Supporting information

Morphology and selectivity of hydrated alkali metal ions as depth of discharge in 1T-MoS_2 electrode with aqueous electrolytes

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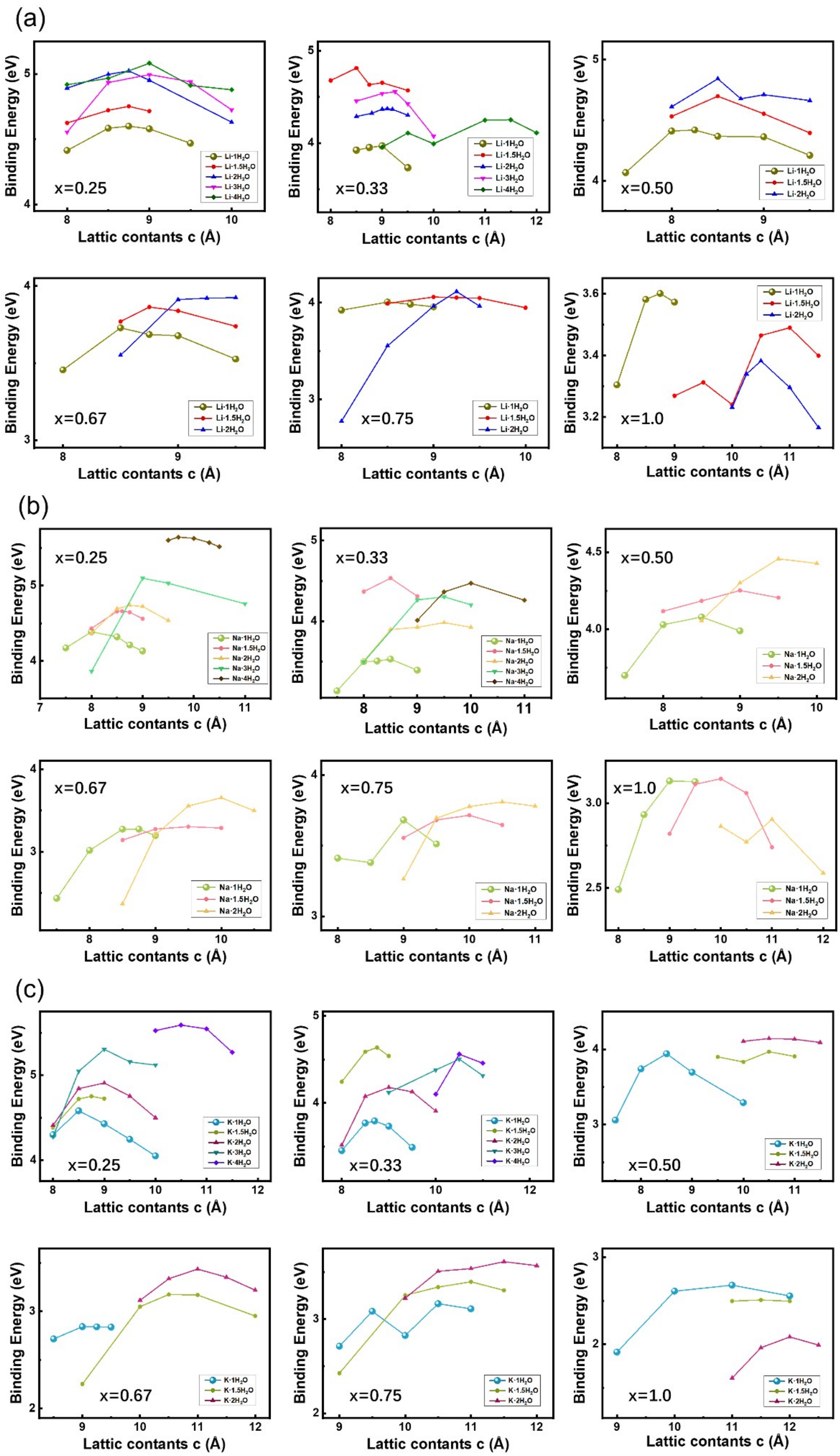
	coordination number (chemistry)	Ionic bond type	symbolic
Y-O ionic bond	≤2	Li-O	
		Na-O	
		K-O	
	≥3	Li-O	
		Na-O	
		K-O	

Table S1. The characteristics of Y-O ionic bonding in the morphology diagrams are listed. For oxygen coordination number≤2, and the ionic bonding types are indicated by different colored lines. For oxygen coordination number≥3, different ionic bonding situations and ionic bonding types are more clearly indicated by different colored facets.

		spacing	symbolic
Water molecule interactions	oxygen-oxygen interaction (d_{OO})	d_{OO}>3.5Å	
		d_{OO}≤3.5Å	
	hydrogen bond (d_{OH})	d_{OH}>2.5Å	unmarked
		d_{OH}≤2.5Å	

Table S2. The characteristics between water molecules in the morphology diagram are listed; oxygen-oxygen spacing>3.5Å, no interaction, indicated by light red dashed lines; oxygen-oxygen spacing≤3.5Å, mutual repulsion exists, indicated by red dashed lines. Hydrogen bond length>2.5Å, no hydrogen bonding, not labeled; hydrogen bond length≤2.5Å, hydrogen bonding, indicated by blue dashed line. Water molecules O-H have interactions with each other to form hydrogen bonding conditions d_{OH}≤2.5Å (d_{OH} denotes the distance between O-H), θ_{OHO}≥150°, d_{OO}≤3.5Å, θ_{HOO}≤30°.



(a)
Binding Energy (eV)
Lattic contants c (Å)
x=0.25
x=0.33
x=0.50
x=0.67
x=0.75
x=1.0
Li·1H₂O
Li·1.5H₂O
Li·2H₂O
Li·3H₂O
Li·4H₂O
(b)
x=0.25
x=0.33
x=0.50
x=0.67
x=0.75
x=1.0
Na·1H₂O
Na·1.5H₂O
Na·2H₂O
Na·3H₂O
Na·4H₂O
(c)
x=0.25
x=0.33
x=0.50
x=0.67
x=0.75
x=1.0
K·1H₂O
K·1.5H₂O
K·2H₂O
K·3H₂O
K·4H₂O

Figure S1. The binding energies of different systems of $[Y \cdot mH_2O]_x MoS_2$ (Y=Li, Na, K; x=0.25, 0.33, 0.50, 0.67, 0.75, 1.0; *m*=1, 1.5, 2, 3, 4) were obtained by varying the strain in the direction of the z-axis. (a) Optimized free energies of $[Li \cdot mH_2O]_x MoS_2$ system. (b) Optimized free energies of $[Na \cdot mH_2O]_x MoS_2$ system. (c) Optimized free energies of $[K \cdot mH_2O]_x MoS_2$ system.

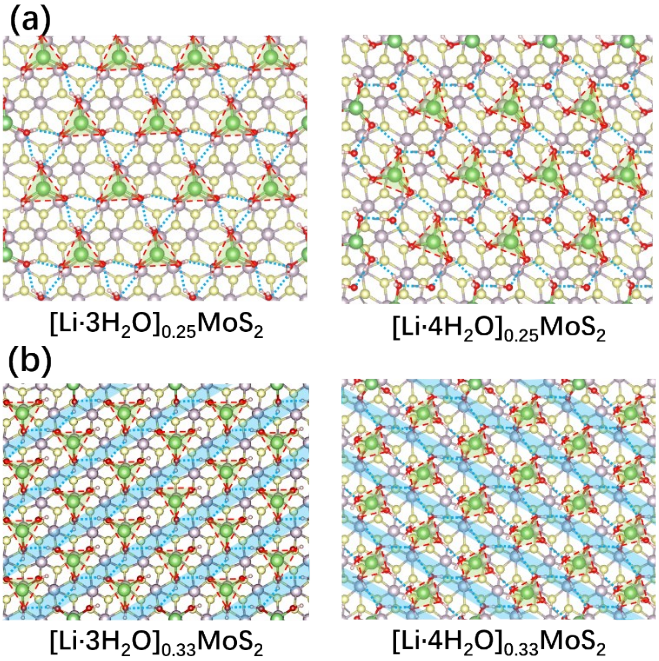


Figure S2. Hydrated lithium ion morphology of $[Li\cdot mH_2O]_xMoS_2$ intra-layer intercalation at low discharge depths. (a) Top view of 3 and 4 water molecules bound respectively for a discharge status of x=0.25. (b) Top view of 3 and 4 water molecules bound respectively for a discharge status of x=0.33.

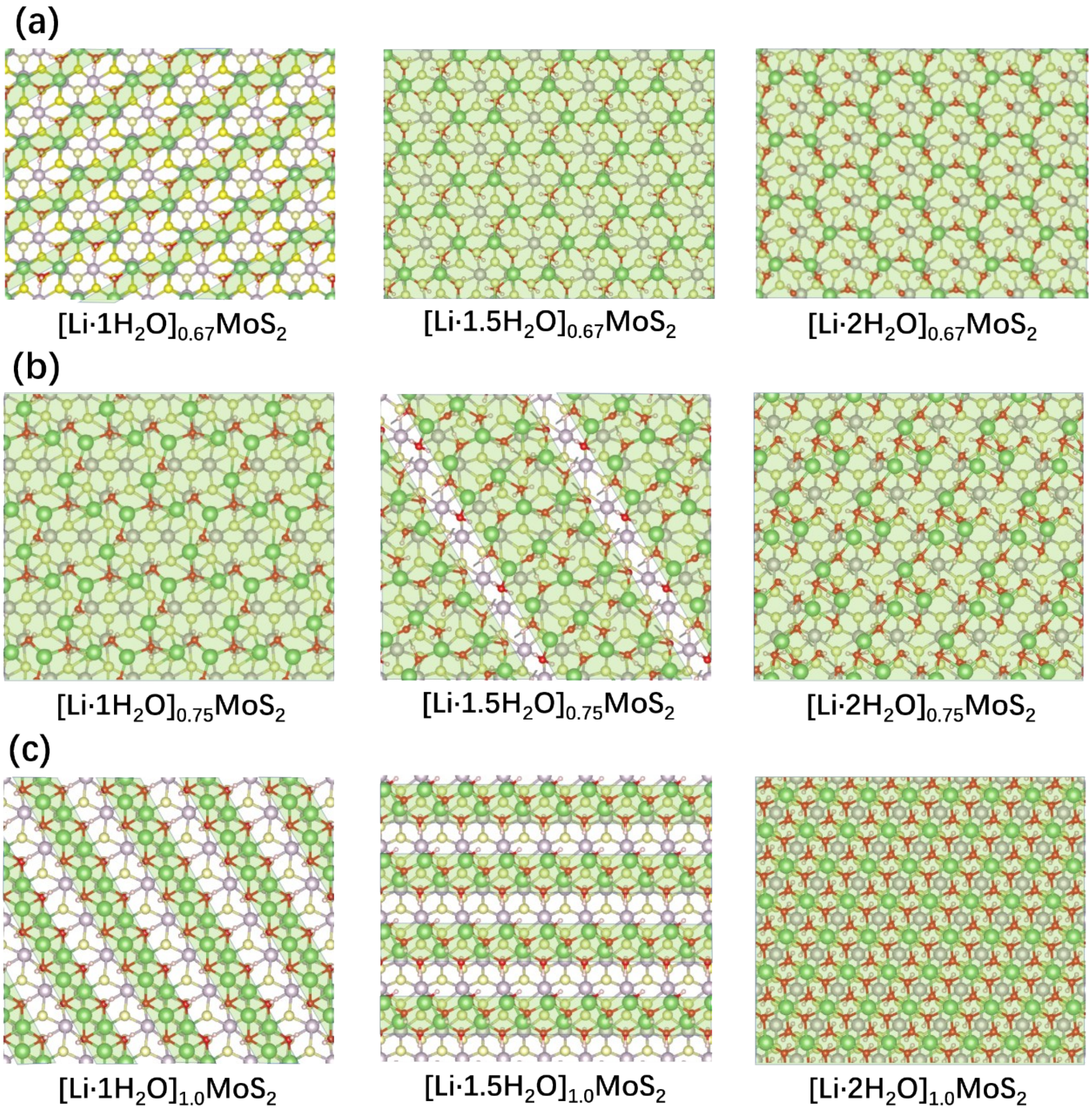


Figure S3. Hydrated lithium ion morphology of $[Li\cdot mH_2O]_xMoS_2$ intra-layer intercalation at high discharge depths. (a) Top views of 1, 1.5, and 2 water molecules bound respectively for a discharge status of x=0.67. (b) Top views for discharge status of x=0.75 combining 1, 1.5, and 2 water molecules, respectively. (c) Top views of 1, 1.5, and 2 water molecules combined for a discharge status of x=1.0, respectively.

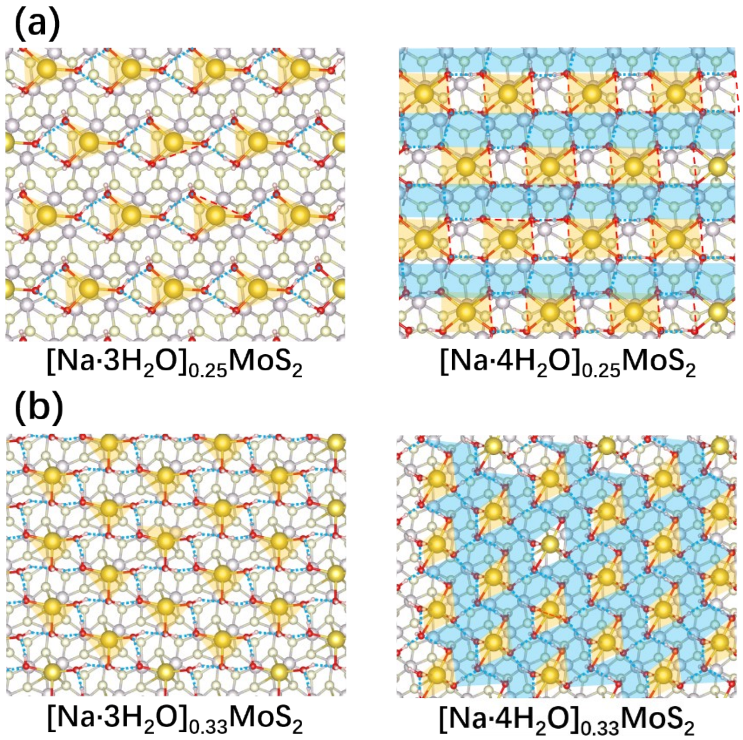


Figure S4. Hydrated sodium ion morphology of $[Na{\cdot}mH_2O]_xMoS_2$ intra-layer intercalation at low discharge depths. (a) Top view of 3 and 4 water molecules bound respectively for a discharge status of x=0.25. (b) Top view of 3 and 4 water molecules bound respectively for a discharge status of x=0.33.

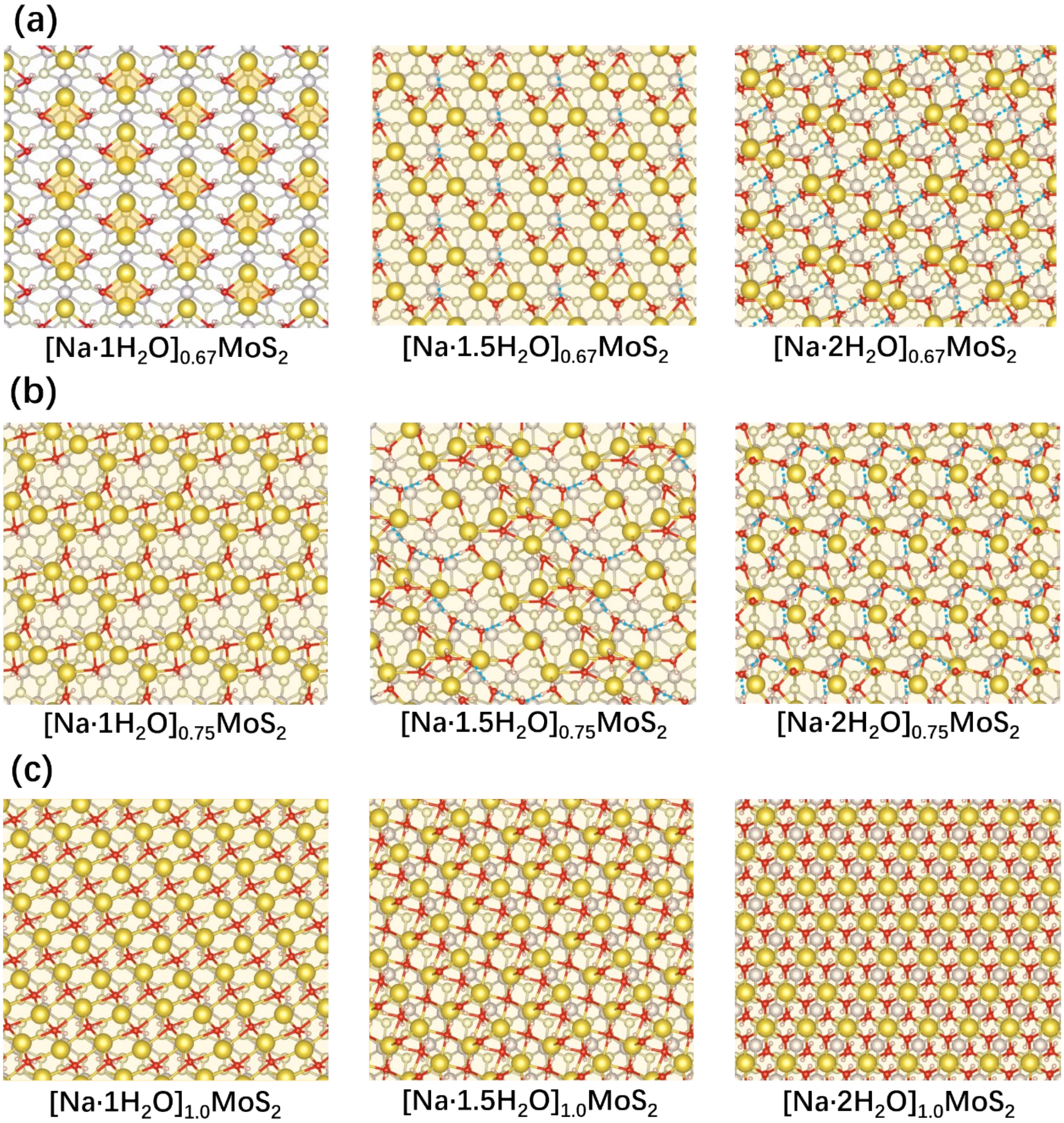


Figure S5. Hydrated sodium ion morphology of $[Na\cdot mH_2O]_xMoS_2$ intra-layer intercalation at high discharge depths. (a) Top views of 1, 1.5, and 2 water molecules bound respectively for a discharge status of x=0.67. (b) Top views of 1, 1.5, and 2 water molecules bound for a discharge status of x=0.75, respectively. (c) Top views of 1, 1.5, and 2 water molecules bound for a discharge status of x=1.0, respectively.

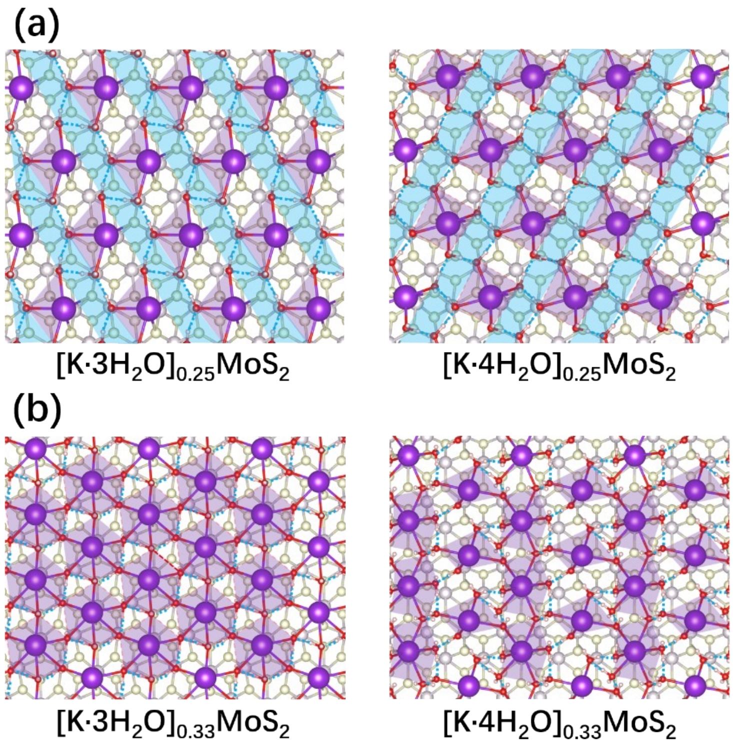


Figure S6. Hydrated potassium ion morphology of $[K\cdot mH_2O]_xMoS_2$ intra-layer intercalation at low discharge depths. (a) Top view of 3 and 4 water molecules bound respectively for a discharge status of x=0.25. (b) Top view of 3 and 4 water molecules bound respectively for a discharge status of x=0.33.

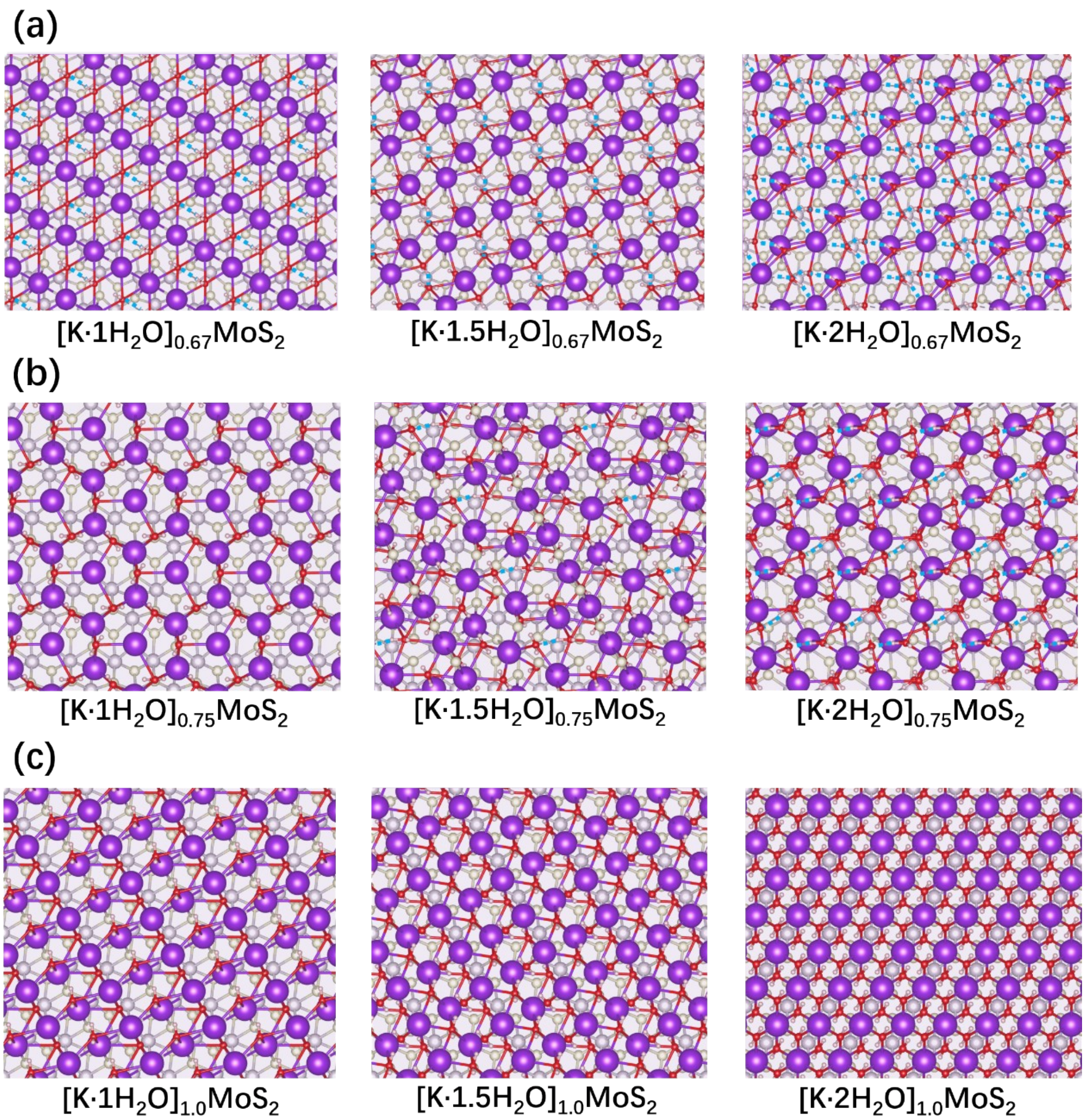


Figure S7. Hydrated potassium ion morphology of $[K \cdot mH_2O]_xMoS_2$ intra-layer intercalation at high discharge depths. (a) Top views of 1, 1.5, and 2 water molecules bound respectively for a discharge status of x=0.67. (b) Top views for discharge status of x=0.75 binding 1, 1.5, and 2 water molecules, respectively. (c) Top views of 1, 1.5, and 2 water molecules bound for a discharge status of x=1.0, respectively.

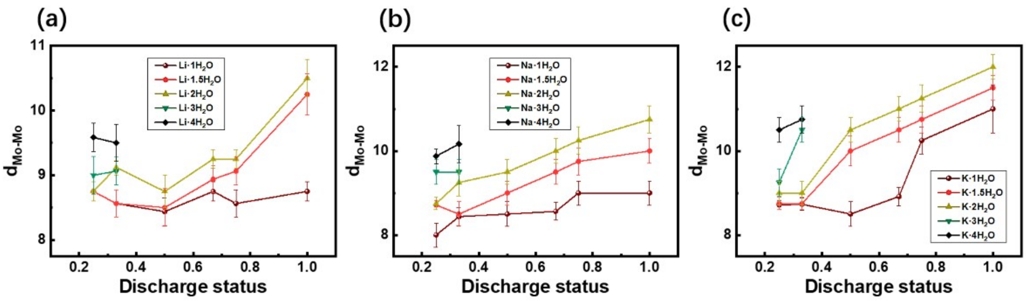


Figure S8. Effect of the status of discharge in hydrated ions on MoS_2 layer spacing. (a) the role of $[Li\cdot mH_2O]_xMoS_2$ (m=1, 1.5, 2, 3, 4) on layer spacing at different degrees of hydration. (b) the role of $[Na\cdot mH_2O]_xMoS_2$ (m=1, 1.5, 2, 3, 4) on layer spacing at different status of hydration. (c) the role of $[K\cdot mH_2O]_xMoS_2$ (m=1, 1.5, 2, 3, 4) on layer spacing at different status of hydration.

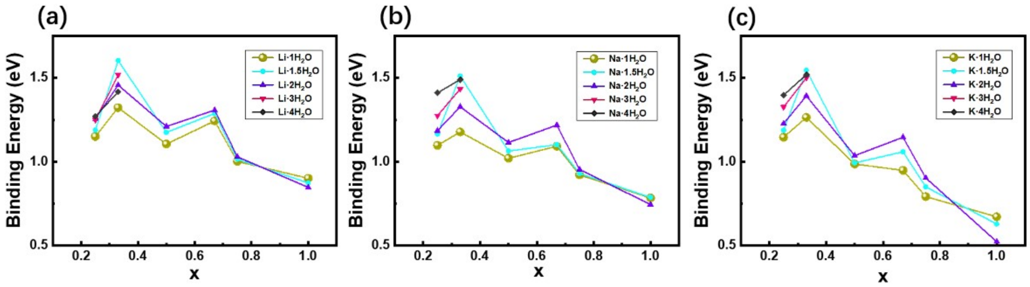
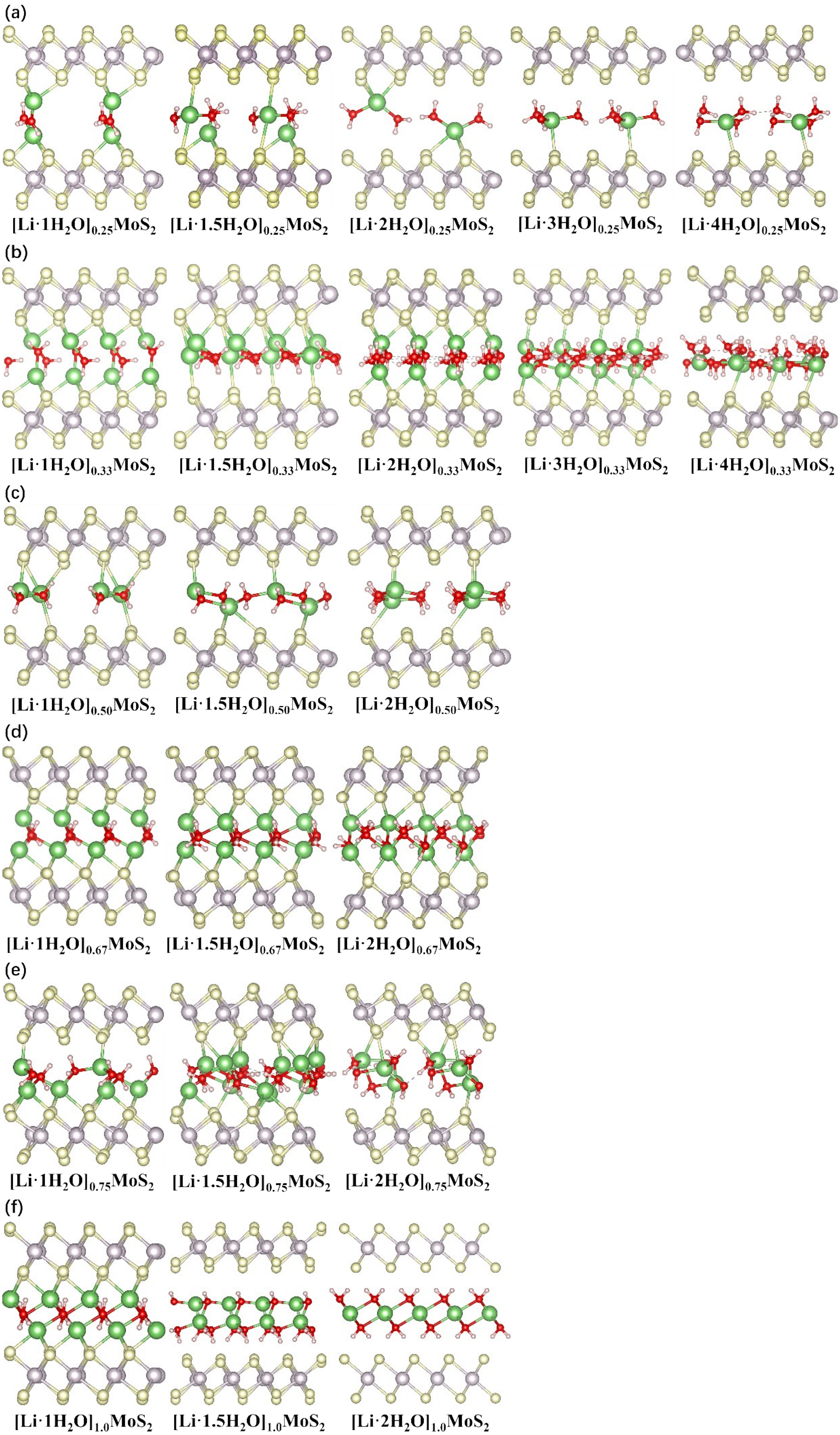
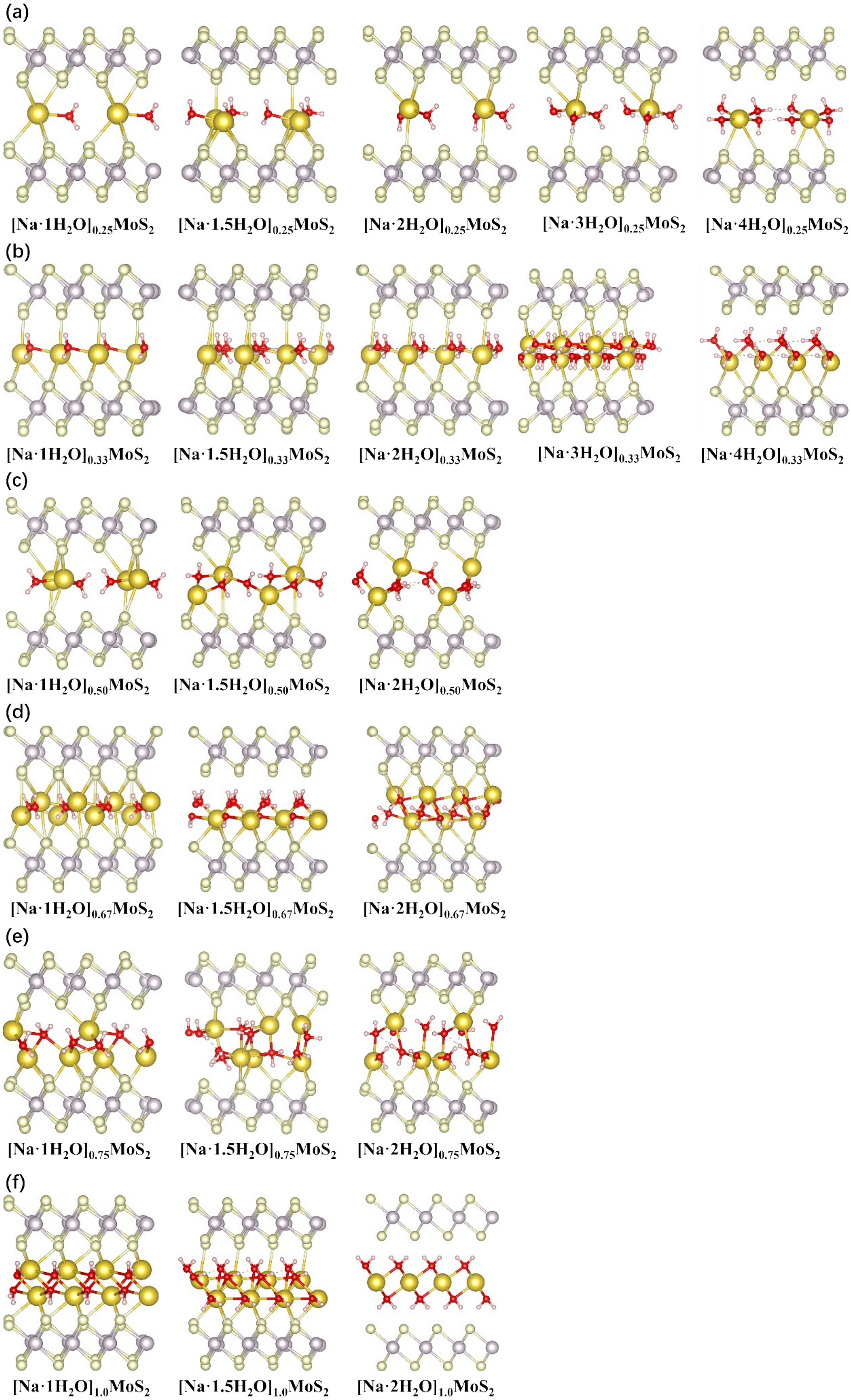


Figure S9. Effect of discharge status on the binding energy of the system. (a) $[Li{\cdot}mH_2O]_xMoS_2$ (m=1, 1.5, 2, 3, 4) at different levels of hydration decreases with increasing discharge status. (b) $[Na{\cdot}mH_2O]_xMoS_2$ (m=1, 1.5, 2, 3, 4) at different levels of hydration increases the binding energy of the system decreases with increasing discharge status. (c) $[K{\cdot}mH_2O]_xMoS_2$ (m=1, 1.5, 2, 3, 4) The binding energy of the system increases linearly with the increase of the discharge status.



(a)
[Li·1H2O]0.25MoS2
[Li·1.5H2O]0.25MoS2
[Li·2H2O]0.25MoS2
[Li·3H2O]0.25MoS2
[Li·4H2O]0.25MoS2
(b)
[Li·1H2O]0.33MoS2
[Li·1.5H2O]0.33MoS2
[Li·2H2O]0.33MoS2
[Li·3H2O]0.33MoS2
[Li·4H2O]0.33MoS2
(c)
[Li·1H2O]0.50MoS2
[Li·1.5H2O]0.50MoS2
[Li·2H2O]0.50MoS2
(d)
[Li·1H2O]0.67MoS2
[Li·1.5H2O]0.67MoS2
[Li·2H2O]0.67MoS2
(e)
[Li·1H2O]0.75MoS2
[Li·1.5H2O]0.75MoS2
[Li·2H2O]0.75MoS2
(f)
[Li·1H2O]1.0MoS2
[Li·1.5H2O]1.0MoS2
[Li·2H2O]1.0MoS2

Figure S10. Side view of $[Li \cdot mH_2O]_xMoS_2$ intra-layer intercalation. (a) Side views of 1, 1.5, 2,3 and 4 water molecules bound respectively for a discharge status of x=0.25. (b) Side views of 1, 1.5, 2,3 and 4 water molecules bound respectively for a discharge status of x=0.33. (c) Side views of 1, 1.5 and 2 water molecules bound respectively for a discharge status of x=0.50. (d) Side views of 1, 1.5 and 2 water molecules bound respectively for a discharge status of x=0.67. (e) Side views of 1, 1.5 and 2 water molecules bound respectively for a discharge status of x=0.75. (f) Side views of 1, 1.5 and 2 water molecules bound respectively for a discharge status of x=1.0.



(a)
$[Na\cdot 1H_2O]_{0.25}MoS_2$
$[Na\cdot 1.5H_2O]_{0.25}MoS_2$
$[Na\cdot 2H_2O]_{0.25}MoS_2$
$[Na\cdot 3H_2O]_{0.25}MoS_2$
$[Na\cdot 4H_2O]_{0.25}MoS_2$
(b)
$[Na\cdot 1H_2O]_{0.33}MoS_2$
$[Na\cdot 1.5H_2O]_{0.33}MoS_2$
$[Na\cdot 2H_2O]_{0.33}MoS_2$
$[Na\cdot 3H_2O]_{0.33}MoS_2$
$[Na\cdot 4H_2O]_{0.33}MoS_2$
(c)
$[Na\cdot 1H_2O]_{0.50}MoS_2$
$[Na\cdot 1.5H_2O]_{0.50}MoS_2$
$[Na\cdot 2H_2O]_{0.50}MoS_2$
(d)
$[Na\cdot 1H_2O]_{0.67}MoS_2$
$[Na\cdot 1.5H_2O]_{0.67}MoS_2$
$[Na\cdot 2H_2O]_{0.67}MoS_2$
(e)
$[Na\cdot 1H_2O]_{0.75}MoS_2$
$[Na\cdot 1.5H_2O]_{0.75}MoS_2$
$[Na\cdot 2H_2O]_{0.75}MoS_2$
(f)
$[Na\cdot 1H_2O]_{1.0}MoS_2$
$[Na\cdot 1.5H_2O]_{1.0}MoS_2$
$[Na\cdot 2H_2O]_{1.0}MoS_2$

Figure S11. Side view of $[Na \cdot mH_2O]_x MoS_2$ intra-layer intercalation. (a) Side views of 1, 1.5, 2,3 and 4 water molecules bound respectively for a discharge status of x=0.25. (b) Side views of 1, 1.5, 2,3 and 4 water molecules bound respectively for a discharge status of x=0.33. (c) Side views of 1, 1.5 and 2 water molecules bound respectively for a discharge status of x=0.50. (d) Side views of 1, 1.5 and 2 water molecules bound respectively for a discharge status of x=0.67. (e) Side views of 1, 1.5 and 2 water molecules bound respectively for a discharge status of x=0.75. (f) Side views of 1, 1.5 and 2 water molecules bound respectively for a discharge status of x=1.0.

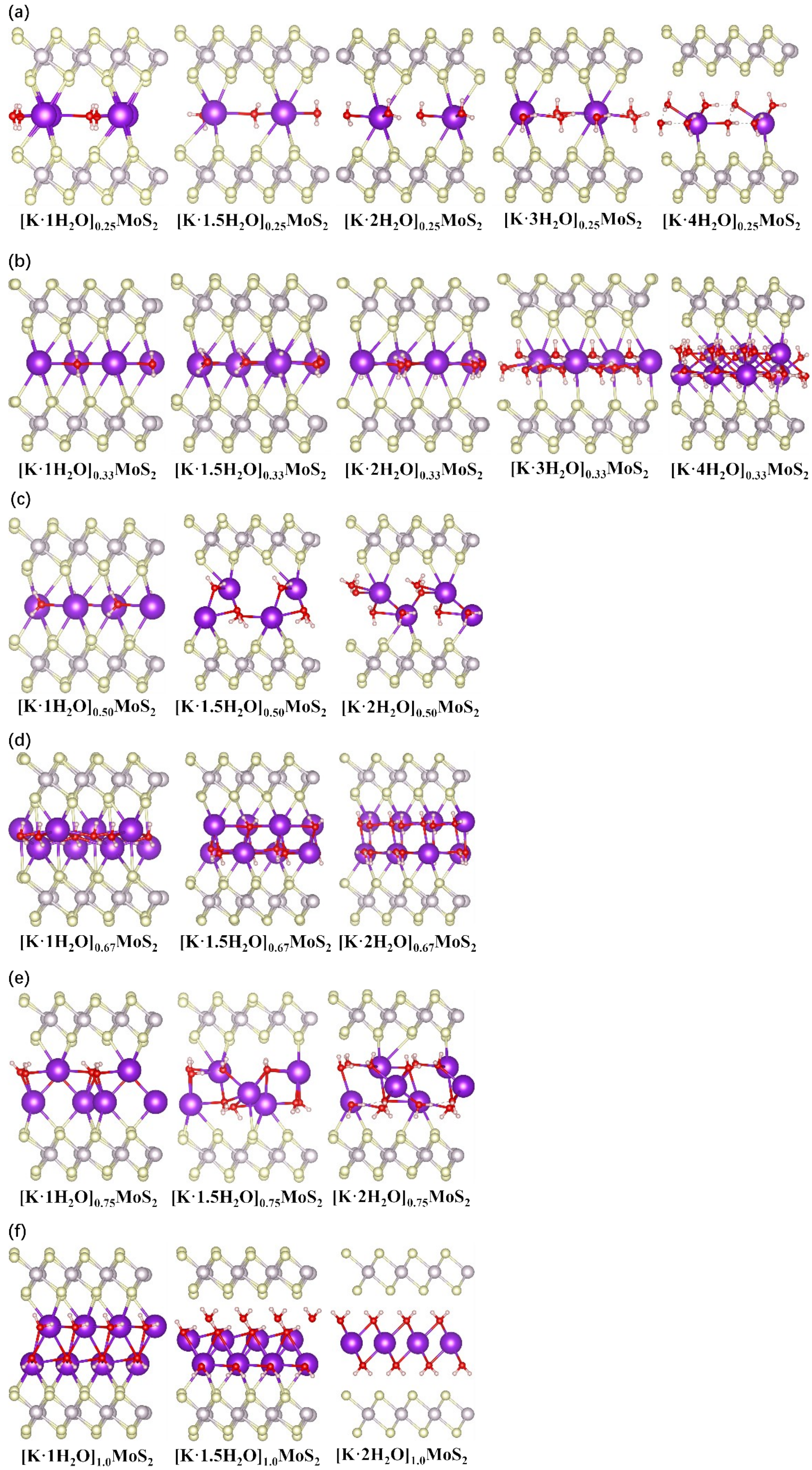

(a)
$[K\cdot 1H_2O]_{0.25}MoS_2$
$[K\cdot 1.5H_2O]_{0.25}MoS_2$
$[K\cdot 2H_2O]_{0.25}MoS_2$
$[K\cdot 3H_2O]_{0.25}MoS_2$
$[K\cdot 4H_2O]_{0.25}MoS_2$
(b)
$[K\cdot 1H_2O]_{0.33}MoS_2$
$[K\cdot 1.5H_2O]_{0.33}MoS_2$
$[K\cdot 2H_2O]_{0.33}MoS_2$
$[K\cdot 3H_2O]_{0.33}MoS_2$
$[K\cdot 4H_2O]_{0.33}MoS_2$
(c)
$[K\cdot 1H_2O]_{0.50}MoS_2$
$[K\cdot 1.5H_2O]_{0.50}MoS_2$
$[K\cdot 2H_2O]_{0.50}MoS_2$
(d)
$[K\cdot 1H_2O]_{0.67}MoS_2$
$[K\cdot 1.5H_2O]_{0.67}MoS_2$
$[K\cdot 2H_2O]_{0.67}MoS_2$
(e)
$[K\cdot 1H_2O]_{0.75}MoS_2$
$[K\cdot 1.5H_2O]_{0.75}MoS_2$
$[K\cdot 2H_2O]_{0.75}MoS_2$
(f)
$[K\cdot 1H_2O]_{1.0}MoS_2$
$[K\cdot 1.5H_2O]_{1.0}MoS_2$
$[K\cdot 2H_2O]_{1.0}MoS_2$

Figure S12. Side view of $[K \cdot mH_2O]_xMoS_2$ intra-layer intercalation. (a) Side views of 1, 1.5, 2,3 and 4 water molecules bound respectively for a discharge status of x=0.25. (b) Side views of 1, 1.5, 2,3 and 4 water molecules bound respectively for a discharge status of x=0.33. (c) Side views of 1, 1.5 and 2 water molecules bound respectively for a discharge status of x=0.50. (d) Side views of 1, 1.5 and 2 water molecules bound respectively for a discharge status of x=0.67. (e) Side views of 1, 1.5 and 2 water molecules bound respectively for a discharge status of x=0.75. (f) Side views of 1, 1.5 and 2 water molecules bound respectively for a discharge status of x=1.0.

A: Proof of Equation (8)

In order to get Eq. (8), take $\alpha \geq \beta$ as an example: a replacement reaction in the presence of β times as many hydrated ions will actually participate in the reaction, then:

$$\beta \quad X \cdot nH_2O \qquad Y \cdot mH_2O \quad \rightarrow \quad \Delta G^{X \cdot nH_2O}_{MoS_2} > \Delta G^{Y \cdot mH_2O}_{MoS_2}$$

where,

$$\mu_{MoS_2(s)} + \mu_{e^-} + \mu_{X^+(aq)} + \mu_{nH_2O} - \mu_{(X \cdot nH_2O)MoS_2(s)} > \mu_{MoS_2(s)} + \mu_{e^-} + \mu_{Y^+(aq)} + \mu_{mH_2O} - \mu_{(Y \cdot mH_2O)MoS_2(s)}$$

Substituting the following equations ito yields the above chemical potentials:

$$\mu_{X^+(aq)} = \mu^0_{X^+(aq)} + KTIn[X^+] \quad , \quad \mu_{Y^+(aq)} = \mu^0_{Y^+(aq)} + KTIn[Y$$

And we get:

$$\mu_{MoS_2(s)} + \mu_{e^-} + \mu^0_{X^+(aq)} + KTIn[X^+] + \mu_{nH_2O} - \mu_{(X \cdot nH_2O)MoS_2(s)} > \mu_{MoS_2(s)} + \mu_{e^-} + \mu^0_{Y^+(aq)} + KTIn[Y^+] + \mu_{mH_2O} - \mu_{(Y \cdot mH_2O)MoS_2(s)}$$

Simplify it to:

$$\mu^0_{X^+(aq)} + KTIn[X^+] + \mu_{nH_2O} - \mu_{(X \cdot nH_2O)MoS_2(s)} > \mu^0_{Y^+(aq)} + KTIn[Y^+] + \mu_{mH_2O} - \mu_{(Y \cdot mH_2O)MoS_2(s)}$$

$$\Downarrow$$

$$KTIn[X^+] - KTIn[Y^+] > \mu^0_{Y^+(aq)} - \mu^0_{X^+(aq)} + \mu_{mH_2O} - \mu_{nH_2O} - \mu_{(Y \cdot mH_2O)MoS_2(s)} + \mu_{(X \cdot nH_2O)MoS_2(s)}$$

$$\Downarrow$$

$$KTIn[X^+] - KTIn[Y^+] > -(\mu^0_{X^+(aq)} - \mu^0_{Y^+(aq)} + \mu_{nH_2O} - \mu_{mH_2O}\mu_{(X \cdot nH_2O)MoS_2(s)}$$

Then we define:

$$\Delta = \mu_{X^+ \, (aq)}^{0} - \mu_{Y^+ \, (aq)}^{0} + \mu_{nH_2O} - \mu_{mH_2O}\mu_{(X \cdot nH_2O)MoS_2(s)} + \mu_{(Y \cdot mH_2O)MoS_2}$$

Then:

$$KTIn[X^+] - KTIn[Y^+] > -\Delta$$

$$In[X^+] - In[Y^+] > -\frac{\Delta}{KT}$$

$$\frac{[X^+]}{[Y^+]} > e$$