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Density Functional Theory Study of Selectivity of Crown Ethers to Li^+ in Spent Lithium-Ion Batteries Leaching Solutions

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It is a challenge to recover lithium from the leaching solution of spent lithium-ion batteries, and crown ethers are potential extractants due to their selectivity to alkali metal ions. The theoretical calculations for the selectivity of crown ethers with different structures to Li ions in aqueous solutions were carried out based on the density functional theory. The calculated results of geometries, binding energies, and thermodynamic parameters show that 15C5 has the strongest selectivity to Li ions in the three crown ethers of 12C4, 15C5, and 18C6. B15C5 has a smaller binding energy but more negative free energy than 15C5 when combined with Li^+ , leading to that the lithium ions in aqueous solutions will combine with B15C5 rather than 15C5. The exchange reactions between B15C5 and hydrated Li^+ , Co^{2+} , and Ni^{2+} were analyzed and the results show that B15C5 is more likely to capture Li^+ from the hydrated ions in an aqueous solution containing Li^+ , Co^{2+} , and Ni^{2+} . This study indicates that it is feasible to extract Li ions selectively using B15C5 as an extractant from the leaching solution of spent lithium-ion batteries.

Key words: Density functional theory, Crown ether, Geometry, Binding energy, Thermodynamic parameter

I. INTRODUCTION

In the past few decades, a large number of lithium-ion batteries (LIBs) were produced and applied in various portable electronic devices such as mobile phones, laptops, and video cameras [1]. In addition, with the rapid development of electric vehicles in recent years, a huge demand and a steady growth for LIBs output is predictable. Corresponding to the tremendous production and application of LIBs, it is inevitable that a large number of spent LIBs will be generated. It was predicted that more than 500 thousand tons of spent LIBs will be generated in 2020 in China [2]. Large quantities of valuable metals (Li, Co, Ni, Mn, Cu, Al, Fe) exist in the spent LIBs. Up to now, many methods have been employed to recycle the valuable metals from various cathode materials such as LiCoO_2 [3], $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (LNCM) [4], and LiFePO_4 [5] based on the points of resource saving.

Among the recycling methods, hydrometallurgical processes are considered to have great potential due to some attractive advantages such as high metal recovery rates and high product purity [6]. In the hydrometal-

lurgical processes, the valuable metals were first leached out and then recovered through various methods including solvent extraction, chemical precipitation, and electrochemical deposition [7]. Generally, Li^+ in the leaching solution is recovered in the form of Li_2CO_3 by a carbonate precipitation process in the last step. However, on the one hand, the Li^+ concentration in the leaching solution is very low and the solubility product of Li_2CO_3 is not low enough, leading to that a satisfactory Li^+ recovery rate was difficult to obtain, and most of the reported Li^+ recovery rates were less than 80% [8, 9]. On the other hand, some metal ions which are not completely removed in the previous steps (*e.g.*, Co^{2+} , Ni^{2+}) will influence the purity of the Li_2CO_3 precipitation. Therefore, it is necessary to develop a new method to effectively gather and separate the Li^+ from the leaching solution.

Crown ethers are an important class of macrocyclic ligands which display a conspicuous selectivity to metal ions based on the host-guest interaction. In the past few decades, crown ethers have been widely researched and applied in diverse areas since it was discovered by Pedersen in 1967 [10], including isotope separations [11, 12], phase transfer catalysts [13, 14], ions determination sensors [15, 16], ions separation [17, 18], and so on. The binding abilities of crown ethers with metal ions are mainly decided by the structures of crown ethers which

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can be adjusted by the crown cavity size, donor atoms and substituent groups (electron withdrawing or electron donating groups). Up to now, many researches about the influence of crown ether structure on the binding abilities with metal ions have been reported theoretically and experimentally [19–21]. Among these researches, some crown ethers exhibit good combination abilities with Li ions [22, 23]. Therefore, it is expectable that the Li⁺ in spent LIBs leaching solution can be recovered by some crown ethers with appropriate structures.

In recent years, with the rapid development of computer hardware and computational technique, theoretical calculation has become an important branch of scientific research. Up to now, the interactions between Li⁺ and some crown ethers, *e.g.*, 12-crown-4 (12C4), 15-crown-5 (15C5), 18-crown-6 (18C6) and their derivatives have been calculated based on different methods [24–27]. Most of these calculations were carried out in gas phase. However, in aqueous solutions, the metal ions exist in the form of hydrated ions and the coordinated water will influence the combination between metal ions and crown ethers. Therefore, the results obtained in gas phase cannot reflect the reality in aqueous solutions. In addition, the impurity ions in the spent LIBs leaching solution can also influence the binding abilities between Li⁺ and crown ethers. In previously reported researches, the main impurity ions of Fe²⁺ and Mn²⁺ can be removed completely by a simple precipitation process [28, 29]. However, the Co²⁺ and Ni²⁺ were generally recovered by solvent extraction and it was very difficult to be up to an extraction rate of 100%. Therefore, the selectivity of crown ethers with different structures to Li⁺ and impurity ions (Co²⁺ and Ni²⁺) in aqueous solutions is calculated in this work, to provide a theoretical basis for the recovery of Li⁺ from the spent LIBs leaching solution.

II. COMPUTATIONAL METHODS

The density functional theory (DFT) was used to study the interactions between the crown ethers with different structures and metal ions (Li⁺, Co²⁺ and Ni²⁺) in this work. All of the calculations were performed by using the Materials Studio 8.0 DMol³ (Accelrys Software Inc.) package. The exchange-correlation interaction was treated with the Perdew-Burke-Ernzerhof (PBE) functional in the generalized gradient approximation (GGA) [30, 31]. A basis set of double numerical plus polarization (DNP) [32] was used for the electronic calculations. To set the type of core treatment, all electrons were adopted because all the atomic numbers of atoms in this study are less than 36. The self-consistent-field (SCF) tolerance was set to 10⁻⁶ to achieve an accurate convergence, and a smearing of 0.005 Ha was applied to improve the computational efficiency. In the geometry optimization calculation, the convergence tolerances of the energy, maximum force,

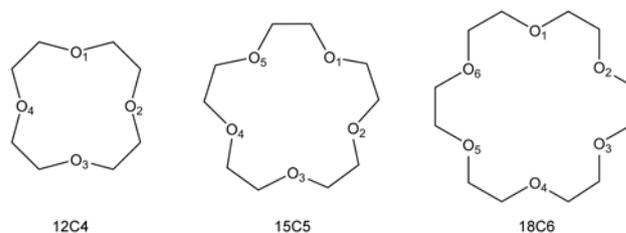


FIG. 1 Molecular structures and oxygen atom serial numbers of 12C4, 15C5, and 18C6.

and maximum displacement are 10⁻⁵ Ha, 0.002 Ha/Å, and 0.005 Å, respectively.

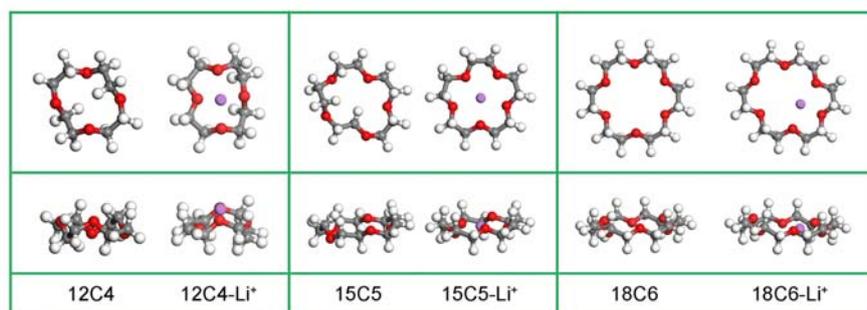
In order to simulate the real conditions in aqueous solutions, the conductor like screening model (COSMO) in DMol³ was used for all the geometry optimizations and energy calculations [33]. The vibration frequencies of crown ethers and their complexes with metal ions were calculated to obtain the thermodynamic parameters (free energy G , enthalpy H , and entropy S). The calculated vibration frequencies should be positive to ensure that the optimized structures are stable.

III. RESULTS AND DISCUSSION

A. Properties of crown ether (12C4, 15C5, and 18C6)-Li⁺ complexes

For the selectivity of crown ethers to metal ions, the matching degree between ion size and cavity size of crown ethers has been considered to be the most important influence factor in earlier researches [10, 34]. However, some other researches demonstrated that the size matching effect is not always effective [35, 36]. Although the size matching effect is uncertain, it is doubtless that the cavity size of crown ethers will influence their selectivity to metal ions in a certain condition. Therefore, we first studied the interaction between the crown ethers with different cavity sizes (12C4, 15C5 and 18C6) and Li ions. FIG. 1 shows the molecular structures of 12C4, 15C5 and 18C6, and the oxygen atoms in the structures are numbered for the geometric parameter description.

The optimized structures of free 12C4, 15C5, 18C6 and their complexes with Li ions are shown in FIG. 2. It can be seen that the Li⁺ in both 15C5 and 18C6 exist in the plane of crown rings, whereas the Li⁺ in 12C4 perches above the ring. From the geometric parameters shown in Table I, 12C4-Li⁺ has the minimum cavity size of 3.228 Å in the three crown ether complexes, which is far less than the sum ionic diameters of Li cation and oxygen anion (4.32 Å) [26]. Therefore, in the coordination process of 12C4 with Li⁺, the cavity of 12C4 cannot accommodate the Li⁺ and then two oxygen atoms bend out of the plane and point to the Li⁺. It also can be seen from Table I that all the three cavity sizes of free 12C4, 15C5 and 18C6 are decreased after they coordinate with Li⁺, due to the dipole-ion interactions

FIG. 2 Optimized geometries of free 12C4, 15C5, 18C6 and their complexes with Li⁺.TABLE I Calculated geometric parameters of crown ether (12C4, 15C5, and 18C6)-Li⁺ complexes.

| Complex | Bond length/Å | | | | | | Cavity size ^a /Å |
|----------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-----------------------------|
| | Li-O ₁ | Li-O ₂ | Li-O ₃ | Li-O ₄ | Li-O ₅ | Li-O ₆ | |
| 12C4-Li ⁺ | 2.067 | 1.982 | 2.072 | 2.017 | | | 3.228 (4.122) |
| 15C5-Li ⁺ | 2.348 | 2.207 | 2.204 | 2.377 | 2.101 | | 4.074 (4.582) |
| 18C6-Li ⁺ | 3.466 | 2.176 | 1.974 | 2.168 | 3.452 | 4.332 | 5.299 (5.699) |

^a The cavity size is the minimum distance between two oxygen atoms located at para-position, and the values in parenthesis are the cavity sizes of free crown ethers.

between the donor O atoms and Li⁺. The Li-O bond lengths of 12C4-Li⁺, 15C5-Li⁺ and 18C6-Li⁺ are 1.982–2.072, 2.101–2.377, and 1.974–4.322 Å, respectively. These Li-O bond lengths lead to that the Li⁺ is centered in the structures of 12C4-Li⁺ and 15C5-Li⁺ but off-center in 18C6-Li⁺. The large range of Li-O bond lengths for 18C6-Li⁺ indicates the weak interactions between Li⁺ and O₁, O₅ and O₆ in 18C6-Li⁺ complex.

The binding energy (ΔE) of the crown ether-metal ion complexation reaction is usually used to characterize the stability of the crown ether-metal complex. Generally, the more negative the binding energy is, the more stable the complex will be, and the more selective the crown ether will be towards the metal ions. The binding energy is defined as follows:

$$M^{n+} + L = L-M^{n+} \quad (1)$$

$$\Delta E = E(L-M^{n+}) - E(L) - E(M^{n+}) \quad (2)$$

where, $E(L-M^{n+})$, $E(L)$, and $E(M^{n+})$ refer to the energies of crown ether-metal ion complexes, free crown ethers, and metal ions respectively.

Generally, metal ions exist in the form of hydrated ions in aqueous solutions. Therefore, the thermal parameters (free energy change ΔG , enthalpy change ΔH and entropy change ΔS) of the crown ether-metal ion complexation reaction were calculated according to the following exchange reaction:



The calculated binding energies and thermodynamic

TABLE II Calculated binding energies (ΔE in kJ/mol) and thermodynamic parameters (ΔG and ΔH in kJ/mol, ΔS in J·mol⁻¹·K⁻¹) of crown ether (12C4, 15C5 and 18C6)-Li⁺ complexes (298.15 K).

| Complex | ΔG^a | ΔH^a | ΔS^a | ΔE |
|----------------------|--------------|--------------|--------------|------------|
| 12C4-Li ⁺ | -6.30 | 45.25 | 307.00 | -120.15 |
| 15C5-Li ⁺ | -70.45 | 24.57 | 318.65 | -141.36 |
| 18C6-Li ⁺ | -21.49 | 74.33 | 321.36 | -91.99 |

^a ΔG , ΔH and ΔS were calculated at $m=4$ according to Eq.(3).

parameters of the crown ethers (12C4, 15C5, and 18C6)-Li⁺ complexation reaction are shown in Table II. It can be seen that the 15C5-Li⁺ has the largest binding energy in the three complexes, which indicates it is more stable than the other two. The Li-O bond lengths of 12C4-Li⁺ shown in Table I are shorter than that of 15C5-Li⁺, which means stronger Li-O bond strength for 12C4-Li⁺. However, 15C5 has more donor O atoms than 12C4, which may be the reason why 15C5-Li⁺ has the greater binding energy than 12C4-Li⁺. As for 18C6-Li⁺, there are only three donor O atoms (the Li-O_{1,5,6} bonds are negligible because of the too long bond lengths), therefore it is reasonable it has the lowest binding energy.

As shown in Table II, the ΔG for the formation of the three complexes are all negative, so the three exchange reactions are spontaneous. The exchange reaction of 15C5-Li⁺ has the most negative ΔG of -70.45 kJ/mol, which indicates that the formation of 15C5-Li⁺ in aque-

TABLE III Calculated geometric parameters of B15C5-Mⁿ⁺ (Li⁺, Co²⁺, Ni²⁺) complexes and their binding energies.

| Complex | Bond length/Å | | | | | Cavity size/Å | ΔE /(kJ/mol) |
|------------------------|------------------|------------------|------------------|------------------|------------------|---------------|----------------------|
| | M-O ₁ | M-O ₂ | M-O ₃ | M-O ₄ | M-O ₅ | | |
| B15C5-Li ⁺ | 2.177 | 2.418 | 2.036 | 2.374 | 2.176 | 3.904 | -137.07 |
| B15C5-Co ²⁺ | 2.017 | 1.917 | 1.911 | 2.004 | 3.016 | 3.321 | -806.46 |
| B15C5-Ni ²⁺ | 2.225 | 2.022 | 2.035 | 2.107 | 2.535 | 3.866 | -868.53 |

ous solutions is more favorable than the other two. It is worth noting that the ΔH for all the three reactions are positive, indicating the exchange reactions are endothermic processes. This is against the formation of the crown ether-Li⁺ complexes due to the equation $\Delta G = \Delta H - T\Delta S$. However, in the exchange reaction process, the ΔS becomes more positive with the dehydration of the hydrated metal ions due to the increased randomness of the free water molecules. And then the ΔS for the three exchange reactions are positive enough to overcome the ΔH , leading to the negative ΔG for the complexation processes.

When crown ethers are used as extractants to separate metal ions in a liquid-liquid extraction system, a portion of the crown ethers will be lost in water because of its water solubility. In order to reduce the crown ether losses and improve the extraction rates, crown ethers are often immobilized on a carrier to form a liquid-solid extraction system [12, 37], for example, the silica gel-crown ether extraction as shown in FIG. 3(a). However, a single crown ether ring is difficult to be immobilized on carriers whereas benzo crown ethers are appropriate candidates, due to that many functional groups can be grafted easily on the benzene rings of the benzo crown ethers. Therefore, in the next section we studied the Li⁺, Co²⁺, and Ni²⁺ selectivity of benzo-15-crown-5 ether (B15C5) who has the same crown ring with 15C5 as shown in FIG. 3(b).

B. Properties of B15C5-Mⁿ⁺ (Li⁺, Co²⁺, Ni²⁺) complexes

The optimized structures of free B15C5 and its complexes with Li⁺, Co²⁺ and Ni²⁺ are shown in FIG. 4. It can be seen that there is a great structure distortion for B15C5-Co²⁺ complex compared with B15C5-Li⁺ and B15C5-Ni²⁺. This distortion leads to the largest M-O distance (1.911–3.016 Å) and the smallest cavity size (3.321 Å) for B15C5-Co²⁺ in the three complexes as shown in Table III. On the contrary, the structures of B15C5-Li⁺ and B15C5-Ni²⁺ are roughly in line with the structure of B15C5, and so these two complexes have narrow M-O distributions (2.036–2.418 Å for B15C5-Li⁺ and 2.022–2.535 Å for B15C5-Ni²⁺) and similar cavity sizes (3.904 Å for B15C5-Li⁺ and 3.866 Å for B15C5-Ni²⁺).

Table III also shows the binding energies of the three complexes. The binding energies of B15C5-Co²⁺ and B15C5-Ni²⁺ are far greater than that of B15C5-Li⁺, which indicates B15C5-Co²⁺ and B15C5-Ni²⁺ are more

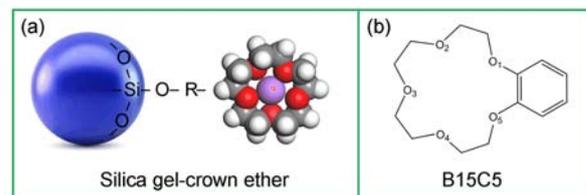


FIG. 3 (a) Schematic diagram of silica gel-crown ether extraction and (b) molecular structure and oxygen atom serial numbers of B15C5.

stable than B15C5-Li⁺. Simultaneously, it is found that the binding energy of B15C5-Li⁺ is slightly less than that of 15C5-Li⁺ despite that they have the same crown ring. This result can be explained by the electron withdrawing effect of the benzene ring of B15C5. FIG. 5 shows the electrostatic potentials of 15C5 and B15C5. Generally, for one region of a molecule, the more negative its electrostatic potential is, the stronger its attraction to metal ions will be. It is clearly shown that the negative electrostatic potential region moves from the crown ring to the benzene ring for B15C5 and its electrostatic potential is more positive than that of 15C5. Therefore, it is reasonable that the binding energy of B15C5-Li⁺ is decreased.

It should be pointed out that the calculated free energy change for the exchange reaction of B15C5-Li⁺ is lower than that of 15C5-Li⁺ (-74.53 kJ/mol for B15C5-Li⁺ and -70.45 kJ/mol for 15C5-Li⁺), which indicates that the lithium ions in aqueous solutions will combine B15C5 preferentially. This result is counter to the results inferred from the binding energies (-137.07 kJ/mol for B15C5-Li⁺ and -141.36 kJ/mol for 15C5-Li⁺), which means that the binding energy criterion is not always valid although it has been widely used. Free energy change, reflecting the direction and degree of a reaction, is a combination of enthalpy and entropy. FIG. 6 shows the thermodynamic parameter changes taking the exchange reaction of B15C5-Li⁺ (hydration number of Li⁺ is 4) for example. First, the dehydration of Li⁺ is an endothermic process, and the entropy of the dehydration process is increased due to the increase of the freedom of the water molecules. Second, in order to combine the dehydrated Li⁺ perfectly, a conformational change happens to the B15C5 which leads to a positive ΔH and a negative ΔS . In the third step, the complexation of B15C5 and Li⁺ is a conspicuous exothermic process, and the entropy of this pro-

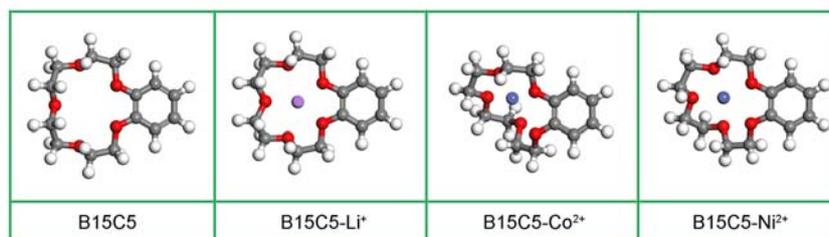


FIG. 4 Optimized geometries of free B15C5 and its complexes with Li⁺, Co²⁺ and Ni²⁺.

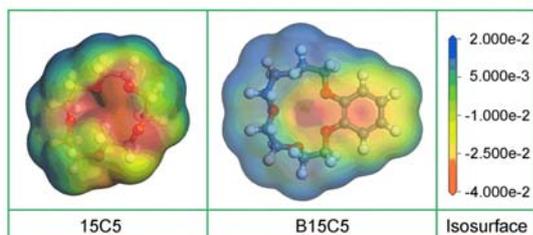


FIG. 5 Electrostatic potentials (in Ha) of 15C5 and B15C5.

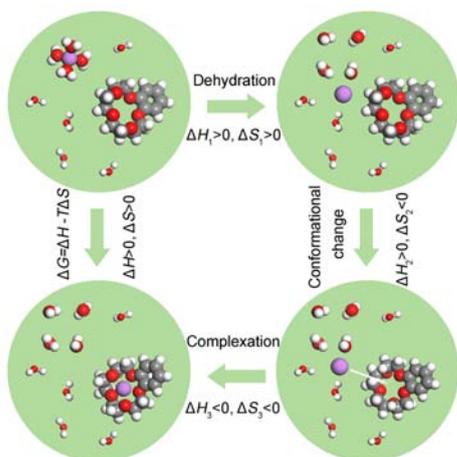


FIG. 6 Thermodynamic parameter changes of the exchange reaction of B15C5-Li⁺.

cess is decreased due to the reduced freedom of the system. B15C5 has a stronger structure rigidity than that of 15C5. Therefore, a less conformational change happens to B15C5 in the whole exchange reaction and the entropic effects in step two and three are reasonable smaller. This is why the ΔG of the exchange reaction of B15C5-Li⁺ is lower than that of 15C5-Li⁺.

All of the three metal ions Li⁺, Co²⁺ and Ni²⁺ exist in the form of hydrated ions in aqueous solutions and their hydration numbers have important effects on the exchange reactions. FIG. 7 shows the influences of hydration numbers of the three metal ions on their thermodynamic parameters of the exchange reactions. As shown in FIG. 7(a), all three ΔH increase with the increase of the hydration numbers, mainly due to that more energies are needed for the dehydration of

the hydrated ions when the hydration number is large. When the hydration numbers are less than or equal to 3, the exchange reactions are exothermic ($\Delta H < 0$). Whereas, they are endothermic ($\Delta H > 0$) when the hydration numbers are larger than 3 which is adverse to the exchange reactions. It is also found that the ΔH of B15C5-Li⁺ is larger than that of B15C5-Co²⁺ and B15C5-Ni²⁺ at $n(\text{H}_2\text{O}) \leq 3$ but smaller at $n(\text{H}_2\text{O}) > 3$. This change is beneficial for the combination of B15C5 and Li⁺ at the large hydration numbers.

The ΔS of the three exchange reactions are mainly from the increased disordered degree of the water molecules after the dehydration of the hydrated metal ions. Therefore, it is reasonable that the three exchange reactions have the similar ΔS and the three ΔS increase with the increase of the hydration numbers, as shown in FIG. 7(b). The calculated ΔG of the three exchange reactions are shown in FIG. 7(c), which shows that the ΔG of B15C5-Li⁺ is more positive than that of B15C5-Co²⁺ and B15C5-Ni²⁺ at $n(\text{H}_2\text{O}) \leq 3$ but more negative at $n(\text{H}_2\text{O}) > 4$. Generally, Li⁺ in aqueous solutions is tetra-coordinated, and Co²⁺ and Ni²⁺ are hexa-coordinated. The ΔG of B15C5-Li⁺ is -74.53 kJ/mol at $n(\text{H}_2\text{O}) = 4$, and the ΔG of B15C5-Co²⁺ and B15C5-Ni²⁺ are -55.35 and -35.21 kJ/mol at $n(\text{H}_2\text{O}) = 6$, respectively. Therefore, it is feasible to extract Li ions selectively using B15C5 as an extractant from the solution containing Li⁺, Co²⁺ and Ni²⁺.

IV. CONCLUSION

The selectivity of crown ethers with different structures to Li ions in aqueous solutions was studied based on the density functional theory. The geometries and binding energies of the crown ether-metal ion complexes, and the thermodynamic parameters of the exchange reactions were calculated. The results show that 15C5 has stronger combining capacity with Li ions than 12C4 and 18C6. B15C5 has a smaller binding energy but more negative free energy than 15C5 when combined with Li⁺ due to the strong structure rigidity of B15C5, which means the lithium ions in aqueous solutions will combine with B15C5 rather than 15C5. The exchange reactions between B15C5 and hydrated Li⁺, Co²⁺ and Ni²⁺ were analyzed according to the thermodynamic parameters. The calculated free energies show that B15C5 is more likely to capture Li⁺ from the

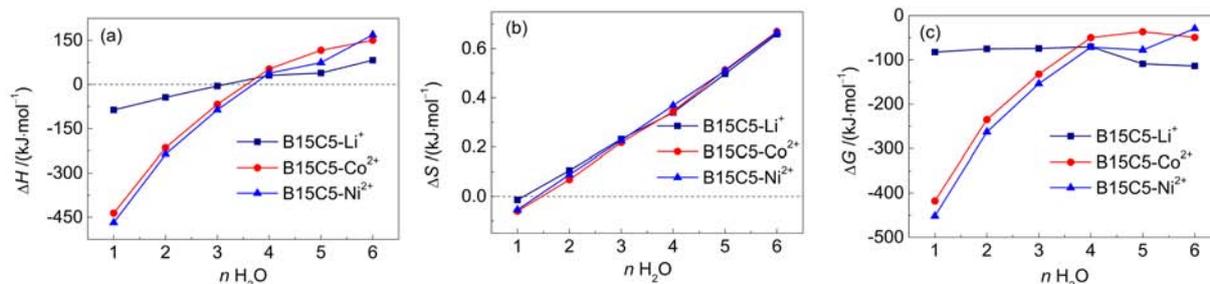


FIG. 7 Influences of hydration numbers of metal ions on the thermodynamic parameters: (a) enthalpy changes ΔH , (b) entropy changes ΔS and (c) free energy changes ΔG for the exchange reaction of B15C5 with Li^+ , Co^{2+} , and Ni^{2+} (298.15 K).

hydrated ions in an aqueous solution containing Li^+ , Co^{2+} and Ni^{2+} . This study provides a potential for the recovery of lithium from the spent LIBs leaching solution.

V. ACKNOWLEDGMENTS

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