling were extracted by using DME and the UV-vis spectra of the DME extract were recorded. The UV-vis spectra in Figure S6 confirmed the formation of significant amounts of polysulfide species, i.e., S₆²⁻, S₄²⁻, in the electrolytes with KTFSI and KPF₆. However, only a small amount of polysulfide was detected in the electrolyte with KFSI, as shown by the blue curve in Figure S6.

Similar to Li-S batteries, the dissolved polysulfide species not only attack the carbonate-based electrolytes but also damage the electrode structure.⁴ On one hand, the nucleophilic polysulfide species are known to attack the carbonate-based electrolytes, resulting in severe side-reactions of electrolyte and electrolyte depletion, further accelerating the capacity decay. On the other hand, the polysulfides dissolution into the electrolyte could leave N-rGO scaffold without mechanical support, and consequently the porous structure of the composite electrode, particular at the edge of SnS₂/N-rGO composites, collapse and clog the access of electrolyte. The TEM images of the SnS₂/N-rGO composites after cycling in various electrolytes were acquired and are shown in Figure S7. The SnS₂/N-rGO composite being cycled in the KFSI-based electrolyte shows numerous SnS₂ particles at the edge the composite electrode, Figure S7a, the same as the pristine electrode before cycling, however, the composites cycled in the other two electrolytes, the SnS₂ particles at the edges of composite disappeared significantly. There are only thin sheets of N-rGO with very little amount of SnS₂ settling in between N-rGO sheets being observed (Figure S7 b&c), which confirms the loss of the active materials and collapse of the structure at the edges. Under the combined influence of continuous loss of support and large volume change of SnS₂ during cycling, the porous structure gradually collapses upon cycling and therefore it obstructs the electrolyte diffusion inside the bulk electrode, which is confirmed by the increasing Z attributed to mass diffusion (1) and increasing cell overpotential. Because of the limited mass transport, the SnS₂ is partially rendered inactive, leading to the capacity decay during cycling.

The peaks in the region of 10⁻³~10⁻² s are assigned to the ion transport across the SEI layer, as shown in Figure 4a. It represents the thickness of SEI layer if we suppose that the compositions and resistance
of SEI remain identical across the layer. Therefore, the increase of the $3$ peak exhibits the growing process of SEI layer. For the KFSI-based cell, the $3$ peak rapidly increases at the beginning of cycling, and becomes constant after 20 cycles, indicating SEI layer stops growing. On the contrary, in the cells with KTFSI and KPF$_6$, the $3$ peaks kept increasing until the death of cells, which indicates the SEI layers in KTFSI and KPF$_6$ cells kept growing thicker and thicker and K$^+$ transport across the SEI films became more and more difficult until the death of cells (Figure 3 e&f).

The SEM images of the electrode after cycling as shown in Figure S8. For simplicity, here, we assume that the SEI layer observed at the electrode/electrolyte interface is identical to the SEI layer formed on the particles surface. For FSI$^-$, a smooth electrode surface coating without pinholes was observed in the KFSI-based cell (Figure S8a&d), which exhibits an excellent protection of the electrode. The FSI$^-$ anion have a higher reduction potential than those of TFSI$^-$ and PF$_6^-$, which is ca. 1.5 V vs. K$^+/K$, therefore it is thermodynamically more favorable reduced at the SnS$_2$ electrode surface compared to TFSI$^-$ and PF$_6^-$ . It is confirmed by XPS spectra in Figure S9. The signals of K–F in the F1s spectra are from salt decomposition on the surface. KF is a key component of SEI because it improves the mechanical property of the SEI and abort the further reactions of electrode and electrolyte as an electronic insulator.

The SEI layer in the KFSI-based cell owns the highest ratio of KF among three samples and thus it forms a thin, dense, and robust film (Figure S8a&d), which prevents the polysulfide dissolution into the electrolyte, traps the sulfide species in the electrode to maintain the electrode structure, and deliver an enhancement of the cycleability and capacity retention of SnS$_2$. However, in the cases of the cells using KTFSI and KPF$_6$, the K-F peaks in the F-spectra (Figure S9a) are much lower than that in KFSI. Due to the lack of KF in the SEI layer, a loose and porous SEI layer forms (Figure S8 b,c,e,f), which is not able to stop the further reduction of electrolytes at the surface, leading to depletion of electrolyte and continuously growing of SEI, in consistence with the increasing $3$ in DRT plots (Figure 3e&f).

Combining with the DRT analysis, at least two competitive processes take place simultaneously in the SEI formation, namely a passivation process and a wetting process. The former is dominant at the beginning of cycling and it is associated with the initiating and growing of the SEI layer which leads to increase of overpotentials (Figure 2a).. The SEI layer in KFSI-based cell stops growing when it reaches a certain thickness and therefore $3$ in DRT plot remains constant after certain cycles as discussed above. Even though the SnS$_2$ particles experienced large volume change during cycling, most of them still are trapped in the electrode by the thin and dense SEI layer, hence the lost of polysulfide is minimized and sandwich structure of the SnS$_2$/N-rGO composite electrode is reinforced. The wetting process is attributing to the gradual diffusion of electrolyte into the porous electrode and wetting of the composite electrode during cycling. Therefore the active surface area of electrode increases steadily with the improved accessibility of electrolytes into the porous electrode structure. For FSI$, as shown in Figure 3d, after the initial passivation process, the wetting process becomes dominant and $1$, representing the ion transport in electrolyte phase, decreases continuously. After 30 cycles, $1$ reaches the minimum and remains constant, which indicates the completion of the wetting process and is in good agreement with the low
overpotential and high capacity retention shown in Figure 1a and Figure 2a, as well as the superior performance at high C-rate (Figure 1b). In comparison, the passivation process is overwhelming in the cells with KTFSI and KPF$_6$ through the entire cycling lifespan. The poor quality and coverage of SEI is not robust enough to accommodate the volume change of the SnS$_2$ upon cycling, hence fresh surface of SnS$_2$ exposes to electrolyte, resulting in continuous decomposition of electrolyte and growth of thick SEI, as shown by the increasing $\delta_{\text{SEI}}$ in Figure 3e&f. At the absence of a sturdy SEI layer, the SnS$_2$ leaches out from the composite electrode as polysulfides intermediates during cycling, leading to electrode structure collapse. Hence, the accessibility of electrolyte to the pores of SnS$_2$ composite electrode is inhibited (as shown by the increasing $\omega$ in Figure 3e&f), which is responsible to the increase of overpotentials and decay of capacities.

**Conclusion**

A study of formation process of SEI on SnS$_2$/N-rGO in KIBs has been successfully assessed by in-situ EIS and DRT analysis. We demonstrate the use of DRT method without establishing a physical-based model of interface to track the formation and evolution process of SEI layer on SnS$_2$/N-rGO, diagnose the failure of cell, and unveil the reaction mechanism in electrolyte containing KFSI, KTFSI and KPF$_6$. DRT analysis shows that ion transport in the liquid phase in the porous electrode is the key factor of the superior electrochemical performance in KFSI-based cells thanks to its sturdy, homogenous, and thin SEI layer. On discharge, SnS$_2$ transforms to Sn and then to KSn, leading to numerous volume changes and crack of the SEI. KFSI reacts with the fresh surface of SnS$_2$, forming a SEI layer containing optimum amount of KF, which improves its mechanical property and results in a thin and dense SEI layer, which does not only inhibit the escape of active materials and the consequent capacity loss but also protects the electrode structure from collapsing hence facilitating the electrolyte diffusion into the porous electrode and improving the capacity retention. A high capacity of 560 mAh g$^{-1}$ is retained after 200 cycles at a current density of 200 mA g$^{-1}$, which is one order of magnitude higher than the cells with KTFSI and KPF$_6$. This study shows a convenient and non-invasive in-situ method, herein DRT analysis, is essential to allow us gaining an in-depth understanding on SEI formation and evolution, facilitates the mechanism studies and rationalize of the cell performance. It lowers the barrier of in-situ EIS and helps researchers to accelerate exploration of high-performance electrode materials.

**Experimental Section**

Experimental Details are described in the Supporting information.

**Declarations**

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### Figures

**Figure 1**

Cycleability of SnS$_2$/N-rGO composite in EC-DEC electrolytes containing 1 M KFSI, KTFSI, and KPF$_6$. (a) Capacity retention of cells with various salts at a current density of 200 mA g$^{-1}$. (b) Rate capability of cells with various salts at current densities from 0.05 mA g$^{-1}$ to 1 A g$^{-1}$.
Figure 2

Load curves for discharge and charge of the 1st, 10th, 20th, and 50th cycles, in (a) KFSI, (b) KTFSI and (c) KPF6. Current density: 200 mA g\textsuperscript{-1}. Arrows indicate the trend of increase of overpotentials.
Figure 3

EIS spectra of the SnS2 electrode at the end of various cycles in three electrolytes. (a-c) Nyquist plots in three electrolytes (a) KFSI, (b) KTFSI, and (c) KPF6. The surface area of the electrode is 1 cm2. (d-f) DRT analysis of the EIS results in three electrolytes.
Figure 4

Schematics of various processes in DRT analysis.

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