

## Supplementary Information

### Electrochemical role of the SEI in Li-ion batteries and design principles for electrode surface modification

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#### A. Some additional figures

##### 1. Cell configurations

Schematic cell configurations are presented in Fig. S1.

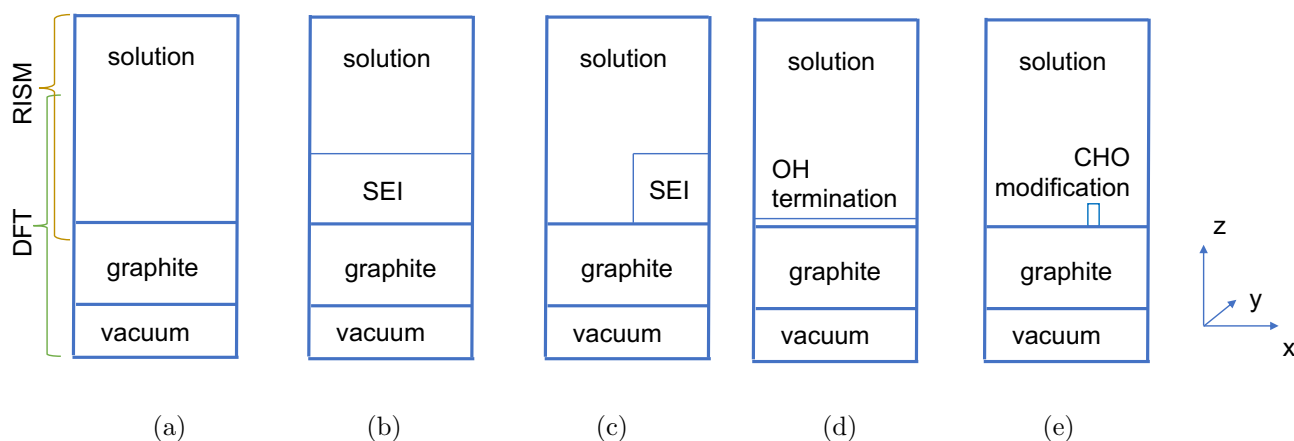


Figure S1: Cell configurations with graphite (a) terminated by H atoms (no SEI), (b) covered by a LiF layer, (c) modified with a LiF cluster, (d) terminated by OH groups, and (e) modified with a single CHO group.

## 2. Solvation shell development

Fig. S2 shows how solvation structures are changed with Li atom/ion movement.

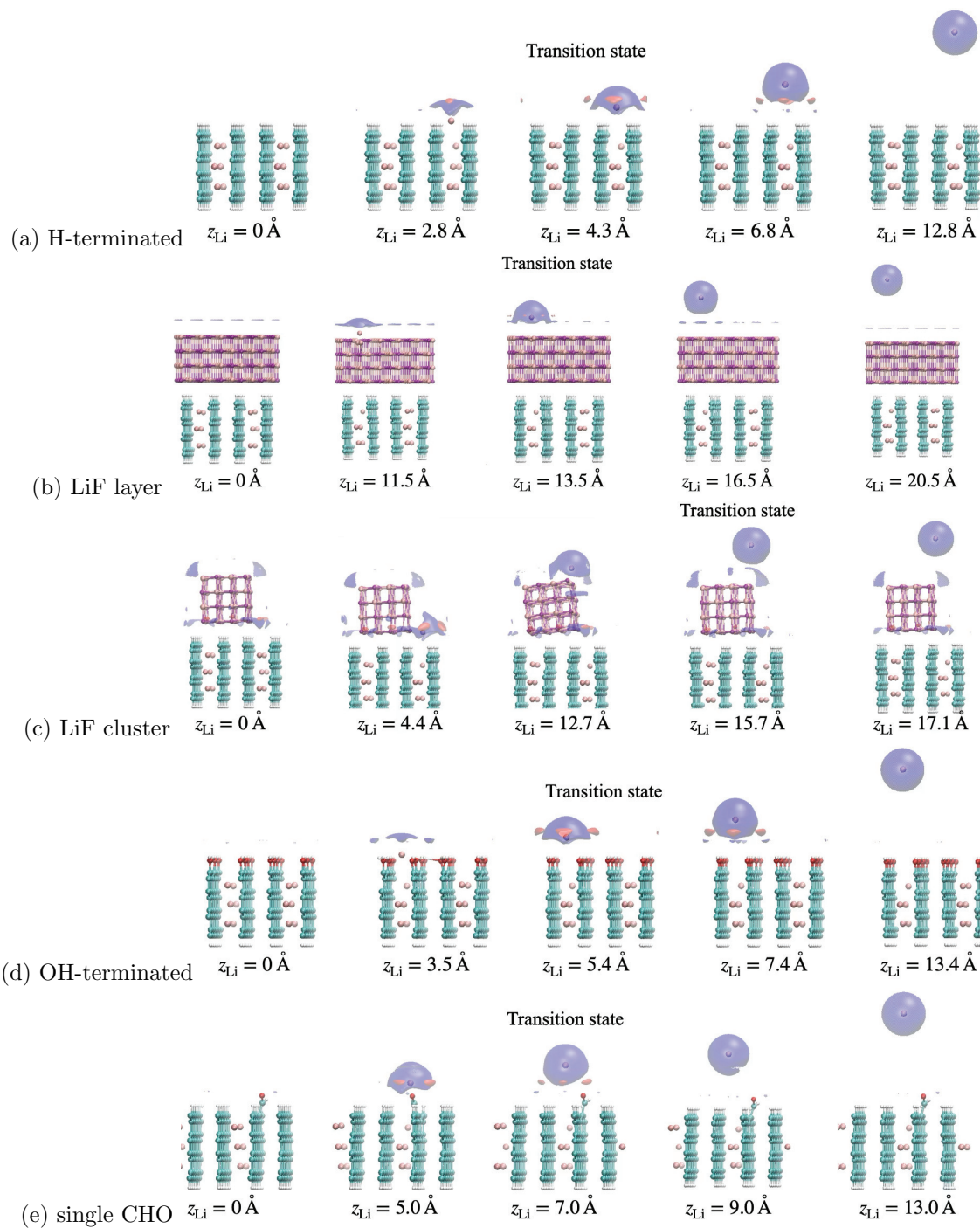


Figure S2: Isovalue surfaces of charge density in electrolyte solutions. Blue cloud, negative charge; red cloud, positive charge.

### 3. Determination of the energy profile with graphite covered by a LiF layer

Movements of a  $\text{Li}^+$  ion from the topmost LiF surface to the solution and from the LiF bottommost to the graphite result in a large energy increase as shown by blue asterisks in Fig. S3. A vacancy is formed on both the LiF surfaces. If the  $\text{Li}^+$  ion moves to the LiF surfaces from the solution or from the graphite, the energy decreases after the transition state are observed as shown by the red crosses in Fig. S3.  $\text{Li}^+$  ion moves toward  $\text{F}^-$  of LiF, forming a stable  $\text{Li}^+ - \text{F}^-$  pair. The energy goes up when the  $\text{Li}^+$  ion enters the LiF medium. The observed energy profile may be that connecting the lower energy marks as shown by the pink line in Fig. S3. This curve is shown in Fig. 2(b) in the main text.

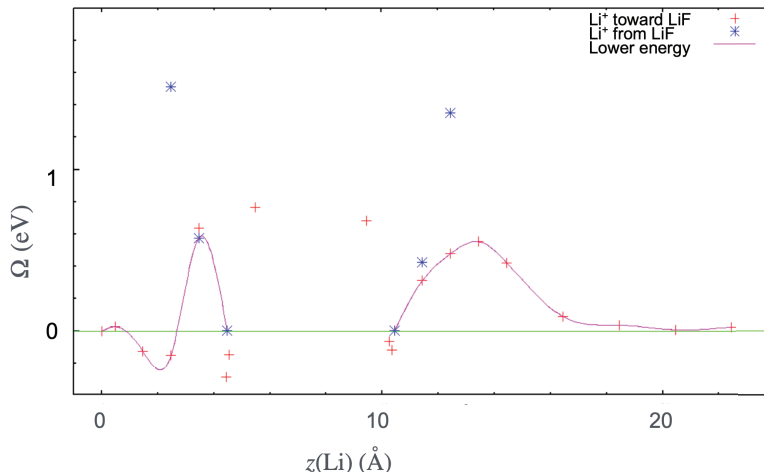


Figure S3: Grand potentials as a function of Li positions. Blue asterisks, energies when Li atoms are moved from LiF to the solution or from LiF to graphite, leaving a vacancy on the LiF surfaces; red crosses, energies when Li atoms are moved toward LiF from the solution or from graphite; pink lines, connecting the lower energy sides between the red crosses and the blue asterisks. The pink line will be observed.

### 4. Ion exchange on LiF layer

After Li is removed from the top of the LiF layer on graphite, the vacant Li site is filled with RISM  $\text{Li}^+$  particles as shown by a density iso-surface in Fig. S4. Ion-exchange takes place.

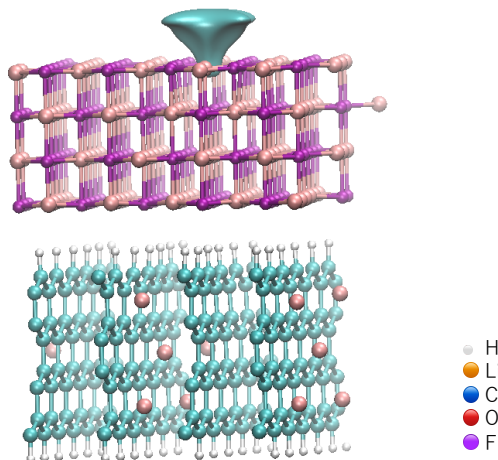


Figure S4: Iso-surface (in ice-blue) of RISM  $\text{Li}^+$  concentration on the Li vacancy.

### 5. $\text{Li}^+$ distribution near the LiF cluster

In order to estimate the  $\text{Li}^+$  path, density distribution of the RISM  $\text{Li}^+$  particles shown in Fig. S5 is used.

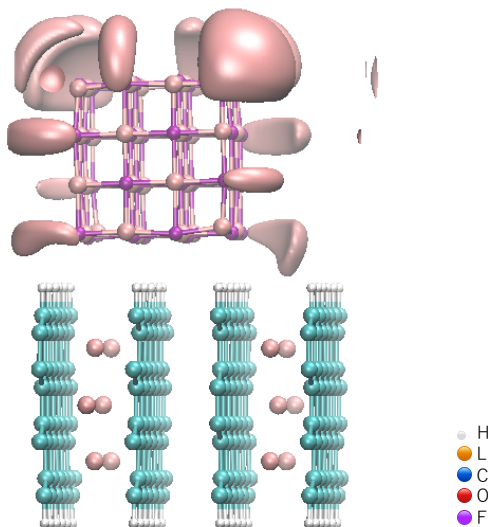


Figure S5: Density distribution of RISM  $\text{Li}^+$  particles near the LiF cluster.

### 6. Potential profiles on the $x - y$ plane at the potential minima

Some potential minima exist between the graphite and the transition state in Figs. 2(c) and 2(e) in the main text. Energy profiles along the perpendicular direction against the  $z$ -coordinate are shown in Fig. S6, in which the moving Li atoms are fixed in all three directions for energy minimization.

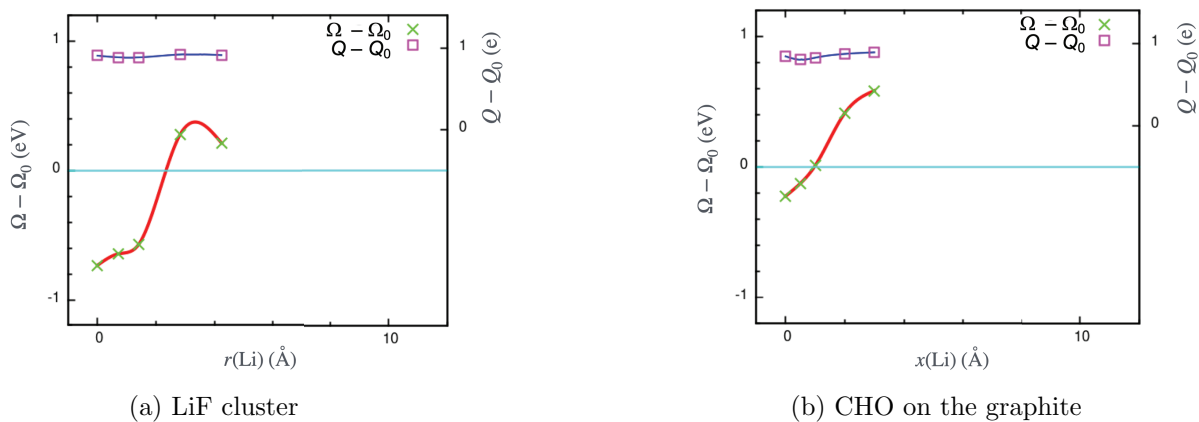


Figure S6: Grand potential profiles in the  $x - y$  plane at the potential minima. (a) along  $r = \sqrt{x^2 + y^2}$  at  $z = 11.58$  Å for the LiF cluster configuration (Fig. 2(c) in the main text), and (b) along the  $x$ -direction at  $z = 6.00$  Å for the CHO modified configuration (Fig. 2(e) in the main text).  $\Omega_0$  and  $Q_0$  are values at  $z_{\text{Li}} = 0$  in the Figs. 2(c) and 2(e).

## 7. Solvent atom distribution around the surface

Distributions of solvent atoms in the  $r$ -direction from certain atoms on the surfaces are shown in Fig. S7. Those along the  $z$ -directions are in Fig. S8. Because the radial distribution from a surface atom includes the electrode region where no solvent exists, the solvent density for large  $r$  is about half of the bulk one. Distributions of  $\text{Li}^+$  in  $\text{LiPF}_6$  show a peak in Fig. S7 (c) and (e) in which the distributions are calculated against a F atom on the LiF vertex and against an O atom the CHO group. On the flat electrode surfaces,  $\text{Li}^+$  peaks are observed in the profile along the  $z$ -direction (Fig. S8).

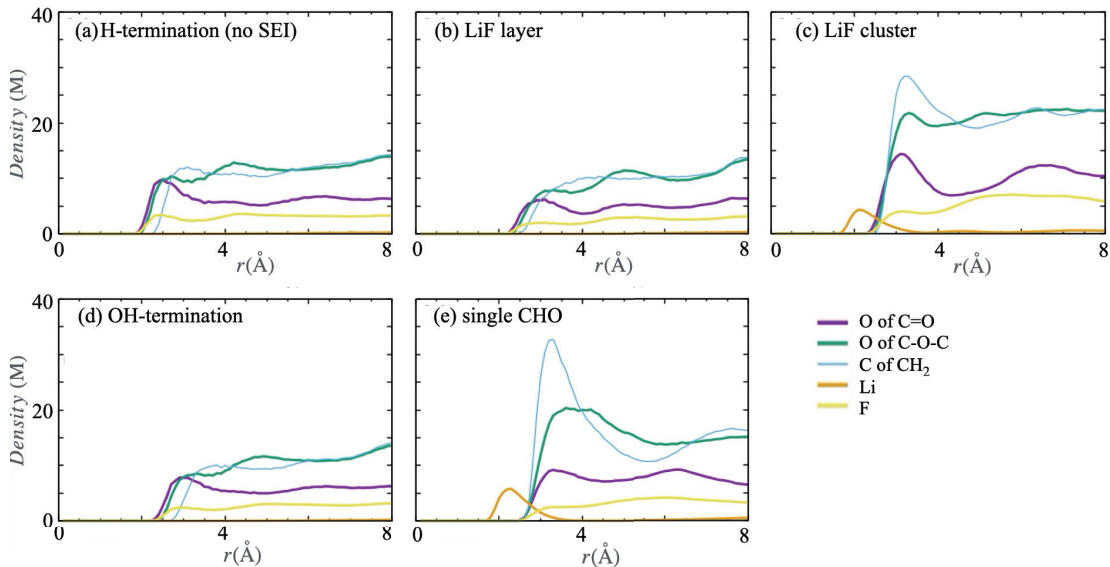


Figure S7: Radial profiles of solvent-atom concentrations from surface atoms H (a), F (b), F at vertex (c), O of OH (d), and O of -CHO.

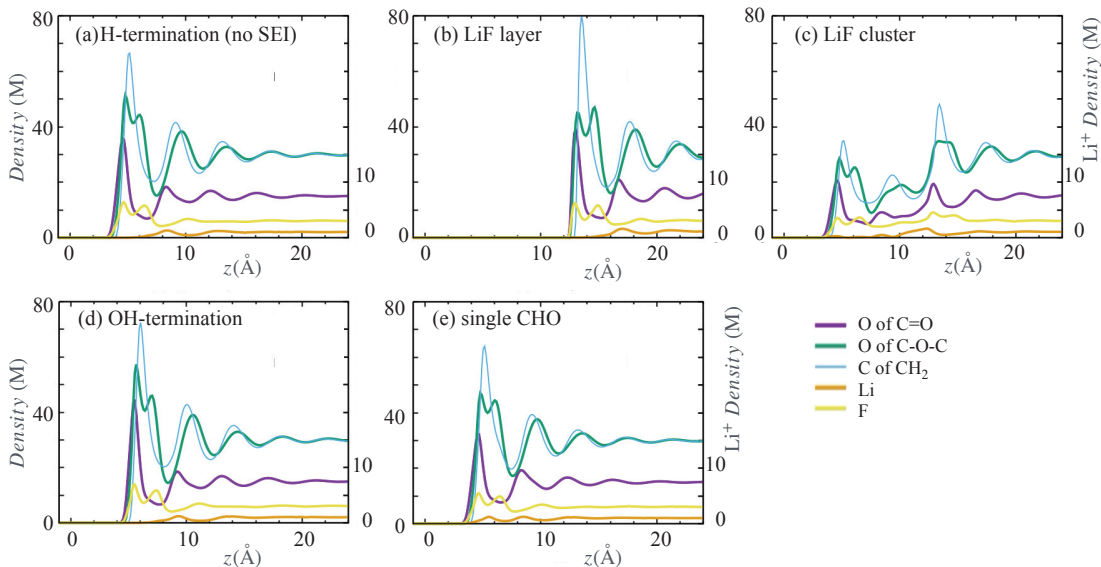


Figure S8: Solvent-atom concentration along the  $z$ -direction.

## B. Grand potential and Activation energy

### 1. Electrode potential dependency of the grand potential

Grand potential  $\Omega$  is defined as

$$\Omega = E_{\text{total}} - QE_e. \quad (1)$$

Electrode potential  $E_e (= -E_F)$  is the derivative of total energy  $E_{\text{total}}$  by charge  $Q$ .

$$E_e = \frac{\partial E_{\text{total}}}{\partial Q} \quad (2)$$

From eq. (1), the derivative of  $\Omega$  by  $E_e$  is

$$\frac{\partial \Omega}{\partial E_e} = \frac{\partial E_{\text{total}}}{\partial E_e} - Q - E_e \frac{\partial Q}{\partial E_e}. \quad (3)$$

By introducing eq. (2) to the last term in eq. (3), it becomes

$$\frac{\partial \Omega}{\partial E_e} = \frac{\partial E_{\text{total}}}{\partial E_e} - Q - \frac{\partial E_{\text{total}}}{\partial Q} \frac{\partial Q}{\partial E_e} \quad (4)$$

$$= -Q. \quad (5)$$

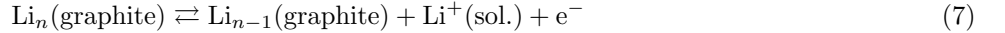
Therefore, it is possible to estimate the  $\Omega$  change by the small change of  $E_e$  as

$$\delta \Omega = -Q \delta E_e. \quad (6)$$

Eq. (6) is used to find the  $\Omega$  after changing  $E_e$  in the main text.

### 2. Transfer coefficient $\alpha$

We consider the following charge transfer reaction which is the same as that of eq. (1) in the main text.



Energy profile at the equilibrium state with electrode potential  $E_e^{\text{eq}}$  is as shown by a black line in Fig. S7. When over-potential  $\eta$  is applied to the electrode potential, the energy profile will change as shown by an orange line in Fig. S6. The grand potential at  $z_{\text{Li}} = 0$  changes from  $\Omega_0$  to  $\Omega_0^\eta$ , and that at  $z_{\text{Li}} = z_a$  changes from  $\Omega_a$  to  $\Omega_a^\eta$ , where  $z_a$  is the position of the transition state. The grand potentials after applying the over-potential will be as follows from eq. (6).

$$\Omega_0^\eta = \Omega_0 - Q_0 \eta \quad (8)$$

$$\Omega_a^\eta = \Omega_a - Q_a \eta \quad (9)$$

$Q_0$  and  $Q_a$  are charges at  $z_{\text{Li}} = 0$  and  $z_{\text{Li}} = z_a$ , respectively. Activation energy  $E_a^\eta$  for the forward reaction after applying  $\eta$  becomes

$$E_a^\eta = \Omega_a^\eta - \Omega_0^\eta \quad (10)$$

$$= \Omega_a - \Omega_0 - (Q_a - Q_0)\eta. \quad (11)$$

$$\text{Introducing } E_a = \Omega_a - \Omega_0, \quad (12)$$

$$E_a^\eta = E_a - (Q_a - Q_0)\eta \quad (13)$$

From Fig. S6,  $E_a^\eta$  and  $E_a$  are in the following relation.

$$\eta + E_a^\eta = E_a + (1 - \alpha)\eta \quad (14)$$

Therefore:

$$E_a^\eta = E_a - \alpha\eta \quad (15)$$

$$\alpha = -\frac{E_a^\eta - E_a}{\eta} \quad (16)$$

From eq. (13):

$$\alpha = Q_a - Q_0 \quad (17)$$

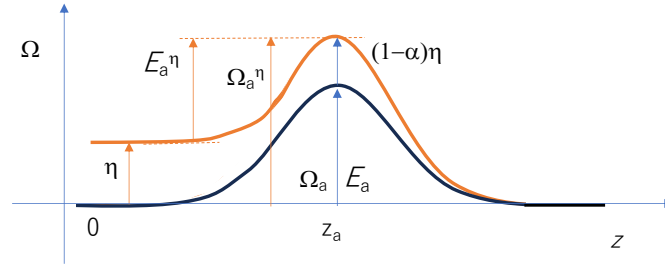


Figure S6: Schematic illustration of activation energy change.

### 3. Butler-Volmer equation

Reaction rate (current density  $J$ ) in the electrochemical cell at electrode potential  $E_e$  is expressed by the following Butler-Volmer equation without the concentration term [1, 2].

$$J = J_0 \left[ \exp\left(\frac{1}{RT}\alpha\eta\right) - \exp\left(-\frac{1}{RT}(1-\alpha)\eta\right) \right] \quad (18)$$

$$J_0 = k \exp\left(-\frac{1}{RT}E_a\right) \quad (19)$$

$$\eta = E_e - E_e^{\text{eq}} \quad (20)$$

$R$  gas constant,  $T$  temperature,  $J_0$  exchange current density, and  $k$  is rate constant.

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[1] A. J. Bard and L. R. Faulker, "Electrochemical Methods: Fundamentals and Applications", John Wiley & Sons, 2nd edn., 2001.

[2] J. O. M. Bockris and A. K. N. Reddy, "Modern Electrochemistry", Plenum, New York, 1973.