## Supporting Information

# Unexpected Electrochemical Behavior of Crown-Based Organic Compounds for LithiumIon Battery Cathodes 

Dae Kyeum Lee, Gyeong Seok Jeong and Ki Chul Kim*

Computational Materials Design Laboratory, Division of Chemical Engineering, Konkuk University, Seoul 05029, The Republic of Korea

## Corresponding Author

*E-mail: kich2018@konkuk.ac.kr (K. C. Kim).
$N$-incorporated B-crown-n
P-incorporated B-crown-n






O-incorporated B-crown-n



S-incorporated B-crown-n



F-incorporated B-crown-n
Cl-incorporated B-crown-n







Figure S1. Structural information. The chemical structures for $x$-incorporated B-crown- $n(x=\mathrm{N}, \mathrm{P}, \mathrm{O}, \mathrm{S}, \mathrm{F}$, and Cl ; $n=4,5$, and 6). The atoms in gray, white, red, blue, pink, purple, yellow, cyan, and light green depict carbon, hydrogen, oxygen, nitrogen, boron, phosphate, sulfur, fluorine, and chlorine, respectively.


Figure S2. Structural modification of B-crown compounds. Li-induced improvement in the redox potentials of Oincorporated B-crown-4 and S-incorporated B-crown-6 compounds. The atoms in gray, white, red, pink, yellow, and violet depict carbon, hydrogen, oxygen, boron, sulfur, and lithium, respectively.


Figure S3. Thermodynamic properties. Binding free energies of $x$-incorporated B -crown- $n$ compounds, namely, $x \mathrm{~B} n(x: \mathrm{S}, \mathrm{P}, \mathrm{O}, \mathrm{N}, \mathrm{F}, \mathrm{Cl} ; n: 4,5,6)$ with the first Li atom in (a) vacuum and (b) solution phase.


Figure S4. Discharging mechanism. The Li-storage mechanism of $S$-incorporated B -crown- 6 during the discharging process.


Figure S5. Recharging mechanism. The self-healing mechanism of $S$-incorporated B -crown- 6 during the recharging process. The dotted green circle shows a C-B bond broken during the discharging process.


Figure S6. Correlations. Changes in the redox potential, electron affinity, and solvation energy for S-incorporated B-crown-6 during the Li-involved discharging process.

$E_{\text {red }}^{E x p}=3.1 \mathrm{~V} \quad E_{\text {red }}^{D E T}=2.9 \mathrm{~V}$


2,6-Diaminoanthraquinone $E_{\text {red }}^{E x p}=2.0 \mathrm{~V} \quad E_{\text {red }}^{D E T}=1.9 \mathrm{~V}$

$E_{\text {red }}^{E x p}=-0.1 \mathrm{~V} \quad \begin{gathered}\text { Thiophene } \\ \text { DET }\end{gathered}=-0.2 \mathrm{~V}$



Anthraquinone-2-carboxylic acid
$E_{\text {red }}^{E x x}=2.3 \mathrm{~V} \quad E_{\text {red }}^{D F T}=2.4 \mathrm{~V}$


$$
E_{r e d}^{E x p}=-1.1 \mathrm{~V} E_{r e d}^{D F T}=-0.8 \mathrm{~V}
$$




9,10-Anthraquinone

$$
E_{r e d}^{E x p}=2.2 \mathrm{~V} \quad E_{r e d}^{D F T}=2.3 \mathrm{~V}
$$

<

$$
\begin{gathered}
1,4 \text {-Benzendicarbonitrile } \\
E_{r e d}^{E x p}=1.7 \mathrm{~V} \quad E_{r e d}^{D E T}=1.7 \mathrm{~V}
\end{gathered}
$$



Benzodyrrole
$E_{\text {red }}^{\text {Exp }}=-0.2 \mathrm{~V} E_{\text {red }}^{D E T}=-0.2 \mathrm{~V}$


Benzo[1,2- $b: 4,5-b^{\prime}$ ]dithiophene-4.8-dione

$$
E_{r e d}^{E x p}=2.5 \mathrm{~V} \quad E_{r e d}^{D F T}=2.6 \mathrm{~V}
$$



Pyrenetetrone
$E_{\text {red }}^{E x p}=2.5 \mathrm{~V} \quad E_{\text {red }}^{D F T}=2.7 \mathrm{~V}$


Anthraquinone-1,5-disulfonic
$E_{\text {red }}^{E x p}=2.4 \mathrm{~V} \quad E_{\text {red }}^{E D T}=2.3 \mathrm{~V}$


Figure S7. Validation of computational protocol. The chemical structures for eleven organic compounds employed to validate the reliability of the computational protocol. The atoms with gray, white, red, blue, yellow, and purple in color depict carbon, hydrogen, oxygen, nitrogen, sulfur, and sodium, respectively.

Table S1. Redox potentials of designed crown-based compounds (Figure 1) and selected compounds with one bound
Li atom.

| Molecule (no Li binding) | Redox potential (V vs. Li/Li ${ }^{+}$) | Molecule (no Li binding) | Redox potential (V vs. Li/Li ${ }^{+}$) |
| :---: | :---: | :---: | :---: |
| O-crown-4 | -0.78 | N-incorporated B-crown-4 | 3.36 |
| O-crown-5 | -0.88 | N-incorporated B-crown-5 | 4.21 |
| O-crown-6 | -1.05 | N-incorporated B-crown-6 | 2.98 |
| B-crown-4 | 0.84 | P-incorporated B-crown-4 | 3.74 |
| B-crown-5 | 0.57 | P-incorporated B-crown-5 | 3.87 |
| B-crown-6 | 0.69 | P-incorporated B-crown-6 | 3.33 |
| N-crown-4 | -0.63 | O-incorporated B-crown-4 | 1.06 |
| N-crown-5 | -0.79 | O-incorporated B-crown-5 | 1.20 |
| N-crown-6 | -0.74 | O-incorporated B-crown-6 | 0.85 |
| P-crown-4 | -0.50 | S-incorporated B-crown-4 | 1.13 |
| P-crown-5 | -0.53 | S-incorporated B-crown-5 | 1.30 |
| P-crown-6 | -0.44 | S-incorporated B-crown-6 | 1.39 |
| S-crown-4 | -0.67 | F-incorporated B-crown-4 | 3.97 |
| S-crown-5 | -0.53 | F-incorporated B-crown-5 | 5.13 |
| S-crown-6 | -0.55 | F-incorporated B-crown-6 | 5.18 |
| paired O-crown-4 | -0.65 | Cl-incorporated B-crown-4 | 4.35 |
| paired O-crown-5 | -0.76 | Cl-incorporated B-crown-5 | 3.87 |
| paired O-crown-6 | -0.38 | Cl-incorporated B-crown-6 | 5.04 |
| 1Li-involved molecule (promising candidacy) | Redox potential (V vs. Li/Li ${ }^{+}$) | 1Li-involved molecule (non-promising candidacy) | Redox potential (V vs. Li/Li ${ }^{+}$) |
| O-incorporated B-crown-4 | 4.12 | N-incorporated B-crown-4 | -0.41 |
| S-incorporated B-crown-6 | 4.74 | N-incorporated B-crown-5 | 1.22 |
|  |  | N-incorporated B-crown-6 | 1.65 |
|  |  | P-incorporated B-crown-4 | 1.17 |
|  |  | P-incorporated B-crown-5 | 0.37 |
|  |  | P-incorporated B-crown-6 | 0.76 |
|  |  | O-incorporated B-crown-5 | 1.58 |
|  |  | O-incorporated B-crown-6 | 2.38 |
|  |  | S-incorporated B-crown-4 | 1.89 |
|  |  | S-incorporated B-crown-5 | 1.30 |
|  |  | F-incorporated B-crown-4 | -0.50 |
|  |  | Cl-incorporated B-crown-4 | -0.57 |
|  |  | Cl-incorporated B-crown-5 | 0.15 |

