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SPECIAL TOPIC — Advanced calculation & characterization of energy storage materials & devices at multiple scale

Understanding the Li diffusion mechanism and positive effect of current collector volume expansion in anode free batteries*

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In anode free batteries (AFBs), the current collector acts as anode simultaneously and has large volume expansion which is generally considered as a negative effect decreasing the structural stability of a battery. Moreover, despite many studies on the fast lithium diffusion in the current collector materials of AFB such as copper and aluminum, the involved Li diffusion mechanism in these materials remains poorly understood. Through first-principles calculation and stress-assisted diffusion equations, here we study the Li diffusion mechanism in several current collectors and related alloys and clarify the effect of volume expansion on Li diffusion respectively. It is suggested that due to the lower Li migration barriers in aluminum and tin, they should be more suitable to be used as AFB anodes, compared to copper, silver, and lead. The Li diffusion facilitation in copper with a certain number of vacancies is proposed to explain why the use of copper with a thickness $\leqslant$ 100 nm as the protective coating on the anode improves the lifetime of the batteries. We show that the volume expansion has a positive effect on Li diffusion via mechanical–electrochemical coupling. Namely, the volume expansion caused by Li diffusion will further induce stress which in turn affects the diffusion. These findings not only provide in-depth insight into the operating principle of AFBs, but also open a new route toward design of improved anode through utilizing the positive effect of mechanical–electrochemical coupling.

Keywords: anode free battery, current collector, Li diffusion mechanism, mechanical–electrochemical coupling, stress-assisted diffusion

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1. Introduction

Due to energy shortage and environmental pollution, the environmentally friendly secondary batteries have attracted considerable attention in recent years with the focus on high energy density, long cycle life, and safety performance of battery materials.[1,2] The current collectors are also an area where improvements are sought,[3–5] including alleviating volume expansion and increasing the contact area with the electrode materials.[6,7]

Recently, Qian *et al.*[9] proposed the concept of the anode free battery (AFB), which is thinner and has the higher capacity than the traditional battery. As shown in Fig. 1, the ideal AFB abandons a Li host anode material but directly uses an ultra-thin metal as both anode and current collector to assemble a rechargeable battery, in which the Li can insert into or extract from the anode current collector to form a Li*M* alloy or intermetallic compound. Notably, the energy density of AFB will therefore be significantly higher than that of the traditional battery, and the absence of a Li host anode material reduces the battery weight and required space for anode. For example, Table 1 lists six AFB systems with the higher energy density, in which three metals (Al,[8,10,11] Cu,[9,12] Sn[13]) rather than Li act as both the anode and current collector in combination with various traditional cathode materials, including $LiCoO_2$, $LiFePO_4$, $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$, and $LiNi_{0.85}Co_{0.10}Al_{0.05}O_2$. These in-principle experiments demonstrate that the current collector participating in the alloying reaction is beneficial to the improvement of the cycle performance of the AFB compared with the lithium directly deposited on the surface. The current collectors used for AFB require high electrical conductivity and long cycle life when forming Li*M* alloys. An

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involuntary concern is whether some high conductivity materials, such as Ag, Pb, and Zn that can form Li*M* alloys, can also be used as the current collectors for AFBs. However, the volume expansion of the anode remains a problem. In this study, the Li diffusion mechanism and positive effect of current collector volume expansion in AFBs will be investigated by multi-scale computation methods.[14–16] In order to facilitate the discussion of electrochemical–mechanical coupling, Li diffusion refers specifically to Li migration, excluding the formation of carriers.

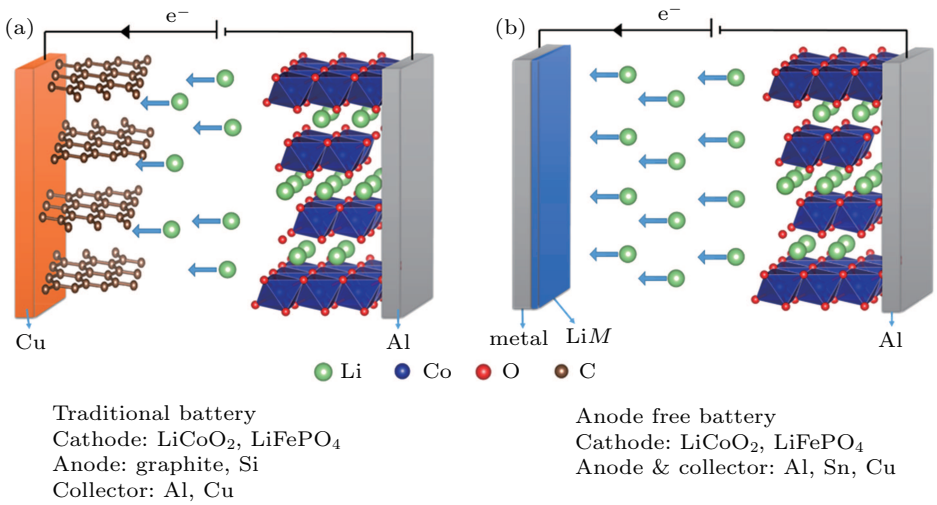


Fig. 1. Schematic illustration of the charging process of (a) traditional lithium ion battery using graphite anode and $LiCoO_2$ cathode material, and (b) anode free battery using metal *M* (*M* = Al, Cu, Sn, etc.) as current collector in combination with $LiCoO_2$ cathode material.[8]

Table 1. Literature data on the cathode and anode current collector materials tested in anode free batteries and corresponding electrochemical performance.

Anode current collector	Cathode	Measured capacity/(mA·h/g)	Cycle number	Ref.
Al	$LiCoO_2$, $LiFePO_4$, $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$	92–160	200	[8,10,11]
Cu	$LiFePO_4$, $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$	150	100	[9,12]
Sn	$LiNi_{0.85}Co_{0.10}Al_{0.05}O_2$	66–71	300	[13]

In general, the current collectors are not considered as lithium storage materials because of the difficulty of lithiation-delithiation. Nevertheless, based on the first-principles calculation, the lithium migration barriers in several current collectors and their alloys have been reported, for example, 0.67 eV for Cu[17] and 0.11 eV for LiAl.[18] The time-of-flight secondary-ion mass spectrometry (TOF-SIMS) technology has proven that lithium can indeed diffuse in Cu.[19] These results indicate that Li can insert into the Al and Cu current collectors successfully. Therefore, it is interesting to further systematically study the feasibility of Li insertion into metal current collectors and understand the underlying mass transfer processes. Furthermore, in order to have a more comprehensive understanding of the Li diffusion mechanism beyond the atomic scale, we study the effect of volume expansion on Li diffusion via stress-assisted diffusion equations from the perspective of mechanical–electrochemical coupling. The relevant theoretical background was laid out in 1961 by Prussin who developed the theory of the diffusion-induced stress (DIS) and the corresponding formulas.[20] Based on the von Mises' theory of plasticity, Bower found the DIS was an important driving force for Li diffusion in lithium-ion batteries.[21] When lithium inserts into or extracts from the active materials, the electrochemical reaction causes stress, and the DIS further assists the Li diffusion. The process that the stress and diffusion are strongly associated with each other is called mechanical–electrochemical coupling.

In the previous studies, the coupling effect on a layered electrode,[22–24] nanowire electrode,[25] and buckling electrode[26] has been discussed. Song *et al.* summarized the factors that affected the coupling for the common active materials, and studied the concentration changes caused by DIS in various electrodes.[27] By accounting for the large strains and effects of pressure gradients on diffusion, Ryu *et al.* modeled DIS in Si nanowires and demonstrated the coupling effect between stress and Li diffusion.[28] These studies on the coupling effect are mainly based on the traditional battery materials and can be described in terms of the coupling parameter β, elastic modulus, dimensions, and other factors of electrode materials.[23,29] Alternatively, far less is known about the effect of volume expansion on Li diffusion in AFB. In this paper, by using first-principles calculation and solving the coupling equations, insights into the coupling effect in AFBs will be provided, and the positive effect of large volume expansion on the stress-assisted diffusion will be discussed. Especially, during the Li diffusion in AFB current collectors, the theoretical

volume expansion rate is up to 142%–268%, which in turn assists Li diffusion significantly but is neglected in the previous AFB studies.

2. Computational details

2.1. First-principles calculation of lithium diffusion in anode free batteries

2.1.1. Structural model

To investigate the insertion mechanisms and diffusion behavior of Li in the metals (Al, Cu, Ag, Pb, etc.) and the corresponding alloys LiM (M = Al, Cu, Ag, Pb, etc.), we build the supercells with appropriate size which depends on the conventional unit cell of these metals and the alloys, i.e., $2\times2\times2$ supercell for Al, Cu, Ag, Pb, etc., and $2\times2\times2$ supercell for LiM. The studied current collector materials are listed in Table 2. All the initial crystal structures are obtained from the Materials Project (MP) database.[30] In this work, we only consider the vacancy diffusion because previous studies suggested that vacancy diffusion is the most common mechanism in metals and alloys.[18,31,32] For the pure metal M systems, one of the metal atoms is replaced by one Li atom and then another metal atom, adjacent to the Li atom, is removed for Li diffusion. For the alloy LiM systems, only one Li atom is removed to create a vacancy required for Li diffusion.

2.1.2. Computational methods

All first-principles calculations are performed with the Vienna *ab initio* simulation package (VASP)[33] with the projector augmented wave (PAW) method.[34] The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA)[35] is adopted for the exchange–correlation functional. The valence electron configurations for the elemental constitutions are as follows: Ag, $3d^{10}5s^1$; Al, $3s^23p^1$; Cu, $3d^{10}4s^1$; Li, $2s^1$; Pb, $6s^26p^2$; Sn, $5s^25p^2$; Zn, $3d^{10}4s^2$. The k-point grid is selected depending on the supercell size, e.g., $2\times1\times2$ for Zn and LiAl, $2\times2\times1$ for Ag and LiAg, $2\times2\times2$ for Al, Cu, Pb, LiSn, and LiZn, $2\times2\times3$ for Sn, $3\times2\times2$ for LiCu, and $3\times3\times2$ for LiPb. The cutoff energy for the plane-wave basis $E_{\rm cut}$ is set to 320 eV. The total energy is converged to within 1×10^{-5} eV/atom[36] and the force on each atom is converged to within 0.01 eV/Å.[37] The relaxation of the cell volume and atom positions has been carried out for every composition. The data of volume expansion rate is obtained by structure relaxation. The minimum energy paths (MEPs) of Li diffusion are obtained by means of the CI-NEB method[38] using three images and two endpoint structures and the threshold for the total force is set to 0.01 eV/Å.

2.2. Mechanical–electrochemical coupling equations

The mechanical–electrochemical coupling process begins with an electrochemical reaction, when Li inserts into (or extracts from) an active material replaced by the current collector in AFB.[20] Figure 2 schematically illustrates the case of a plate electrode model. When Li inserts into active material A, a new component $\mathrm{Li}_x A_y$ is produced as follows:

$$x\mathrm{Li}+yA=\mathrm{Li}_xA_y, \tag{1}$$

where x and y represent the amounts of lithium and active material, respectively. Following Fick's law,[22] the diffusion equation of Li in the electrochemical process is written as follows:

$$\frac{\partial c}{\partial t}+\nabla\cdot J=0, \tag{2}$$

where c is the molar concentration of Li and J is the Li flux in the active material.

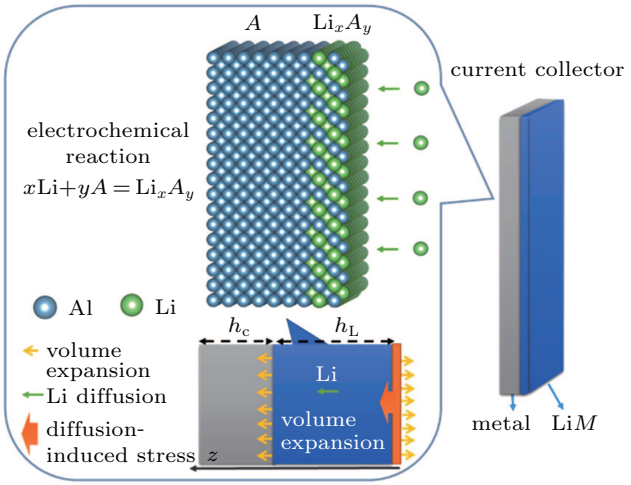


Fig. 2. Schematic diagram of diffusion-induced stress generation in a plate current collector.

The flux is a key physical quantity for the Li diffusion behavior,[39] and its relationship with the electrochemical potential μ is given by

$$J=-Mc\cdot\nabla\mu, \tag{3}$$

where M is the mobility of the mobile moiety in the solute limit. During a stress-assisted diffusion process, the electrochemical potential in the ideal solute can be described as

$$\mu=\mu_0+RT\ln c-\Omega\sigma_{\rm h}, \tag{4}$$

where μ_0 is an invariant reference potential, $R=8.314472\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ is the universal gas constant, T is the temperature, and Ω is the partial molar volume of the solution, and $\sigma_{\rm h}$ is the hydrostatic stress. The third term is responsible for the elastic energy induced by Li insertion. Equations (3) and (4) indicate that $\sigma_{\rm h}$ is an important parameter for Li diffusion. The $D=M\cdot RT$ relation is introduced in Eq. (3). According to Eqs. (2)–(4), the governing equation of diffusion takes the following form:

$$\frac{\partial c}{\partial t}-D\frac{\partial^2 c}{\partial z^2}+\frac{D\Omega}{RT}\frac{\partial c}{\partial z}\frac{\partial\sigma_{\rm h}}{\partial z}+\frac{D\Omega}{RT}c\frac{\partial^2\sigma_{\rm h}}{\partial z^2}=0. \tag{5}$$

Equation (5) describes the mechanical–electrochemical coupling, reflecting the relationship between stress and diffusion. The third and fourth terms of Eq. (5) indicate that σ_h is related to the Li concentration. To solve the diffusion equation, the expression of σ_h must be obtained first.

As shown in Fig. 2, for the AFB regarded as a plate model, the Li concentration is a function of z, i.e., $c = c(z)$. It is assumed that the diffusion coefficient D of Li is constant.[22] The diffusion of lithium produces diffusion strain via volume expansion of the active material.[40] In a large electrode plate, the strain components in two planes, i.e., $\varepsilon_{xx} = \varepsilon_{yy}$ are a function of z. The strain equation in the plate model is written as follows:

$$\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_0 + \kappa z, \tag{6}$$

where ε_0 is the in-plane stain at $z = 0$ and κ is the electrode curvature.[41] In real battery systems, there are mechanical constraints on the electrode, thus the electrode cannot bend freely. In other words, $\kappa = 0$.[41] In this case, the constitutive equation for the biaxial stress reads

$$\sigma_{xx} = \sigma_{yy} = E'\left(\varepsilon_0 - \frac{1}{3}\Omega c\right), \tag{7}$$

where $E' = E/(1-\upsilon)$ is the biaxial modulus. Since there is no stress component in the z direction, the hydrostatic stress σ_h of the plate model can be obtained as

$$\sigma_h = \frac{1}{3}(\sigma_{xx} + \sigma_{yy}) = \frac{2}{3}E'\varepsilon_0 - \frac{2}{9}E'\Omega c. \tag{8}$$

In Eq. (8), the concentration-dependent term $\frac{2}{9}E'c$ represents the stress caused by inhomogeneous Li concentration. By considering the mechanical boundary of zero resultant force and zero curvature, the strain ε_0 can be written as follows:[41]

$$\varepsilon_0 = \frac{2}{3}\left[\frac{1}{2 + (h_c/h_1)(E_c'/E_1')}\right]\frac{\Omega}{h_1}\int_0^{h_1} c(z)\mathrm{d}z, \tag{9}$$

where $E_1' = E_1/(1-\upsilon)$ and $E_c' = E_c/(1-\upsilon)$ are the biaxial moduli of the active material and the current collector, h_1 and h_c are the thicknesses of the active material and the current collector. Assuming both the active material and the current collector are the same material in AFB, we have $E_1' = E_c'$. According to Eqs. (8) and (9), the hydrostatic stress σ_h can be obtained, as long as the concentration distribution is known.

Combining Eqs. (5) and (8), the stress-assisted diffusion equation can be rewritten as

$$\frac{\partial c}{\partial t} = (D + \beta c)\frac{\partial^2 c}{\partial z^2} + \beta\left(\frac{\partial c}{\partial z}\right)^2, \tag{10}$$

where β is the coupling parameter and expresses as

$$\beta = 2E_1' D\Omega^2/9RT. \tag{11}$$

Equation (10) reveals that β is a key influencing factor of Li diffusion. In the second and third terms of Eq. (10), the concentration gradient of Li is positively correlated to the value of β. Meanwhile, in Eq. (11), the β value is related to the quadratic of the partial molar volume, with the partial molar volume Ω expressed as

$$\Omega = \frac{\varepsilon_V F}{C\rho \times 3.6 \times 10^8}. \tag{12}$$

The partial molar volume is related to $\varepsilon_V = V_{max}/V$ which is the volume strain at maximum concentration.[42] $F = 96485.3$ C/mol is Faraday's constant. C is the rechargeable specific capacity. The Ω is obtained by volume strain ε_V divided by the maximum molar and is proportional to the volumetric strain. Therefore, the volumetric strain is also an essential factor.

The initial Li concentration in the AFB anode is assumed to be zero, i.e.,

$$c = 0, \quad \text{for} \quad t = 0. \tag{13}$$

For galvanostatic charging, the boundary conditions for the active plate are

$$J = -D\frac{\partial c}{\partial z} + \frac{D\Omega}{RT}c\frac{\partial \sigma_h}{\partial z} = -\frac{i_n}{F} \quad \text{for} \quad z = h_1, \tag{14}$$

$$J = -D\frac{\partial c}{\partial z} + \frac{D\Omega}{RT}c\frac{\partial \sigma_h}{\partial z} = 0 \quad \text{for} \quad z = 0, \tag{15}$$

where i_n is the current density. Equations (11), (13), (14), and (15) describe the stress-assisted diffusion and reveal the Li concentration variation in the AFB.

3. Results and discussion

3.1. Lithium diffusion mechanism in current collectors of anode free batteries

When lithium inserts into the current collector, an electrochemical reaction occurs. As shown in Fig. 3, the potential of the LiM alloys in AFB is usually lower than the bottom of the electrochemical window, and a thin, amorphous solid/electrolyte-interface layer will be formed.[14,44] For example, the potentials of LiAl alloy[45] and LiSn alloy[46,47] reaction in the AFBs are 0.31 V and 0.42 V vs. Li/Li$^+$, respectively. As a comparison, we list the electrochemical potentials of the common current collector materials in Table 2.[43] Since the electrolyte reduction at the anode does not occur, metals with a high potential, such as copper, tin, etc., can be used as a lithium protective layer.

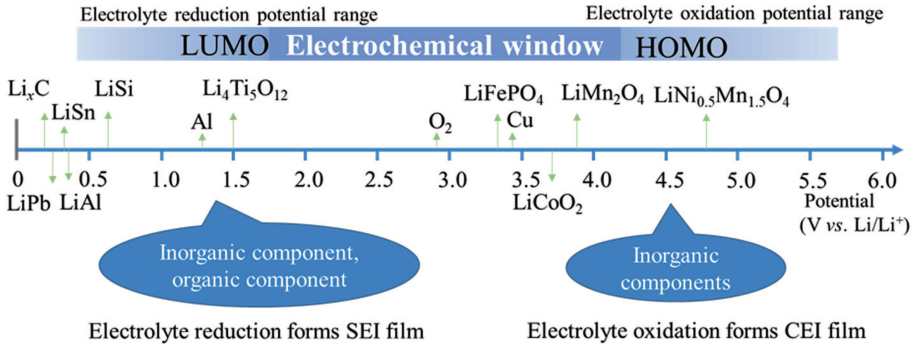


Fig. 3. Schematic illustration of the potential (V vs. Li/Li^+) of some common electrode materials in comparison with current collector metals (Al and Cu) and alloys (LiSn, LiPb, and LiAl). The general range on the electrochemical window of the common liquid organic electrolytes is also shown at the top.[43]

Table 2. Summary of the Li migration barriers, redox potential, volume expansion rate, and theoretical capacity of lithium in the current collectors *M* and corresponding Li*M* alloys.

Materials	Li migration barriers for *M*/eV	Li migration barriers for Li*M*/eV	Redox potential[43] /V vs. Li/Li^+	Volume expansion rate/%	Theoretical capacity/(mA·h/g)	Experiment? (Yes/No)
Ag	0.98	0.49	3.83	167	248.4	No
Al	0.63	0.18	1.36	190	992.5	Yes[8,10,11]
Cu	0.65	1.14	3.43	142	140.4	Yes[9,12]
Pb	0.10	1.73	2.91	501	129.3	No
Sn	0.25	0.65	2.89	262	993.3	Yes[13]
Zn	0.45	0.25	2.28	190	409.7	No

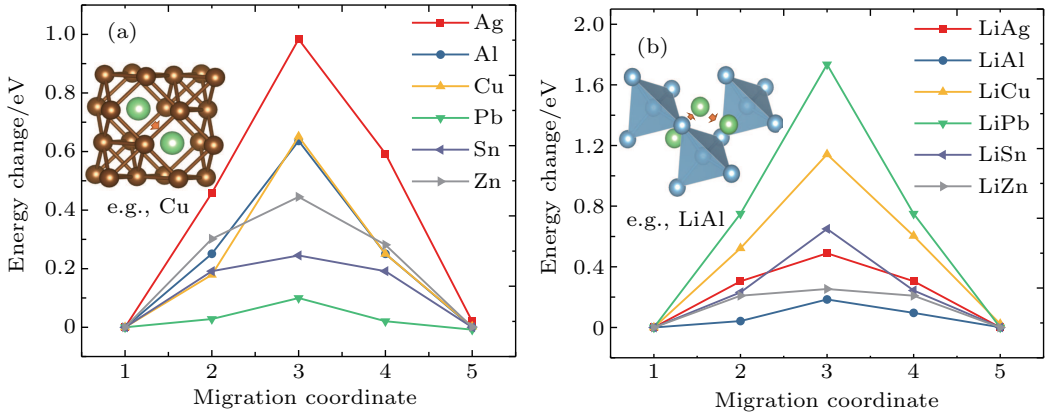


Fig. 4. Comparison of Li migration barriers in (a) metals and (b) alloys.

Before analyzing the coupling effect, we calculate the Li migration barriers for the metals and the corresponding alloys and compare the volume expansion rate on lithium insertion into several metals. This is an important step for in-depth analysis of the Li diffusion in AFBs. As shown in Fig. 4, the Li migration barriers for *M* metals are less than 1.00 eV. The barrier of Li diffusion in Ag is as high as 0.98 eV, making Li diffusion more difficult, while Cu and other metals have the lower migration barriers. The Li migration barrier of 0.65 eV for Cu is in agreement with the value of 0.68 eV obtained by Rupp *et al.* as measured by TOF-SIMS.[19] This proves that lithium can diffuse in copper, which was previously considered to be difficult. It breaks the conventional knowledge in previous experiments that Li cannot diffuse in Cu due to no formation of LiCu alloy phase at room temperature. However, the actual situation is that Li can diffuse as long as there exist a certain number of vacancies in Cu. Therefore, the insight we gain from our calculations can be used to explain the experimental phenomenon that the use of Cu with a thickness $\leqslant$ 100 nm as the protective coating on the anode significantly improves the lifetime of the battery due to the fast Li diffusion,[48–50] which has complicated implications for Cu coating to enhance the interfacial protection and kinetics of the electrode. This is also supported by the experiments of copper-based AFBs.[9,12] As a comparison, the Li migration barriers for Cu and Pb are lower than those for the LiCu alloy and LiPb alloy, respectively, which means that it is more difficult for Li to pass through the LiCu alloy and LiPb alloy layers. However, the Li migration barriers for the LiAg, LiAl, LiSn, and LiZn alloys are lower than those for the parents Ag, Al, Sn, and Zn, respectively. Espe-

cially for the LiAl alloy and LiZn alloy, the migration barriers are 0.18 eV and 0.25 eV, respectively, which are lower than the barriers for Al and Zn. This suggests that the formation of the LiAl alloy and LiZn alloy will not hinder the Li diffusion. Overall, when the migration barriers of these current collectors are close, the current collector with relative higher theoretical capacity and smaller volume expansion as shown in Table 3 should be selected for AFB. The results suggest that Al, Sn, and Zn are the better AFB current collectors than Cu or Ag. This is consistent with the experimental result that Al and Sn show the better energy density and cycling performance.[8,11]

At the same time, the volume expansion rates of several materials after lithiation are shown in Table 3. The results show that the volume expansion rates of most metals on lithiation are usually between 150% and 300% with the exception of lead with the value of 501%, which makes it unsuitable as the anode material.

Table 3. Summary of Young's modulus (E'), specific capacity (C), volume specific mass density (ρ), volume strain at maximum concentration (ε_v), partial molar volume (Ω), and coupling parameter (β) in mechanical–electrochemical coupling on some electrode materials and current collectors. The values of Young's modulus are obtained from database in Materials Project.[30,52]

Materials	E'/GPa[30,52]	C/(mA·h/g)	ρ/g·cm^{-3}	ε_v/%	Ω/m^3·mol^{-1}	β/nm^3
Graphite	10	372	1.83	9	3.54×10^{-6}	0.36[27]
$LiVO_2$	43	314	4.3	10	1.99×10^{-6}	0.49[27]
$LiCoO_2$	375	140	5	−2	-7.66×10^{-7}	0.64[27]
$LiFePO_4$	120	170	3.5	7	3.15×10^{-6}	3.45[27]
$Li_4Ti_5O_{12}$	240	175	3.5	1	4.38×10^{-7}	0.13[27]
$LiMn_2O_4$	142	136	4.1	7	3.36×10^{-6}	4.65[27]
Ag	123	248	9.92	167	1.82×10^{-5}	118
Al	109	993	2.7	190	1.90×10^{-5}	115
Cu	230	140	8.89	142	3.05×10^{-5}	620
Pb	55	129	10.7	501	9.71×10^{-5}	1511
Sn	82	993	5.37	262	1.32×10^{-5}	41
Zn	139	410	6.98	190	1.78×10^{-5}	128

3.2. Mechanical–electrochemical coupling facilitates lithium diffusion in anode free batteries

The alloying reaction between metallic materials and lithium leads to a large volume expansion (Table 2). The developing stress and strain in turn affect Li diffusion via mechanical–electrochemical coupling. By solving the diffusion Eq. (10), the Li concentration distribution along the z direction is shown in Fig. 5(a) (at $t = 900$ s) and its evolution is shown in Fig. 5(b) (at $z = 0.8$). The impact of the coupling parameter β is evaluated. The results show that when $\beta = 0$, which means no coupling, it shows a significant concentration gradient. With the increase of β, the concentration becomes uniform, which is caused by the stress-assisted diffusion. However, when $\beta > 100$ nm^3, the coupling effect is not further strengthened (Fig. 5(a)). Similarly, as shown in Fig. 5(b), when $z = 0.8$, the coupling effect makes the Li concentration change with time, approaching a linear regime for $t > 500$ s. As can be also seen, the pronounced effect on stress-assisted diffusion is achieved when $\beta = 0$–100 nm^3 and saturates at higher values.

Equations (11) and (12) indicate that β depends on the Young's modulus, density, and volume expansion rate of the materials. In Table 3, the related factors affecting the coupling of the studied materials are presented in which the volume expansion data is calculated in Subsection 2.2. It can be seen from Table 3 that there are obvious differences in the coupling parameter for different materials. Song[27] has studied the coupling of conventional battery materials, which are listed as a comparison with the metals in Table 3. It can also be seen from Table 3 that the metal current collectors which can be used for AFB have large volume expansion which in turn results in high value of β (> 40 nm^3). The β of Cu is 620 nm^3, revealing that fast Li diffusion in current collector such as Cu is affected by large volume expansion. The positive effect of high stress-assisted Li diffusion in the AFB anodes also explains their good cycling performance.[8] The β values of Al, Sn, and Zn are 115 nm^3, 41 nm^3, and 128 nm^3, respectively, indicating pronounced coupling effects. Overall, considering the capacity, migration barriers, and coupling effect, the Al, Sn, and Zn are more suitable than other metals for AFB. Among them, Sn has a larger volume expansion than Al and Zn, but lower β due to the low Young's modulus and the high density. In addition, Al has higher capacity and larger β with lower volume expansion than Sn, so Al offers the best application prospect in AFBs, followed by Zn and Sn as mentioned in Section 1.[8,11,13,51] Therefore, the optimal materials for AFBs should be assessed from three aspects: the energy density, volume expansion, and coupling effect. As an example, Pb and Ag have lower capacities and higher migration barriers than those of other metals, and even $\beta > 100$ nm^3 cannot compensate these drawbacks, so they are not preferred for AFB.

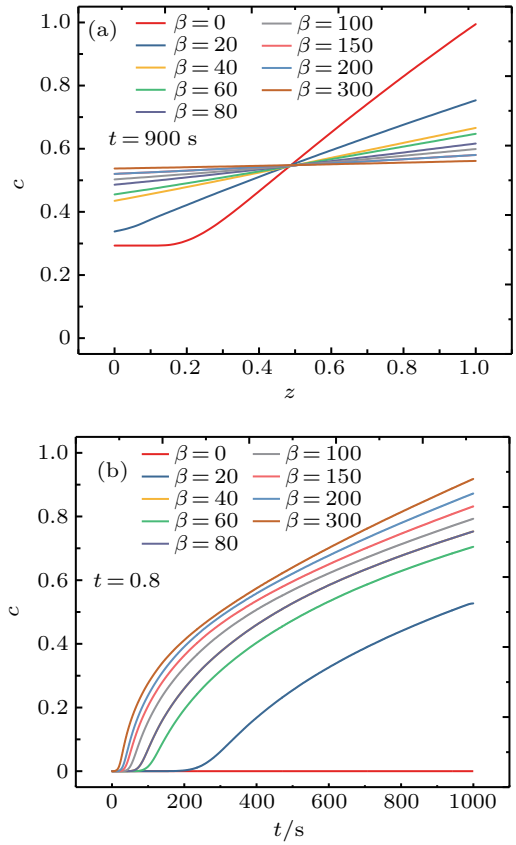


Fig. 5. (a) Distribution of Li concentration along the z direction with various values of the coupling parameter β after the 900 s diffusion. (b) Distribution of Li concentration against diffusion time t at a distance of 0.8 from the surface toward the current collector with various values of the coupling parameter β. For the convenience of comparison, both the Li concentration and diffusion distance along the z direction are normalized.

4. Concluding remarks and perspectives

The AFB is a new concept proposed in recent years, which uses metal as both current collector and anode. However, there are only a few in-depth studies on the effect of the volume expansion during charge on the electrochemical performance. In this paper, using first-principles calculation and solving the stress-assisted diffusion equations, we have demonstrated that the volume expansion facilitates Li diffusion in AFBs via mechanical–electrochemical coupling. We also compare the migration barriers in metals and the corresponding alloys and show that for Al, Sn, and Zn, the barriers in the corresponding alloys LiM (M = Al, Sn, etc.) are lower than those for Ag, Cu, and Pb, which has implications on their suitability for AFBs.

Through the analysis of the coupling equations, we obtain the volume expansion rates and the corresponding coupling parameters of these metals. Combining the migration barriers, coupling, and volume expansion rates, we find that Al is the most suitable for AFB, followed by Sn and Zn. By showing the importance of volume expansion via mechanical–electrochemical coupling in anode materials, this work establishes a new way to assess materials for AFBs. In general, the analysis of stress assisted diffusion can be applied to any other anode materials, including conventional batteries. In addition, multi-scale calculation models can be used to deeply study the manifestation of stress in the entire diffusion process even in sodium and zinc batteries. Compared with the traditional batteries, the AFB occupies the smaller space and exhibit the higher energy density. As a feasible research direction in the future, the migration mechanism of ions and the effect of mechanical–electrochemical coupling on diffusion can be studied in the corresponding sodium, magnesium, and zinc based AFBs. Our results will undoubtedly provide some support for researchers working on current collectors as well as energy storage technologies.

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