A Reaction Model for Li Deposition at the Positive Electrode of the Braga-Goodenough Li-S Battery

To cite this article before publication: Masanori Sakai 2020 J. Electrochem. Soc. in press https://doi.org/10.1149/1945-7111/abcf53

Manuscript version: Accepted Manuscript

Accepted Manuscript is "the version of the article accepted for publication including all changes made as a result of the peer review process, and which may also include the addition to the article by IOP Publishing of a header, an article ID, a cover sheet and/or an 'Accepted Manuscript' watermark, but excluding any other editing, typesetting or other changes made by IOP Publishing and/or its licensors"

This Accepted Manuscript is © 2020 The Author(s). Published by IOP Publishing Ltd.

As the Version of Record of this article is going to be/has been published on a gold open access basis under a CC 4.0 licence, this Accepted Manuscript is available for reuse under the applicable CC licence immediately.

Everyone is permitted to use all or part of the original content in this article, provided that they adhere to all the terms of the applicable licence referred to in the article – either https://creativecommons.org/licenses/by/4.0/ or https://creativecommons.org/licenses/by-nc-nd/4.0/

Although reasonable endeavours have been taken to obtain all necessary permissions from third parties to include their copyrighted content within this article, their full citation and copyright line may not be present in this Accepted Manuscript version. Before using any content from this article, please refer to the Version of Record on IOPscience once published for full citation and copyright details, as permissions may be required. All third party content is fully copyright protected and is not published on a gold open access basis under a CC licence, unless that is specifically stated in the figure caption in the Version of Record.

View the article online for updates and enhancements.
A Reaction Model for Li Deposition at the Positive Electrode of the Braga-Goodenough Li-S Battery

| Journal:            | Journal of The Electrochemical Society |
|---------------------|----------------------------------------|
| Manuscript ID       | JES-102562.R1                          |
| Manuscript Type:    | Research Paper                         |
| Date Submitted by the Author: | 10-Nov-2020                           |
| Complete List of Authors: | Sakai, Masanori; Showa Denko Materials Co Ltd, Advanced Technology Research and Development Center |
| Keywords:           | Batteries - Lithium, Batteries – Li-ion, Electrode Kinetics, Electrocatalysis, Thermodynamics, Energy Storage, Dielectrics - High-k |

https://mc04.manuscriptcentral.com/jes-ecs
A Reaction Model for Li Deposition at the Positive Electrode of the Braga-Goodenough Li-S Battery

Masanori Sakai

Advanced Technology R&D Center, Showa Denko Materials Co., Ltd., Tsukuba-shi, Ibaraki-ken, 300-4247 Japan

E-mail: sakaimasanori144@gmail.com

Abstract

The Braga-Goodenough all-solid-state Li-S battery demonstrates Li deposition at the positive electrode during discharge. This Li deposition behavior is explained herein in terms of a newly proposed multi-stage mechanism that can be summarized by the shorthand formula E[(ECC)c]n in which E stands for an electrochemical step, C stands for a chemical step, c indicates steps that are catalytic and n indicates a part of the process that is repeated n times. The catalytic part of the reaction, (ECC)c, cycles the deposition of Li. The n in the E[(ECC)c]n formula represents the number of cycles of the Li deposition step, (ECC)c. An intermediate radical S₈⁻ formed during the first E step, the one-electron reduction of S₈, plays an essential catalytic role in the process. The thermodynamics of the second E step were examined by taking account of the electrochemistry involving two consecutive one-electron steps and of the theory of generalized charge neutrality levels in respect of Schottky barriers. The thermodynamics relating to the Li deposition in the second E step was considered to result in a free energy change of at least ΔG < -2.34eV. The thermodynamics relating to the overall steps of the mechanism were also examined.

Introduction

A Li-S secondary battery with a newly developed solid electrolyte was reported recently ¹. Two other batteries, which were equipped with Li and Na negative electrodes respectively, were reported at the same time ¹. All three batteries exhibited metal (Li or Na) depositions in the positive active mass during their discharge reactions. The most detailed data provided for these
systems were those revealed for the Li-S type battery with the newly
developed Li-glass solid electrolyte, \( \text{Li}_{2.99}\text{Ba}_{0.005}\text{O}_{1+x}\text{Cl}_{1-2x} \). This battery was
demonstrated to provide a capacity of more than ten times that of
conventional Li-ion batteries, while depositing Li metal in the positive active
mass during discharge. In this Li-S type, the battery reactions and their
characteristics were thought to be quite different from the conventional view
of battery function. The paper describing these batteries\(^1\) raises a number of
questions. One relates to the thermodynamics of the Li deposition at the
positive electrode. Despite the remarkable performance characteristics of this
battery, hitherto, the chemistry of the system has never been disclosed, apart
from consideration of electrostatic behavior, capacitor equivalent circuits and
so on\(^1-4\).

\( \text{S}_8 \) positive electrodes exhibit higher specific energy than those of Li-
metal oxides for the conventional Li-ion batteries. The enhancement of the
positive electrode capacity of a battery equipped with a metal negative
electrode is of great importance for energy storage devices to achieve high
specific power and energy. Therefore, enthusiastic research and
development have been reported with regard to the Li-S type batteries\(^5-14\).
However, this Braga-Goodenough battery behavior had never been observed
before.

In this paper, an \( E[(\text{ECC})^c]^n \) mechanism to elucidate the Braga-
Goodenough battery characteristics is proposed. In this formulation of the
mechanism \( E \) stands for an electrochemical step, \( C \) stands for a chemical step,
\( c \) indicates steps that are catalytic and \( n \) indicates a part of the process that
is repeated \( n \) times. The catalytic part of the reaction, \( (\text{ECC})^c \), cycles the
deposition of Li. The \( n \) in the \( E[(\text{ECC})^c]^n \) formula represents the number of
cycles of the Li deposition step, \( (\text{ECC})^c \). An intermediate radical \( \text{S}_8^- \) formed
during the first \( E \) step, the one-electron reduction of \( \text{S}_8 \), plays an essential
catalytic role in the process. \( \text{S}_8^- \) adsorbs at a surface state, \( \text{Li}^{+}(\text{sf}) \), of the newly
developed Li-glass solid electrolyte. The \( \text{Li}^{+}(\text{sf}) \) side of the adsorbent \( \text{S}_8\text{Li}^{+}(\text{af}) \)
accepts a one-electron reduction, and deposits Li. This \( E \) process of Li
deposition is repeatedly cycled via the \( (\text{ECC})^c \) step. Through this \( E[(\text{ECC})^c]^n \)
mechanism, it is possible to account for the one-electron reduction step of the
adsorbent of \( \text{S}_8\text{Li}^{+}(\text{af}) \). In this paper, its thermodynamics are examined by
taking account of both the electrochemistry with regard to two consecutive
one-electron charge transfer steps and the theory of generalized charge
neutrality levels with regard to Schottky barriers. Then the behavior of the Braga-Goodenough battery is examined by means of this E[(ECC)c]n mechanism in many respects, e.g., Li deposition thermodynamics, Li deposition cycle numbers, a cycle limit, and thermodynamics cycle on this mechanism.

Concerning Li deposition cycles, the number of its cycles corresponding to the Braga-Goodenough battery capacity of ten with respect to S$_8$ was determined to be 18 by means of this mechanism. Li deposition cycles on the basis of this mechanism indicate a capacity of greater than the ten times advantage previously reported$^1$.

**Experimental**

In order to evaluate the electronic states and the critical radius corresponding to the intermediate radical S$_8^-$ and the molecule S$_8$, quantum chemistry calculations using Gaussian 09, Revision E.01, were performed with the accuracy of APFD/6-311+G(2d,p). S$_8^-$ is a radical species, so that its calculations are to be expressed as SOMO calculations hereinafter.

Concerning experimental data relating to the Braga-Goodenough battery, all data in this paper are referred to those from reference 1$^1$. The mechanism proposed herein is examined on the basis of the data in 1$^1$.

**An E[(ECC)c]n Model of Li Deposition at the Positive Electrode**

Figure 1 shows the Braga-Goodenough battery diagrams. Li deposition during discharge takes place at interfaces between the discharge reaction intermediate S$_8^-$ and Li$^+$gl as described below.

Reaction steps from [1] to [4] correspond to the model relating to the Li deposition at the positive electrode during discharge of this battery. In this paper, this mechanism is to be expressed in E[(ECC)c]n as follows:
K₁ and K₂ are equilibrium constants of [3] and [4], respectively. This mechanism consists of mainly two consecutive one-electron EE process steps [1] and [2], equilibrium CC steps [3] and [4], and these combined in the catalytic step, (ECC)c. The Li deposition step corresponds to step [2]. The subscript c in the (ECC)c part means a catalytic reaction, and n in E[(ECC)c]n means the number of cycles of the (ECC)c part. This integer n (n≥1) of cycle number corresponds to n times deposition of Li. An intermediate radical S₈⁻ formed at the first E of the one-electron reduction of S₈ plays an essential role in the (ECC)c part as a mediator of a catalyst.

In the positive active mass, S₈ has contact interfaces with the Li-glass solid electrolyte, Li⁺gl⁻, and carbon black. In step [1], S₈Li⁺(ad) represents the solid/solid contact between S₈ and surface states Li⁺(ad) of Li⁺gl⁻. In step [2], S₈⁻Li⁺(ad) represents the adsorbent between S₈⁻ and Li⁺(ad). S₈⁻ Li in the step [2] is the product of the second one-electron reduction of S₈⁻Li⁺(ad). In this step [2], the reduction of S₈⁻Li⁺(ad) takes place at the Li⁺(ad) side of the group, forming Li on discharge. The reaction step [3] shows the equilibrium between S₈⁻Li and both S₈⁻ and Li. Then after the equilibrium step [4], the rest of Li⁺(ad) contacting S₈⁻ continues to cycle the Li deposition from steps [2] to [4] until a cycle number n. As described in the following, the reformation of S₈⁻Li⁺(ad) in this equilibrium step [4] depends on the S₈⁻ catalysis and the cycle number n.

This cycle number n is thought to depend on the formation of S₈⁻ in step [1]. This n relates to the number of contacts between S₈⁻ and Li⁺(ad) surface states. This number of contacts is considered to be large since the ratio of the critical radius of S₈⁻ to that of Li⁺ is ca.10. The critical radius, 483pm, of S₈⁻ is obtained by means of the SOMO calculations. Once S₈⁻ forms at a S₈ site in the positive active mass, the number of contacts relating to the possible number of cycles becomes evident. That is, the arrow from step [4] to step [2],
signifies a change in the reaction site of Li$^{+\,(ad)}$ contacting the same S$_8^-$. Then the one-electron reduction of each Li$^{+\,(ad)}$ contacting S$_8$ takes place n times until the number of contacts between the two is completely utilized thus demonstrating the role of S$_8$ as a catalyst.

Figure 2 shows a schematic representation of the above role of S$_8$ as a catalyst and the cycle number n corresponding to the number of depositions of Li. Three species in the figure are illustrated with circles. The radii of the three circles as shown represent the radii of the three spherical species. The critical radius of 483pm S$_8^-$ is based on the SOMO calculations and the radii of 59pm Li$^+$ and 152pm Li can be referred to elsewhere. In this figure, a total of ten Li and Li$^{+\,(ad)}$ sites are illustrated. Five of the ten are already discharged to form Li, indicating the end of five cycles (n=5). In this case in Fig.2, the remaining 5 Li$^{+\,(ad)}$ are still contacting S$_8^-$, so that there is a possibility of a total Li deposition cycle number of ten. Another significant factor of the S$_8^-$ role as a catalyst is its characteristics as a good conductor (0.64eV $E_g$ as indicated by the SOMO calculations). If S$_8^-$ was a poor conductor, then all the continued one-electron reduction of Li$^{+\,(ad)}$ would be difficult, as shown in Fig.2. On the other hand, the $E_g$ of S$_8$ is an insulator of 5.21eV by the calculation.

The overall reaction of E[(ECC)c]n can be expressed by taking account of the summation from [1] to [4] as follows:

$$S_8 + (n+1)Li^{+\,(ad)} + (n+1)e \rightarrow S_8^- Li^{+\,(ad)} + nLi$$ [5]

That is, the products of the overall reaction from [1] to [4] correspond to one mole of S$_8^-$ Li$^{+\,(ad)}$ and n mole of Li. When the cycle number n=1, incidentally, [5] is replaced by [6].

$$S_8 + 2Li^{+\,(ad)} + 2e \rightarrow S_8^- Li^{+\,(ad)} + Li$$ [6]

In this E[(ECC)c]n mechanism the first step [1] corresponding to the first one-electron charge transfer step controls the overall kinetics from the viewpoint of the formation of S$_8^-$. This dependence on step [1] is based on the kinetics of the two consecutive one-electron charge transfer reactions in the E[(ECC)c]n mechanism. An overall two-electron electrochemical reaction has been considered elsewhere$^{15-24}$. In this study of S$_8$, there is also an overall two-electron reduction. In this respect, the EE mechanism for S$_8$
two-electron reduction is also thought to correspond to the kinetics of the Braga-Goodenough battery. That is, from the viewpoint of electrochemical kinetics, the first charge transfer step of \( S_8 \) is thought to be a one-electron reduction to form the intermediate radical \( S_8^- \).

In the all-solid-state Li-S battery, the coordinates of the reduction site of \( S_8 \) and that of \( S_8^- \) are to be equivalent to each other from a viewpoint of kinetics because \( S_8^- \) is formed at \( S_8 \) coordinates. As described above and in Fig.2, on forming \( S_8^- \), many contacts with \( \text{Li}^+(\text{ad}) \) of \( \text{Li}^+\text{gl}^- \) are formed because the critical ion radius of \( S_8^- \) is nearly one order of magnitude greater than that of \( \text{Li}^+ \). In the Braga-Goodenough battery, once \( S_8^- \) forms, it is considered that \( S_8^- \) adsorbs \( \text{Li}^+(\text{ad}) \) of \( \text{Li}^+\text{gl}^- \) due to their coulombic affinity and thus the adsorbent \( S_8^- \text{Li}^+(\text{ad}) \) is formed. Then the consecutive one-electron reduction will occur in step [2]. This reaction step [2] corresponds to the essential one to explain the Braga-Goodenough battery behavior because Li deposition occurs in this step.

Here, there are two possibilities for further one-electron reduction schemes. One is the consecutive reduction of the \( S_8^- \) side in \( S_8^-\text{Li}^+(\text{ad}) \) to form \( S_8^{2-} \). The other is the reduction of the \( \text{Li}^+(\text{ad}) \) side in \( S_8^-\text{Li}^+(\text{ad}) \) to form metal Li. In this study, \( \text{E}[(\text{ECC})\text{c}]n \), the latter reaction was chosen. When the former scheme is chosen, the Braga-Goodenough battery behavior is not observed, and the reactions are those of conventional Li-S type batteries. This diagnostic criterion is based on the behavior of the Braga-Goodenough battery forming metal Li on discharge.

Accordingly, the second charge transfer step must rely on the thermodynamics of \( \Delta G<0 \), i.e., \( eV_2 < eV_0 \), where \( eV_0 \) is the electron energy level for \( \text{Li}^+/\text{Li} \) of the negative electrode and \( eV_2 \) is that for \( S_8^-\text{Li}^+(\text{ad}) \) of \( S_8^-\text{Li} \). Otherwise, as a spontaneous reaction of the battery discharge, no energy flow and no Li deposition would occur in this mechanism. According to the discharge behavior of the Braga-Goodenough battery \(^1\), the battery voltage of 2.34V was the threshold for the observation of Li deposition in the positive active mass under discharge conditions. That is, as long as the battery voltage is higher than 2.34V on discharge, the cycling of reactions [2] to [4] continues to deposit Li in the positive active mass.

The negative electrode reaction corresponding to the overall positive electrode reaction [5] of this \( \text{E}[(\text{ECC})\text{c}]n \) mechanism is to be expressed as follows:
\[(n+1)\text{Li} \rightarrow (n+1)\text{Li}^+ + (n+1)e\]  \[7\]

\[(n+1)\text{Li}^+ \leftrightarrow (n+1)\text{Li}\text{^+}_\text{(ad)}\]  \[8\]

Therefore, the overall reaction of the negative electrode is as follows:

\[(n+1)\text{Li} \rightarrow (n+1)\text{Li}^\text{+}_\text{(ad)} + (n+1)e\]  \[9\]

The overall reaction of this battery under battery voltages higher than 2.34V conditions can be expressed by \[10\] taking account of the summation of \[5\] and \[9\].

\[\text{S}_8 + \text{Li} \rightarrow \text{S}_8\text{^+}_\text{(ad)}\]  \[10\]

This overall reaction product of \(\text{S}_8\text{^+}_\text{(ad)}\) is the same as the product of the 1st one-electron charge transfer step \[1\]. As long as Li deposits by the reaction cycle from \[2\] to \[4\] in the positive active mass on discharge, the reduction of \(\text{S}_8\) is limited to a one-electron reduction. Then the product of \(\text{S}_8\text{^-}\) of the one-electron reduction of \(\text{S}_8\) plays an essential role as a catalyst in the reaction cycle steps from \[2\] to \[4\]. The product of \(\text{S}_8\text{^-}\text{Li}_\text{(ad)}\) in \[10\] is still an intermediate from the viewpoint of the \(\text{S}_8\) two-electron reduction. When the battery voltage is less than 2.34V, this E[(ECC)c]\text{n} mechanism is over, i.e., Li deposition stops during discharge\textsuperscript{1}). The Braga-Goodenough battery reactions after the termination of E[(ECC)c]\text{n} mechanism are shown in the Appendix.

Concerning the charge reactions of the E[(ECC)c]\text{n} mechanism, those of the positive and the negative electrodes correspond to the reverse reactions of both \[5\] and \[9\]. Thus, the overall charge reaction \[11\] corresponds to the reverse reaction of \[10\] as follows:

\[\text{S}_8\text{^-}\text{Li}_\text{(ad)} \rightarrow \text{S}_8 + \text{Li}\]  \[11\]

Figure 3 shows schematic representation of the step \[2\] for Li deposition cycle in E[(ECC)c]\text{n}. This figure emphasizes the one-electron reduction cycle through \(\text{S}_8\text{^-}\) in the mechanism. As described above, according to the SOMO
calculations, $S_8$ behaves as a good conductor, and this property is to be of importance to play a role of a catalyst in this mechanism. Incidentally, the conductivity of $Li^+$ of $Li^+gl^-$ is greater than $10^{-2} \text{ S cm}^{-1}$ at $25^\circ C$ \(^1\). Thus, the resistance of $Li^+$ transfer in the $Li^+gl^-$ is considered to be sufficiently small compared with the battery kinetics, that it does not affect the steps in the $E[(ECC)c]n$ mechanism. In respect of the practical discharge rate of the Braga-Goodenough battery, it was estimated to be 0.018C by taking account of the data in\(^1\).

**Thermodynamics of Li deposition in the $E[(ECC)c]n$ mechanism**

The thermodynamics of the Li deposition is a fundamental issue to elucidate the positive electrode reactions of the Braga-Goodenough battery. In the potential regions of the positive electrode, the well-known electrode reaction of $Li^+/Li$ redox couple never takes place. In the $E[(ECC)c]n$ mechanism, it is considered that the thermodynamics issue is integrated into the one-electron reduction of $S_8 Li^+ (ad)$ in step [2].

In order to elucidate the electron energy states of the adsorbent $S_8 Li^+ (ad)$ formed in the 1$^{st}$ charge transfer step [1], two procedures from different viewpoints are employed herein. One is the thermodynamics in electrochemistry with regard to a two consecutive one-electron charge transfer reaction, the so-called EE mechanism\(^{15-24}\). The other is the theory of the generalized charge neutrality level $\phi^{G_{CNL}}$\(^{25-29}\). This theory of $\phi^{G_{CNL}}$ newly emerged from the recent consideration of Schottky barriers, especially, for the understanding of effective work functions with electronic structures at interfaces between metals and high-k dielectric insulators\(^{25-29}\). Elucidating electron energy levels of the adsorbent of $S_8 Li^+ (ad)$ by taking account of both electrochemistry and heterojunction physics is considered to be of great importance to clarifying the behavior of the Li deposition thermodynamics in terms of this $E[(ECC)c]n$ mechanism. The thermodynamics $\Delta G<0$ for the Li deposition in step [2] are equivalent to an indication that the electron energy levels of $S_8 Li^+ (ad)$ are lower than those of $Li^+/Li$ of the negative electrode. In practice, on discharge, electrons relating to this $E[(ECC)c]n$ mechanism are all transferred from the negative electrode of $Li^+/Li$, so that the energy levels of the Li deposition in step[2] must be lower than those of $Li^+/Li$.

At first, we examine the situation from the viewpoint of a two consecutive one-electron charge transfer reaction. As is well known, $S_8/S_8^{2-}$ demonstrates
a redox potential, so that its kinetics can be considered to involve an intermediate radical $S_8^{-15-24)}$. Then we employ the theory of the generalized charge neutrality level $\phi_{\text{GCNL}}^{G}$ to continue to examine the electron energy states of the adsorbent formed at interfaces between $S_8^{-}$ and $Li^{+}(sf)$. When this mechanism is appropriate for Li deposition behavior of the Braga-Goodenough battery, it is considered that these two types of examinations from different viewpoints will be consistent with each other.

From the first point of view of the redox potential with regard to $S_8/S_8^{2-}$, the electron energy levels of an intermediate radical of $S_8^{-}$ are to be examined$^{15-24)}$. However, it is already known that the electron energy levels of $S_8^{-}$ should be intermediate between those of $S_8$ and $S_8^{2-}$. In particular, $S_8^{-}$ has two levels in the orbitals occupied with unpaired electrons$^{15)}$. One is corresponding to the level of redox potential of $S_8/S_8^{-}$ and the other is corresponding to that of $S_8^{-}/S_8^{2-}$. Thus, the electron energy level of $S_8^{-}$ is lower than $S_8$ and higher than $S_8^{2-}$. $S_8^{2-}$ is the lowest of the electron energy levels and the highest in potential among the three species.

In the E[(ECC)c]n mechanism, the chemical forms of $S_8 Li^{+}(sf)$, $S_8^{-} Li^{+}(sf)$, and $S_8^{-} Li$ in steps [1] and [2] are different from those of $S_8$, $S_8^{-}$, and $S_8^{2-}$, so that the absolute values of these levels, e.g., between $S_8^{-} Li^{+}(sf)$ and $S_8^{-}$, cannot be identical to each other. However, the potential relationship with regard to these species in the E[(ECC)c]n mechanism is considered to be of the same order of $S_8^{-} Li^{+}(sf)< S_8^{-} Li^{+}(ad)< S_8: Li$ as that of $S_8^{-}< S_8< S_8^{2-}$. That is, the energy level of $S_8^{-} Li^{+}(ad)$ is explicitly lower than that of the negative electrode $Li^{+}/Li$.

Figure 4 shows the images of electron energy levels versus density of states for each reaction species of steps [1] and [2] in the E[(ECC)c]n mechanism. As described above, in particular, the electron energy levels of $S_8^{-} Li^{+}(ad)$ are separated into two Gaussians. Here, $E_1$ and $E_2$ are equilibrium electrode potentials in the EE processes corresponding to the steps [1] and [2], respectively. $e_1$ and $e_2$ are the Fermi levels corresponding to $E_1$ and $E_2$, respectively. The relationship between $E_1$ and $E_2$ is $E_1< E_2^{15, 16-24)}$. As long as the battery voltage is higher than 2.34V, this E[(ECC)c]n mechanism can continue. Thus, the thermodynamics relating to the Li deposition in step [2] is considered to be $\Delta G< -2.34eV$ at least.

In this paper, this symbol $\phi_{\text{GCNL}}^{G}$, the generalized charge neutrality level, has two meanings. One is the theory itself and the other is a charge neutrality level itself evaluated by this $\phi_{\text{GCNL}}^{G}$ theory. There is a conventional base theory.
of a charge neutrality level of $\varphi_{\text{CNL}}$, also relating to Schottky barriers\textsuperscript{25-29}. However, this $\varphi_{\text{CNL}}$ could not clarify the Schottky barriers at interfaces between metals and high-$k$ materials like HfO$_2$. In the case of the interfaces of metals/HfO$_2$, the penetration of MIGS into HfO$_2$ was observed at most one to two atomic layers\textsuperscript{25-29}, so that the full contact of electronic states could not be realized at metals/HfO$_2$ interfaces. One of the causes of this shallow penetration of MIGS into HfO$_2$ was ascribed to the high ionicity of HfO$_2$\textsuperscript{25-29}. HfO$_2$ is a typical high-$k$ insulator with a band gap of greater than 5eV. The Li-glass electrolyte used in the Li-S type battery also demonstrates a band gap of greater than 8eV with typical ionic bond glass structure\textsuperscript{1}. Then Braga et al. described that high dielectric property of this glass electrolyte is the significant factor in this battery performance\textsuperscript{1}.

The theory $\varphi_{\text{GCNL}}$ is built on an orbital hybridization between unoccupied and occupied states of two materials at an interface\textsuperscript{25-29}. In this theory of $\varphi_{\text{GCNL}}$, the charge transfer between S$_8^-$ and Li$^+$gl$^-$ is realized only by such orbital hybridization between unoccupied and occupied states. This electron transfer is absolutely confined to just interfaces between S$_8^-$ and Li$^+$($\alpha_0$) because the insulator of the ionic bond structure Li$^+$gl$^-$ demonstrates greater than 8eV band gap. S$_8^-$, however, demonstrates metal like characteristics with a 0.64eV band gap as indicated by the SOMO calculations. Since Li$^+$gl$^-$ is an ionic bond insulator material, its conduction band contains the frontier orbitals of Li$^+$ cation and the valence band mainly comprises the frontier orbitals of O$^2-$, Cl$^-$\textsuperscript{30} in Li$^+$gl$^-$. Therefore, the heterojunction generated by the contact between S$_8^-$ and Li$^+$($\alpha_0$) is an analogy to the case of heterojunctions between metals and HfO$_2$. It is considered that the algorithm of the analysis of the Schottky barriers between metals and HfO$_2$ can also be applied to the analysis of electron levels of heterojunctions appearing in the E[(ECC)c]n mechanism.

The energy states of S$_8^-$ before/after contacting Li$^+$($\alpha_0$) of the insulator of Li$^+$gl$^-$ are examined by employing the $\varphi_{\text{GCNL}}$ in the following. In the case of S$_8^-$ Li$^+$($\alpha_0$) (ad) in steps [1] and [2], $\varphi_{\text{GCNL}}$ is expressed on the basis of the physics of metal/high-$k$ interfaces\textsuperscript{25-29} as follows:

$$\varphi_{\text{GCNL}} = E_{\text{VB}} + E_g \cdot \text{D}_{\text{UNOCC}} \cdot \text{D}_{\text{VB}} \cdot |t_{\text{S-O,Cl}}|^2 / (\text{D}_{\text{UNOCC}} \cdot \text{D}_{\text{VB}} \cdot |t_{\text{S-O,Cl}}|^2 + \text{D}_{\text{OCC}} \cdot \text{D}_{\text{CB}} \cdot |t_{\text{S-Li}^+}|^2) \quad [12]$$
where $E_{VB}$, $E_{g}$, $D_{VB}$, and $D_{CB}$ are the level of the valence-band top, the band gap, density of states of the valence bands, and density of states of the conduction bands of Li$^{+}\text{gl}$, respectively; $D_{\text{UNOCC}}$ and $D_{\text{OCC}}$ are the density of states for unoccupied and occupied molecular orbitals of S$_{8}^{-}$, respectively; $|t_{S-O,\text{Cl}}|$ is the transfer energy between unoccupied states of S$_{8}^{-}$ and occupied states of O$^{2-}$ and Cl$^{-}$ of Li$^{+}\text{gl}$; and $|t_{S-Li^{+}}|$ is the transfer energy between occupied states of S$_{8}^{-}$ and unoccupied conduction-band states of Li$^{+}\text{gl}$. S, O, and Cl in the term of the transfer energies designate S$_{8}^{-}$, O$^{2-}$, and Cl$^{-}$, respectively.

The second term of the right-hand side involves the intrinsic points to examine the electron energy level at a heterojunction. That is, in this study, in order to know the direction of a Fermi level shift of S$_{8}^{-}$ after contacting Li$^{+}(\text{sf})$ of Li$^{+}\text{gl}$, the right-hand side of the second term in Eq.[12] is examined. When the second term increases, an electron level of $\phi_{\text{GCNL}}$ goes up, demonstrating that the Fermi level of the metal side of S$_{8}^{-}$ also goes up with the contact.

The equation [12] is obtained by $\Delta \rho=0$ in Eq.[13], which was derived by applying the second-order perturbation theory of quantum mechanics. $\Delta \rho$ means transfer charges from metals to insulators and is proportional to the right hand side of the equation. At $\Delta \rho=0$ in Eq.[13], the $E_{\text{f}}$ reveals the Fermi level of S$_{8}^{-}$ after contacting Li$^{+}(\text{sf})$ of Li$^{+}\text{gl}$ and it is identical to $\phi_{\text{GCNL}}$ of Eq.[12]. The expression of $E_{\text{f}}$ in Eq.[13] corresponds to the S$_{8}^{-}$ side as a metal-like electronic structure and that of $\phi_{\text{GCNL}}$ in Eq.[12] corresponds to the insulator side.

$$\Delta \rho \propto D_{\text{OCC}}D_{\text{CB}}|t_{S-Li^{+}}|^{2}/(E_{CB}-E_{\text{f}}) \cdot D_{\text{UNOCC}}D_{VB}|t_{S-O,\text{Cl}}|^{2}/(E_{\text{f}}-E_{VB}) \quad [13]$$

where $E_{CB}$ is the conduction-band bottom of Li$^{+}\text{gl}$ in this study. When $D_{\text{UNOCC}}=D_{\text{OCC}}$ and $|t_{S-Li^{+}}|^{2}=|t_{S-O,\text{Cl}}|^{2}$ are assumed in [12], $\phi_{\text{GCNL}}$ is consistent with the conventional charge neutrality level $\phi_{\text{CNL}}$ expressed in equation [14] and this $\phi_{\text{CNL}}$ is capable of demonstrating neither the effects of the adsorption nor those of the hybridization of orbitals between S$_{8}$ and Li$^{+}(\text{sf})$.

$$\phi_{\text{CNL}}=E_{VB}+E_{g}D_{VB}/(D_{VB}+D_{CB}) \quad [14]$$
In this study, the magnitude of the second term of the right-hand sides of Eq.[12] is compared with that of Eq.[14] in order to evaluate the effects of the adsorption and the hybridization of orbitals and to know the energy levels of the adsorbent. Here, D_{UNOC} of S_8^{-} is to be equivalent to its D_{OCC}, D_{UNOC} = D_{OCC}, compared with d-orbital metals like Au of being D_{OCC} >> D_{UNOC}. Then the relationship between |t_{S-Li^{+}}| and |t_{S-O,Cl}| is of |t_{S-Li^{+}}| >> |t_{S-O,Cl}| because S_8^{-} demonstrates coulombic affinity with Li^{+}(_{sf}). By contrast, S_8^{-} demonstrates coulombic repulsion with O^{2-} and Cl^{-} of the Li^{+}gl^{-} electrolyte.

Under these conditions, from Eq.[12], the second term of the right-hand side decreases compared with that of Eq.[14], so that φ_{GCNL} and E_{f} demonstrate a decrease in the case of taking account of the effects of the adsorption and the hybridization of orbitals. A decrease in φ_{GCNL} and E_{f} means that a charge transfer from S_8^{-} occupied states to unoccupied states of Li^{+}(_{sf}) occurs within S_8^{-}Li^{+}(_{sf}) (ad) orbitals. This charge transfer generates a dipole potential at the heterojunction between S_8^{-} and Li^{+}(_{sf}). Then the potential of the electron donor side S_8^{-} increases as the positive charge side of the dipole and the negative charge of the dipole is the Li^{+}(_{sf}) side of S_8^{-} Li^{+}(_{sf}) (ad). This dipole is restricted at just the heterojunction where S_8^{-} Li^{+}(_{sf}) (ad) is formed between S_8^{-} and Li^{+}(_{sf}) and is essentially different from a dipole generated by dielectric polarization. Therefore, dipoles described by Braga et al. 1-4) are related to those induced by dielectric polarization of Li^{+}gl^{-}, which are different from the dipole explained here. In this paper, hybridization of orbitals and charge transfers between S_8^{-} and Li^{+}(_{sf}) cause the dipole generation at the heterojunction interfaces.

Figure 5 shows the schematic diagrams with regard to the hybridization of orbitals and the directions of charge transfers between S_8^{-} and Li^{+}(_{sf}) in the theory of φ_{GCNL}. Two arrows are shown in the figure and the direction of the bold one demonstrates the finding obtained by the φ_{GCNL} analysis herein. That is, the Fermi level of S_8^{-} after contacting Li^{+}(_{sf}) and the φ_{GCNL} of S_8^{-} Li^{+}(_{sf}) formed after the contact decreases, indicating that the potential of S_8^{-} Li^{+}(_{sf}) is higher than that of S_8. The relationships of S_8^{-} Li^{+}(_{sf}) > S_8 Li^{+}(_{sf}) in potential were already considered above from the viewpoint of the EE process in the E[(ECC)c]n mechanism. From the different viewpoint of φ_{GCNL} analysis of S_8^{-} Li^{+}(_{sf}), the same finding was obtained. That is, electron levels of the absorbent S_8^{-} Li^{+}(_{sf}) in steps [1] and [2] involving the intermediate radical S_8^{-} indicate higher levels than those of S_8^{-} before the formation of the absorbent S_8^{-}Li^{+}(_{sf}).
Taking all into account described above, the relationship between $S_8^- Li^{+(sf)}$ and $S_8 Li^{+(sf)}$ in potential is to be $S_8^- Li^{+(sf)} > S_8 Li^{+(sf)}$ in the $E[(ECC)\text{cn}]$ mechanism. As described, as long as the battery voltage is higher than 2.34V, this $E[(ECC)\text{cn}]$ mechanism can continue. Thus, on the basis of the analysis of $\varphi^{G\text{CNL}}$, the thermodynamics relating to the Li deposition in step [2] is also considered to be $\Delta G < -2.34$ eV at least.

The amorphous electronic structure of the Li-glass electrolyte is considered not to conflict with the findings discussed on the basis of the $E[(ECC)\text{cn}]$ mechanism. Amorphous band alignment seems to be more appropriate to the $E[(ECC)\text{cn}]$ mechanism since the surface states of $Li^{+(sf)}$, i.e., electron levels of $Li^{+(sf)}$, may demonstrate a wider range that can be ascribed to the effects of diffuse band tail states$^{33,34}$. In other words, the density of $S_8 Li^{+(sf)} (\text{ad})$ adsorbent formation may be increased since the electron levels of $Li^{+(sf)}$ of amorphous $Li^{+gl}$ are thought to be rather wider than those of an equivalent crystal structure of $Li^{+gl}$. A band model of amorphous materials consists of the mobility edge level for electrons, the mobility edge for holes, the diffuse band tail states, the mobility gap, and the gap states$^{33,34}$. The mobility gap corresponds to the energy gap between the mobility edge level of electrons and the mobility edge of holes and consists of three terms which are diffuse band tail states from mobility edges for electrons, diffuse band tail states from mobility edges for holes, and the gap states. Although more than 8eV band gap of this $Li^{+gl}$ is a typical insulator and the above band model is based on semiconductor amorphous materials, this band model is considered to be fundamentally applicable to $Li^{+gl}$.

The detailed relations of $E_1$, $E_2$ in Fig.4, the equilibrium constants of $K_1$ and $K_2$, and an overall positive electrode potential of $E^{(+)}$ will be discussed in the section on thermodynamics cycle.

**Li Deposition Cycle of the Braga-Goodenough Battery**

On the basis of this $E[(ECC)\text{cn}]$ mechanism from equations [1] to [4], when the discharge reaction initiates, at first, the one-electron reduction of $S_8$ proceeds and then the Li deposition cycle is repeated. As shown in Appendix, after the termination of this mechanism, the final product of $S_8^- Li^{+(sf)} (\text{ad})$ is reduced by further one-electron reduction to form Li$_2$S and to the final form of Li$_x$S. Thus, the Braga-Goodenough Battery consists of two kinds of discharge reactions. One is the $E[(ECC)\text{cn}]$ mechanism to form the
discharge product of \( S_8^{8-} \) (ad) and the total discharges within this mechanism corresponds to \((n+1)e\) from Eq.[5]. The other discharge reaction is to form the discharge product of \( Li_2S \) by the one-electron reduction of \( S_8^{8-} \) (ad). In other words, the total amount of discharge can be expressed in terms of the number of electrons, as \((n+2)e\) for this Li-S type battery where \( n \) corresponds to \( nF \) discharge per \( nLi \) deposition in terms of the cycle number \( n \) in the \( E[(ECC)c]n \) mechanism and \( 2e \) corresponds to \( 2F \) discharge per \( S_8 \). \( F \) is the Faraday constant. Therefore, the ratio of the total amount of discharge to the theoretical amount of capacity of \( S_8 \) in the positive active mass can be expressed in percentage as follows:

\[
100\frac{(n+2)}{2} \quad \text{%} \quad [15]
\]

Figure 6 shows the relationship between total battery discharge capacity/\( S_8 \) capacity versus the cycle number \( n \) by Eq.[15]. As shown in Fig.6, as long as the battery reaction obeys this \( E[(ECC)c]n \) mechanism, tenfold capacity against the theoretical capacity of \( S_8 \) can be observed at cycle 18.

**Thermodynamics Cycle**

In general, on the basis of the energy cycle, the Gibbs free energy \( \Delta G \) of the overall reaction [5] is consistent with each step \( \Delta G \) summation in the \( E[(ECC)c]n \) mechanism. That is, \( \Delta G = \sum \Delta G_i \) (i=1-4) where \( \Delta G_i \) corresponds to each step [i] from the step [1] to [4]. Here, from the steps from [1] to [5], \( \Delta G_1 = -FE_1, \Delta G_2 = -nFE_2, \Delta G_3 = -RT\ln(K_1)^n, \Delta G_4 = -RT\ln(K_2)^n \), and \( \Delta G = -(n+1)FE^{(+)} \) can be expressed, where \( E^{(+)} \) corresponds to the positive electrode potential in the overall reaction step [5]. That is, Eq.[16] is obtained as follows:

\[
E^{(+)} = E_1/(1+n) + E_2/(1+(1/n)) + (RT/(n+1)F)\ln(K_1K_2)^n \quad [16]
\]

where \( n \) is the cycle number of the \( E[(ECC)c]n \) mechanism; \( R, T, \) and \( F \) are their usual significance. At 25 \(^\circ\)C, Eq.[14] is rewritten in the form in Eq.[17] as follows:

\[
E^{(+)} = E_1/(1+n) + E_2/(1+(1/n)) + 0.059/(1+(1/n)) \log(K_1K_2) \quad [17]
\]

where \( E^{(+)}, E_1, \) and \( E_2 \) are all corresponding to equilibrium potentials not
including kinetics information, i.e., overpotential. Here, \( K_1 K_2 \) is the product of \( K_1 \) and \( K_2 \) and is corresponding to the equilibrium constant of the following reaction [18] on the basis of the steps [3] and [4] as follows:

\[
S_8^{2-} \text{Li}^+ + \text{Li}^+ \leftrightarrow S_8^{2-} \text{Li}^+ + \text{Li} \tag{18}
\]

Thus, \( K_1 K_2 \) with non-dimension corresponds to [19].

\[
K_1 K_2 = \frac{[S_8^{2-} \text{Li}^+][\text{Li}]}{[[S_8^{2-} \text{Li}][\text{Li}^+]]} \tag{19}
\]

where \([K_1]\) and \([K_2]\) are in mol/cm\(^2\) and (mol/cm\(^2\))\(^{-1}\), respectively. Here, Eq.[20] is derived from Eq.[16] at \( n \to \infty \).

\[
E^{(+)} = E_2 + \frac{RT}{F} \ln(K_1 K_2) \tag{20}
\]

According to the E[EC]c mechanism, cycle number \( n \) corresponds to \( n \) number of Li deposition. Then the deposited Li is all transported from the negative electrode of the battery. In Eq.[20], \( E_1 \) and \( n \) are eliminated from the derived general form of \( E^{(+)} \) in Eq.[16]. Thus, in order to obtain the practical relationship between the cycle number \( n \) and \( K_1 K_2 \), the rest of the parameters of \( E^{(+)} \), \( E_1 \), and \( E_2 \) must be fixed. In order to examine the cycle number \( n \) versus \( K_1 K_2 \), \( E^{(+)} \), \( E_1 \), and \( E_2 \) have to be estimated by taking account of the battery practical data\(^1\).

The positive and negative electrode potentials are \(-0.40 \text{ V}_{\text{SHE}}\)\(^1\) and \(-3.05 \text{ V}_{\text{SHE}}\)\(^1\), respectively. Incidentally, the Fermi level of SHE corresponds to \(-4.44\text{eV} \) versus the absolute potential. On the basis of these data, \( E_1 \) is considered to correspond to \(-0.40 \text{ V}_{\text{SHE}} \) because no \( S_8^{2-} \text{Li}^+ \text{(ad)} \) is formed before the battery discharge. Before the formation of \( S_8^{2-} \text{Li}^+ \text{(ad)} \), the potential of the positive electrode is thought to be established by \( S_8 \) alone. After discharge, the maximum voltage of the Braga-Goodenough battery was \(2.68 \text{ V}\)\(^1\). If this value did not involve overpotential components, the positive electrode potential after discharge would be \((-3.05 \text{ V}_{\text{SHE}} + 2.68 \text{ V}) = -0.37 \text{ V}_{\text{SHE}}\). In practice, the value of \(2.68 \text{ V} \) explicitly includes overpotential components during discharge. On the basis of the discharge performance data\(^1\), the negative electrode dominates the overall overpotential components of this battery discharge behavior. That is, the estimated positive electrode potential
of -0.37 V is to be considered to be the minimum of possible potential of the positive electrode under the 2.68 V cell voltage conditions. When \( S_8 \text{Li}^{+\text{ad}} \) is formed by the discharge reaction, \( E_2 \) can be defined as shown in Fig. 4. Then, \( \alpha \) of Eq.[21] is introduced here on account of the relationship \( E_2 > E_1 \).

\[
\alpha = E_2 - E_1 \tag{21}
\]

Here, by employing the above estimated \( E_1 \) of -0.40 V SHE and \( E^{(+)} \) of -0.37 V SHE, the relationship between the cycle number \( n \) and \( K_1K_2 \) can be examined by employing Eq.[17]. By introducing the above values and \( \alpha \) at 25 °C, Eq.[17] is to be rewritten as Eq.[22] as follows:

\[
-0.37 = -0.40/(n+1) + (-0.40+\alpha)/(1+1/n) + 0.059/(1+1/n) \log(K_1K_2) \tag{22}
\]

Figure 7 shows the relationship between the cycle number \( n \) and \( K_1K_2 \) when \( \alpha = 0.06 \) V corresponding to twice \( (E^{(+)} - E_1) \). In accordance with the increase in the cycle number, \( K_1K_2 \) decreases, and after around cycle 10 the trend of \( K_1K_2 \) decrease is almost saturated. In the E[(ECC)c]n mechanism, the cycle number 18 corresponding to the observed capacity of ten with respect to \( S_8 \) was determined as described. At this cycle 18, \( K_1K_2 \) is the almost saturated value of 0.33 as shown in Fig. 7.

Table I shows the relationship between \( \alpha \) and \( K_1K_2 \). As shown in this table, \( K_1K_2 \) values at cycle 20 and 30 already reach to 95% and 97% of those of cycle 100, respectively. When the cycle number is fixed, \( K_1K_2 \) decreases in accordance with the increase in \( \alpha \). Thus, the equilibrium of the reaction [18] is to move to the left of the reaction when \( \alpha \) increases.

Table II shows the relationship between \( \alpha \) and the logarithm of \( K_1K_2 \) under \( E^{(+)} = -0.37 \) V SHE and \( E_1 = -0.4 \) V SHE conditions as shown in Eq.[22]. That is, it is demonstrated that the summation of \( E_2 \) at each \( \alpha \) and 0.059 Log \( (K_1K_2) \) at cycle 100 of corresponding \( \alpha \) asymptotically approaches to the potential of \( E^{(+)} = -0.37 \) V SHE as expected by Eq.[20] at 25 °C.

**A Limit of the Li Deposition Cycle**

In the E[(ECC)c]n mechanism, a limit of cycle number \( n \) of the Li deposition is determined in terms of the number of contacts of \( \text{Li}^{+\text{ad}} \) with
Li⁺/gl⁻ per S₈⁻. In order to estimate a cycle limit, geometrical contact numbers between the two are to be examined by assuming spheres for S₈⁻ and Li⁺ (gl⁻).

Here, when Li⁺ cations are arranged on the sphere surface of S₈⁻, the maximum number of Li⁺ per S₈⁻, (Li⁺/S₈⁻)_{max}, under closest packing conditions is to be approximated by Eq.[23].

\[
(Li^+/S_8^-)_{max} = \pi (r_1/r_2)^2 + 2\pi (r_1/r_2) + 4\pi/3 \tag{23}
\]

where \(r_1\) and \(r_2\) are the S₈⁻ and Li⁺ ion radius, respectively. Eq.[23] is based on the calculation of \([4\pi(r_1+2r_2)^3/3 - 4\pi r_1^3/3]/(2r_2)^3\). On the basis of the SOMO calculations, the critical ion radius of S₈⁻ was 483pm which was slightly larger than that of 474pm of S₈. The radius of Li⁺ is 59pm. Therefore, (Li⁺/S₈⁻)_{max} =266 is obtained from Eq.[23].

As shown in Fig.1, the positive active mass consists of mainly three kinds of components involving 47 S₈⁻, 43 Li⁺/gl⁻, and 10 carbon black in weight % \(^1\). Thus, the ratio of S₈⁻ volume to the total volume and the porosity of these materials are thought to be the practical factors to affect (Li⁺/S₈⁻)_{max}. When the volume and the porosity factor are designated by \(f_v\) and \(f_p\), respectively, \(n_{lim}\), the limit of Li deposition cycle number is obtained by Eq.[24] as follows:

\[
n_{lim} = f_v f_p (Li^+/S_8^-)_{max} \tag{24}
\]

Eq.[24] shows \(n_{lim} = 44\), provided that \(f_v=1/3\), \(f_p=0.5\), and (Li⁺/S₈⁻)_{max} =266. These numbers correspond to the probability of 1/3 and the porosity of 50%, respectively, which are considered to be reasonable values. Since the cycle number corresponding to the battery capacity of ten with respect to S₈ was 18, the \(n_{lim} = 44\) value is more than twice this cycle number.

According to Braga et al., this battery was not optimized \(^1\), and the rate determining electrode of the battery discharge was apparently its negative electrode \(^1\). On optimizing the design of this battery in accordance with the capacity determining factor of \(n_{lim}\) and \(n_{lim} = 44\), a capacity could be 23 times S₈ by Eq. [15].

In this mechanism, the morphology of the deposited Li is thought to be a dispersion of deposited Li nuclei unless explicit susceptibility to coalescence of deposited Li nuclei occurs. It is thought that this is consistent with
Conclusions

An E[(ECC)c]n mechanism was proposed in order to clarify the Braga-Goodenough battery reactions. This mechanism consists of two consecutive one-electron EE processes, equilibrium CC steps, and these combined in a catalytic cycle that can be repeated. The Li deposition step corresponds to the second E of the EE process. The (ECC)c part is a catalytic reaction and this part cycles the deposition of Li. The n in E[(ECC)c]n means the number of cycles of the (ECC)c part, corresponding to n times deposition of Li. An intermediate radical S₈⁻ formed at the first E step of the mechanism by a one-electron reduction of S₈ plays an essential role in the (ECC)c part as a mediator of a catalyst. S₈ adsorbs surface states Li⁺(sf) of the Li-glass solid electrolyte, and the Li⁺(sf) side of S₈Li⁺(sf) takes a one-electron reduction to deposit Li. This catalytic function of S₈⁻ was ascribed to the affinity between S₈⁻ and the Li⁺ surface states of Li⁺gl⁻, which resulted in hybridization of orbitals with a shallow MIGS due to both S₈⁻ metal like band structures and the ionic bond structures of Li⁺gl⁻. Another significant factor of the S₈⁻ role as a catalyst was its characteristic as a good conductor. The number of Li deposition cycles corresponding to the Braga-Goodenough battery capacity of ten with respect to S₈ was determined to be 18 by means of this mechanism.

The thermodynamics of Li deposition at the second E step was examined by taking account of electrochemistry with respect to two consecutive one-electron steps and of the theory of generalized charge neutrality levels in respect of Schottky barriers. Consequently, the thermodynamics relating to the Li deposition in the second E step was considered to bring forth at least ΔG< -2.34eV.

The thermodynamics cycle of the overall mechanism was also examined. Overall equilibrium potentials of the positive electrode were expressed by a function of Li deposition cycles, two equilibrium potentials relating to the EE steps, and two equilibrium constants. In accordance with the progress of Li deposition cycles, it was found that the overall positive electrode potentials converged to [E₂+(RT/F) Ln(K₁K₂)] where E₂ and K₁K₂ corresponded to the E of the 2nd E step corresponding to Li deposition and the product of each equilibrium constant, respectively. Then K₁K₂ depended on the values of n and (E₂-E₁) where E₁ corresponded to the 1st E step of S₈ reduction to form S₈⁻.
A limit of the number of reaction cycles equivalent to the limit of the amount of Li deposition was investigated by means of the $\text{E}[(\text{ECC})\text{c}]n$ mechanism. According to this mechanism, a limit of cycle number $n$ is determined in terms of the number of contacts of $\text{Li}^{+\text{(sf)}}$ per $\text{S}_8^-$. This limit of the cycle number was discussed with ion radii of the intermediate $\text{S}_8^-$ and $\text{Li}^{+\text{(sf)}}$ by taking account of the compositions of the materials of the positive active mass and their porosity.

**Acknowledgements**

The author thanks Mr. Takahiro Hidaka for the calculation and discussions on the quantum chemistry and Dr. Ueda Suguru for discussions on the quantum chemistry and the generalized charge neutrality level.

**List of Symbols**

- Li$^{+\text{gl-}}$: Li-glass solid electrolyte of $\text{Li}_{2.99}\text{Ba}_{0.005}\text{O}_{1+x}\text{Cl}_{1-2x}$
- EE: electrochemical-electrochemical
- CC: chemical-chemical
- $c$ in $\text{E}[(\text{ECC})\text{c}]n$: $(\text{ECC})\text{c}$ denoting catalytic reaction steps
- $n$ in $\text{E}[(\text{ECC})\text{c}]n$: cycle number $n$ of $(\text{ECC})\text{c}$ corresponding to $n$ Li deposition
- SHE: standard hydrogen electrode
- $V_{\text{SHE}}$: electrode potential versus SHE
- $\text{Li}^{+\text{(sf)}}$: surface states of $\text{Li}^+\text{ of }\text{Li}_{2.99}\text{Ba}_{0.005}\text{O}_{1+x}\text{Cl}_{1-2x}$
- $\text{S}_8^-\text{ Li}^{+\text{(sf)}}$: adsorbent between $\text{S}_8^-$ and $\text{Li}^{+\text{(sf)}}$
- $\text{S}_8^-\text{ Li}$: initially deposited Li form by one-electron reduction of $\text{S}_8^-\text{ Li}^{+\text{(sf)}}$
- high-$k$: high relative permittivity
- $\varphi_{\text{CNL}}$: charge neutrality level
- $\varphi_{\text{GCNL}}$: generalized charge neutrality level
- $|t_{\text{S\-Li+}}|$: transfer energy between occupied $\text{S}_8^-$ states and conduction-band states of $\text{Li}^+$
- $|t_{\text{S\-O\-Cl}}|$: transfer energy between unoccupied $\text{S}_8^-$ states and valence-band states of $\text{Li}^{+\text{gl-}}$
- $E_F$: Fermi level
- $E_{\text{CV}}$: energy level of conduction band bottom
- $E_{\text{VB}}$: energy level of valence band top
Appendix

Discharge reaction of the positive electrode after the termination of $E[(ECC)_c]n$

The rate determining electrode of this battery discharge is apparently the negative electrode$^1)$. On the basis of the reaction steps [7] and [8] of the negative electrode, if the provision of $(n+1)Li^+$ is not sufficient to sustain the reaction [5], the overpotential of the negative electrode increases and the battery voltage is to reach the threshold of 2.34V. The part of $(ECC)c$ of $E[(ECC)_c]n$ is incapable of cycling under the voltage of less than 2.34V. That is, the $E[(ECC)_c]n$ mechanism terminates under these conditions. After the termination of the $E[(ECC)_c]n$ mechanism, instead of $Li^+_{(ad)}$ reduction to $Li$, $S_8$ in the product $S_8 \cdot Li^+_{(ad)} (ad)$ of the overall reaction [10] should take further one-electron reduction to form $Li_2S_x$ as follows:

$$S_8 \cdot Li^+_{(ad)} (ad) + Li^+_{(ad)} + e \rightarrow Li_2S_x + S_{8-x} \quad [A-1]$$

where $x$ is $1 \leq x \leq 8$. By the summation of [10] and [A-1], [A-2] can be obtained.

$$S_8 + Li + Li^+_{(ad)} + e \rightarrow Li_2S_x + S_{8-x} \quad [A-2]$$

The negative electrode reaction in respect to this [A-2] of the positive electrode reaction is the following [A-3] by taking account $n=0$ in [8].
Li → Li⁺_{(s0)} + e  \text{[A-3]}

That is, after \(E[(ECC)cn]\) mechanism, the overall reaction of the battery is to be expressed by [A-4] with the summation of [A-2] and [A-3], demonstrating the ordinary Li-S type battery overall reaction of \(S_8 + 2Li → Li_2S_8\) with \(x=8\) in [A-4].

\[
S_8 + 2Li → Li_2S_x + S_{8-x} \text{[A-4]}
\]

In general, transient states of the oxidation of \(S_8\) in the positive active mass of conventional Li-S type battery are expressed in a series of chemical forms of e.g., \(S_8 → Li_2S_8 → Li_2S_6 → Li_2S_4 → Li_2S_3 → Li_2S\).

References
1. M. H. Braga, N. S. Grundish, A. J. Murchison, and J. B. Goodenough, \textit{Energy Environ. Sci.}, \textbf{10}, 331 (2017)
2. M. H. Braga, A. J. Murchison, J. A. Ferreira, P. Singh, and J. B. Goodenough, \textit{ibid.}, \textbf{9}, 948 (2016)
3. M. H. Braga, C. M. Subramaniyam, A. J. Murchison, and J. B. Goodenough, \textit{J. Am. Chem. Soc.}, \textbf{140}, 6343 (2018)
4. M. H. Braga, J. E. Oliveira, A. J. Murchison, and J. B. Goodenough, \textit{Appl. Phys. Rev.} \textbf{7}, 011406 (2020)
5. Y. Seino, K. Takada, B.-C. Kim, L. Zhang, N. Ohta, H. Wada, M. Osada, and T. Sasaki, \textit{Solid State Ionics}, \textbf{176}, 2389 (2005)
6. Y. Seino, K. Takada, B.-C. Kim, L. Zhang, N. Ohta, H. Wada, M. Osada, and T. Sasaki, \textit{ibid.}, \textbf{177}, 2601 (2006)
7. Y. Seino, T. Ota, and K. Takada, \textit{J. Power Sources}, \textbf{196}, 6488 (2011)
8. Y. Seino, T. Ota, K. Takada, A. Hayashi, and M. Tatsumisago, \textit{Energy Environ. Sci.}, \textbf{7}, 627 (2014)
9. Y. Seino, M. Nakagawa, M. Senga, H. Higuchi, K. Takada, and T. Sasaki, \textit{J. Mater. Chem. A}, \textbf{3}, 2756 (2015)
10. H. Zhao, N. Deng, J. Yan, W. Kang, J. Ju, Y. Ruan, X. Wang, X. Zhuang, Q. Li, and B. Cheng, \textit{Chem. Eng. J.}, \textbf{347}, 343 (2018)
11. X. Fan, W. Sun, F. Meng, A. Xing, and J. Liu, \textit{Green Energy & Environ.}, \textbf{3}, 2 (2018)
12. W. Ren, W. Ma, S. Zhang, and B. Tang, \textit{Energy Stor. Mater.}, \textbf{23}, 707
13. F. Lanlan, D. Nanping, Y. Jing, L. Zhenhuan, K. Weimin, and C. Bowen, *Chem. Eng. J.*, **369**, 874 (2019)
14. S. Choudhury, *Curr. Opin. Electrochem.*, **21**, 303 (2020)
15. S. R. Morrison, *Surf. Sci.*, **10**, 459 (1968)
16. T. Berzins and P. Delahay, *J. Am. Chem. Soc.*, **75**, 5716 (1953)
17. H. L. Hung and D. E. Smith, *J.Electroanal.Chem.*, **11**, 425 (1966)
18. A. Damjanovic, M. A. Genshaw, and J. O’M. Bockris, *J. Chem. Phys.*, **45**, 4057 (1966)
19. K. J. Vetter, “Electrochemical Kinetics” pp.149-154, Academic Press, New York (1967)
20. J. Jacq, B. Cavalier, and O. Bloch, *Electrochim. Acta*, **13**, 1119 (1968)
21. F. Mizutani, N. Sato, and T. Sekine, *Denki Kagaku*, **5**, 247 (1978)
22. I. Ruzic, *J. Electroanal. Chem.*, **52**, 331 (1974)
23. J. Galvez, M. L. Alcaraz, and S.M.Park, *ibid.*, **247**, 119 (1988)
24. M. Sakai and N. Ohnaka, *This Journal*, **137**, 576 (1990)
25. T. Nakayama, K. Shiraishi, S. Miyazaki, Y.Akasaka, T. Nakaoka, K. Torii, A. Ohta, P. Ahmet, K. Ohmori, N. Umezawa, H. Watanabe, T. Chikyow, Y. Nara, H. Iwai, and K. Yamada, *ECS Transactions*, **3**, Issue 3, 129 (2006)
26. K.Shiraishi, Y. Akasaka, S. Miyazaki, T. Nakayama, T. Nakaoka, G. Nakamura, K. Torii, H. Furutou, A.Ohta, P. Ahmet, K. Ohmori, H.Watanabe, T. Chikyow, M. L. Green, Y. Nara, and K. Yamada, Technical Digest of IEEE International Electron Devices Meeting, p.43, Washington D.C., USA (2005)
27. T. Nakayama and K. Shiraishi, *J. Surf. Sci. Soc. Jpn.*, **28**, 1, 28 (2007)
28. K. Shiraishi and T. Nakayama, *ibid.*, **29**, 2, 92 (2008)
29. T. Nakayama, Y. Kangawa, and K. Shiraishi, “Atomic Structures and Electronic Properties of Semiconductor Interfaces” in “Comprehensive Semiconductor Science and Technology”, Eds. P. Bhattacharya, R. Fornari, and H. Kamimura, Vol.1, pp.157-161, Elsevier Sci. B.V., Amsterdam (2011)
30. N. Sato, “Electrochemistry at Metal and Semiconductor Electrodes” pp.35-37, Elsevier Sci. B.V., Amsterdam (2003)
31. T. Nakayama, *Physica B*, **191**, 16 (1993)
32. M. Cardona and N. E. Christensen, *Phys. Rev., B*, **35**, 6182(1987)
33. N. Sato, “Electrochemistry at Metal and Semiconductor Electrodes” pp.44-45, Elsevier Sci. B.V., Amsterdam (2003)

34. N. F. Mott and E. A. Davis, “Electronic Processes in Non-Crystalline Materials, 2Ed.”, Clarendon Press, Oxford (1979)

35. J. B. Goodenough interview by J. Schroeder, “University of Texas Researchers Develop More Powerful and Long-lasting Battery”, https://www.tun.com/blog/university-of-texas-powerful-and-longlasting-battery/, The University Network Copyright © 2019
Table I. \(K_1K_2\) vs. \(\alpha\) and cycle number \(n\)

| \(\alpha\) \((E_2-E_1)\) | \(K_1K_2\) | \(n1\) | \(n10\) | \(n20\) | \(n30\) | \(n40\) | \(n100\) |
|------------------|----------|-------|-------|-------|-------|-------|-------|
| 0.040            |          |       |       |       |       |       |       |
|                  | 2.183    | 0.761 | 0.718 | 0.704 | 0.697 | 0.685 |
| 0.060            |          |       |       |       |       |       |       |
|                  | 1.000    | 0.349 | 0.329 | 0.322 | 0.319 | 0.314 |
| 0.080            | 0.458    | 0.160 | 0.151 | 0.148 | 0.146 | 0.144 |

Table II. \(0.059 \log(K_1K_2)\) vs. \(\alpha\) and cycle number \(n\)

| \(\alpha\) \((E_2-E_1)\) | \(0.059 \log(K_1K_2)/V\) | \(n1\) | \(n10\) | \(n20\) | \(n30\) | \(n40\) | \(n100\) |
|------------------|-----------------|-------|-------|-------|-------|-------|-------|
| 0.040            | -0.0200         | -0.0070 | -0.0085 | -0.0090 | -0.0092 | -0.0097 |
| 0.060            | 0.0000          | -0.0270 | -0.0285 | -0.0290 | -0.0293 | -0.0297 |
| 0.080            | -0.0200         | -0.0470 | -0.0484 | -0.0490 | -0.0493 | -0.0497 |
Figure 1. Diagrams of positive electrode active mass of the Braga-Goodenough battery under open circuit and discharge conditions reflecting the E[(ECC)c]n mechanism.

Glass electrolyte powder, Carbon black, S₈ before discharge, S₈ covered with Li during discharge.
Figure 2. Two-dimensional schematic representation of S₈ contacting both Li⁺ and deposited Li. Circle radii reflect those of 483 S₈, 59 Li⁺, and 152 Li in pm. Five of ten of Li⁺ contacting S₈ are already reduced to Li, i.e., five cycles of Li deposition were over. In this case, the rest of Li deposition cycles is to be five.

Figure 3. Schematic representation of the step [2] for Li deposition cycle in E[(ECC)ₙ]. The ECC part in the mechanism is a catalytic cycle reaction in which S₈ plays an essential role of a catalyst with an electron conductor.
Figure 4. Images of electron energy level vs. density of states for each equilibrium electrode potential of the EE process in the E([ECO]c)n mechanism. $\varepsilon_1$ and $\varepsilon_2$ of each Fermi level correspond to $E_1$ and $E_2$, respectively.
Figure 5. Two possibilities of hybridization of orbitals in the theory of $\phi^G_{\text{CNL}}$ between $S_8^-$ and $\text{Li}^+\text{gl}^-$. Inset arrows show the direction of possible electron transfers at their interfaces.

Figure 6. Battery capacity / $S_8$ capacity vs. cycle number $n$ of Li deposition in the $[\text{E}[(\text{ECC})c]n$ mechanism.
Figure 7. Equilibrium constant $K_1K_2$ vs. cycle number $n$ by Eq.[20] for $\alpha=0.06\text{V}$.