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# Molecular engineering on a MoS<sub>2</sub> interlayer for high-capacity and rapid-charging aqueous ion batteries†

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Rechargeable aqueous ion batteries (AIBs) play essential roles in the increasing demand for high-performance energy storage systems, and yet they are hampered by the lack of suitable cathode materials because of the sluggish intercalation kinetics. In this work, we develop an effective and feasible strategy to enhance the performance of AIBs by broadening the interlayer spacing by using intercalated CO<sub>2</sub> molecules to promote the intercalation kinetics by using first principles simulations. Compared with pristine MoS<sub>2</sub>, the intercalation of CO<sub>2</sub> molecules with a 3/4 ML coverage significantly increases the interlayer spacing to 9.383 Å from 6.369 Å and the diffusivity is boosted by 12 orders of magnitude for Zn ions, 13 orders for Mg ions and one order for Li ions. Moreover, the concentrations of intercalating Zn, Mg and Li ions are enhanced by 7, 1 and 5 orders of magnitude, respectively. The significantly increased diffusivity and intercalation concentration of metal ions signify that intercalating CO<sub>2</sub> bilayer MoS<sub>2</sub> is a promising cathode material to realize metal ion batteries with a rapid charging capability and high storage capacity. The strategy developed in this work can be generally applied to increase the metal ion storage capacity in transition metal dichalcogenide (TMD)- and other layered material-based cathodes and make them promising for next-generation rapidly rechargeable batteries.

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## Introduction

Renewable and clean energy generation is a promising solution to counter the carbon dioxide emission mainly originating from burning fossil fuels. Several renewable energy harvesting technologies have been well developed.<sup>1–5</sup> The rapid development and high demands of renewable and clean energy sources, portable electronic devices, and electric vehicles have triggered great ambition for low cost, large-scale, and high energy density battery systems for energy storage. Due to the high cost and safety hazards and the scarce source of metal Li, it is desirable to find alternative energy storage systems to replace Li-ion batteries (LIBs). In this regard, aqueous multivalent metal ion batteries (AMMIBs) are attracting tremendous attention and are considered promising substitutes for LIBs.<sup>6–13</sup> Due to high safety, low cost, eco-friendliness, and high ionic conductivity (1000 times higher than organic electrolytes), rechargeable AMMIBs are promising batteries for grid-scale electrochemical

energy storage. Among rechargeable AMMIBs, aqueous zinc-ion batteries (ZIBs)<sup>14–17</sup> and aqueous magnesium-ion batteries (MIBs)<sup>18–20</sup> have attracted remarkable attention worldwide because they exhibit a high volumetric energy density of 5851 mA h mL<sup>−1</sup> for ZIBs<sup>21,22</sup> and 3833 mA h mL<sup>−1</sup> for MIBs.<sup>23–25</sup> However, the main challenge lies in developing suitable cathode materials for AMMIBs.

Several materials have been developed as promising cathode materials for AMMIBs. Vanadium oxides with a tunnel structure as cathode materials show high Zn-ion storage properties,<sup>26–31</sup> but the dissolution of vanadium in water-based electrolytes remains a significant challenge.<sup>32</sup> A composite of manganese dioxide and carbon molecular sieves ( $\delta$ -MnO<sub>2</sub>@CMS) with a core-shell structure and Chevrel phase Mo<sub>6</sub>S<sub>8</sub> were reported as cathode materials for MIBs.<sup>33–35</sup> The practicality of MIBs is hampered by the absence of suitable high-performance cathode materials with rapid Mg ion diffusion.<sup>36</sup> Transition metal dichalcogenides (TMDs) have attracted extensive attention due to their potential applications in cathode materials for rechargeable AMMIBs. The layer structure of TMDs and their weak interlayer interaction *via* van der Waals (vdW) force are appealing properties for multivalent metal ion diffusion and intercalation,<sup>37–41</sup> especially for large metal ion-based AMMIBs. Among TMDs, MoS<sub>2</sub> is considered one of the most promising cathode materials for AMMIBs,<sup>42,43</sup> which suggests the feasibility of employing MoS<sub>2</sub> as a functional AMMIB cathode material. This scarcity in the report suggests the heightened

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challenges in observing reversible metal ion storage in pristine MoS<sub>2</sub>. The high intercalation energy barrier of metal ions leads to the low specific capacities recorded for the MoS<sub>2</sub> systems (for Zn 1–40 mA h g<sup>-1</sup>).<sup>44–46</sup> For example, it was found that Zn<sup>2+</sup> diffusion across the MoS<sub>2</sub> framework was further hampered by its low electrochemical activity and low conductivity.<sup>45</sup> Hence, it is essential to explore effective modification methods to “activate” MoS<sub>2</sub> towards reversible metal ion storage for leveraging the advantages of MoS<sub>2</sub>. Phase engineering was a highly appealing strategy for modulating the chemical and electrical properties. 1T-MoS<sub>2</sub>, with a tetragonal symmetry, in which each Mo atom has an octahedral coordination with S atoms, has metallic conductivity, resulting in a lower metal ion diffusion barrier than in 2H-MoS<sub>2</sub>. However, 1T MoS<sub>2</sub> is a metastable phase, and producing 1T MoS<sub>2</sub> on a large scale remains a big challenge. An alternative strategy is to tune the intercalation energy by changing the interlayer spacing. It was demonstrated that intercalation oxygen could increase their interlayer spacing (9.5 Å) and tune hydrophilicity, resulting in boosting the Zn ion diffusion kinetics by 3 orders of magnitude in MoS<sub>2</sub>.<sup>44</sup> Sandwiched structures consisting of monolayer MoS<sub>2</sub> and carbon (MoS<sub>2</sub>:C)<sup>47</sup> and MoS<sub>2</sub>/graphene<sup>48</sup> were reported to realize high-performance sodium ion and Zn ion batteries thanks to the expanded interlayer spacing (11.6 Å). Although many efforts have been made to study layered MoS<sub>2</sub>, the high capacity and long life-cycle times of MoS<sub>2</sub>-based cathodes have not yet been coexisting for practical utilization. More work needs to be conducted to expand the interlayer spacing further and enhance the hydrophilicity of MoS<sub>2</sub> to realize high reversible capacity and superb durability, which remains a big challenge.

In this study, we demonstrate a feasible and effective strategy to reduce metal ion diffusion barrier by using intercalation of CO<sub>2</sub> molecules to expand the MoS<sub>2</sub> interlayer spacing through density functional theory (DFT) simulations. Our comprehensive DFT results reveal that the intercalated MoS<sub>2</sub> by CO<sub>2</sub> is a promising cathode material for realizing rapidly chargeable metal ion batteries.

## Results and discussion

AA' stacking bilayer MoS<sub>2</sub> was chosen to investigate the metal ion diffusion in this study since it has the lowest relative formation energy among five possible stacking configurations.<sup>49</sup> The optimized unit cell of AA' stacking bilayer MoS<sub>2</sub> is shown in Fig. S1a.† The optimized lattice constants are  $a = b = 3.204$  Å and the layer spacing is 6.37 Å, which is quite close to the reported value of 6.21 Å.<sup>49</sup> The stacking formation  $E_S$  of bilayer MoS<sub>2</sub> was calculated based on the definition of the total energy difference per atom between the bilayer and two individual monolayers  $E_S = \frac{E_{\text{bilayer}} - 2E_{\text{monolayer}}}{N}$ , where  $N$  is the total number of atoms in bilayer MoS<sub>2</sub> unit cell (4 S and 2 Mo atoms). The calculated AA' stacking formation energy is -34.33 meV per atom, well agreeing with the reported value of -25.13 meV.<sup>49</sup> The tiny difference may originate from the van der Waals (vdW) correction methods.<sup>50</sup> The optimized unit cell was expanded to build  $5 \times 5 \times 1$  supercells containing 50 Mo and 100 S atoms

shown in Fig. S1b,† and rectangle supercells ( $a = 22.201$  Å and  $b = 19.224$  Å) with 96 Mo and 192 S atoms shown in Fig. S1b.†

It was well explored that the interlayer spacing and coupling have a strong effect on the intercalation energy of metal ions.<sup>44,47,48</sup> In this study, the intercalating CO<sub>2</sub> molecules were used to expand the interlayer spacing of bilayer MoS<sub>2</sub>. First, the possible embedding configurations of the intercalating CO<sub>2</sub> molecules were investigated, and the optimized configurations and the calculated relative energies are shown in Fig. S2.† In which, the CO<sub>2</sub> molecule has two possible embedding sites, and the computed relative energies reveal that CO<sub>2</sub> prefers to stay at the bridge site rather than the hollow site. The intercalation energy of an intercalating CO<sub>2</sub> molecule  $E_{\text{In}}$  was calculated based on  $E_{\text{In}} = E_{(\text{MoS}_2+\text{CO}_2)} - (E_{\text{MoS}_2} + E_{\text{CO}_2})$ , where,  $E_{(\text{MoS}_2+\text{CO}_2)}$ ,  $E_{\text{MoS}_2}$  and  $E_{\text{CO}_2}$  are the total energies of bilayer MoS<sub>2</sub> with one embedding CO<sub>2</sub> molecule, pristine bilayer MoS<sub>2</sub> and an isolated CO<sub>2</sub> molecule. For an isolated CO<sub>2</sub> molecule energy calculation, we put one CO<sub>2</sub> molecule in a cube model ( $a = b = c = 15$  Å), and the calculated ground state energy is considered the energy of an isolated CO<sub>2</sub> molecule. The calculated intercalation energy of one embedding CO<sub>2</sub> molecule is 2.98 eV at the bridge site. With one intercalating CO<sub>2</sub> molecule, the interlayer spacing slightly increases to 7.61 Å from 6.37 Å (pristine bilayer MoS<sub>2</sub>). The relatively high intercalation energy of the CO<sub>2</sub> molecule may originate from the strong interlayer coupling. Therefore, more CO<sub>2</sub> molecules may need to be intercalated to expand the interlayer spacing and reduce the interlayer coupling further. Meanwhile, we also investigate the intercalating CO<sub>2</sub> molecule diffusion in bilayer MoS<sub>2</sub>. According to the symmetry of the 2H MoS<sub>2</sub> structure, the intercalating CO<sub>2</sub> has three possible diffusion pathways: armchair, zigzag and crossing, as shown in Fig. 1a. The calculated diffusion barriers are 0.209, 0.209 and 0.394 eV as shown in Fig. 1b. The computed results reveal that the CO<sub>2</sub> diffusion barriers along the zigzag and armchair directions are identical, revealing an isotropic diffusivity of the intercalating CO<sub>2</sub> in the bilayer MoS<sub>2</sub>. Also, the direct crossing diffusion is more difficult due to its higher diffusion barrier than zigzag and armchair directions originating from the high relative energy at the hollow site. The calculated diffusion barriers of 0.209 and 0.394 eV also show that the intercalation CO<sub>2</sub> would be kinetically stable in the bilayer MoS<sub>2</sub> since the room temperature is about 0.0256 eV. Temperature and pressure contributions are not included in the results obtained from DFT simulations, which only are valid at  $T = 0$  K and  $P = 0$  atm. The results from DFT simulations can be used as an input to thermodynamics considerations to describe a situation of finite temperature and pressure. To investigate the thermodynamic stability of the CO<sub>2</sub> intercalated MoS<sub>2</sub>, we performed DFT simulations considering appropriate thermodynamic functions, and the CO<sub>2</sub> intercalated stacking Gibbs free energy as a function of the temperature and pressure can be calculated

$$\Delta G(T, P) = E_S + \Delta E_{\text{ZPE}} - T\Delta S_{\text{vib}} + PV \quad (1)$$

where  $E_S$  is the normalized CO<sub>2</sub> intercalated stacking energy directly from DFT simulations, defined as





Fig. 1 (a) Three possible diffusion pathways of the intercalation of CO<sub>2</sub> molecule. (b) The diffusion barrier of CO<sub>2</sub> in bilayer MoS<sub>2</sub>. The CO<sub>2</sub> molecule coverage-dependent intercalation energies (c) and layer spacing (d).

$$E_S = (E_{(\text{MoS}_2+n\text{CO}_2)} - (E_{(\text{MoS}_2)} + nE_{\text{CO}_2}))/n \quad (2)$$

where  $E_{(\text{MoS}_2+n\text{CO}_2)}$ ,  $E_{(\text{MoS}_2)}$  and  $E_{\text{CO}_2}$  are the energies of monolayer or bilayer MoS<sub>2</sub> with  $n\text{CO}_2$  molecules, a clean monolayer, or bilayer MoS<sub>2</sub> and the CO<sub>2</sub> molecule, respectively.  $E_{\text{ZPE}}$  and  $S_{\text{vib}}$  are the zero point energy and the entropy contributed by vibration frequency  $\omega_i$  and  $T = 298$  K.  $E_{\text{ZPE}}$  can be calculated using  $E_{\text{ZPE}} = \sum_i \frac{\hbar\omega_i}{2}$ , and  $S_{\text{vib}}$  can be calculated using

$$S_{\text{vib}} = \sum_i \left[ K_b T \ln \left( 1 - \exp \left( -\frac{\hbar\omega_i}{K_b T} \right) \right) \right], \text{ where } \hbar \text{ is the reduced}$$

Planck's constant and  $\omega_i$  is the  $i$ -th vibrational frequency of the diffusing ion. As a benchmark, we computed the entropy CO<sub>2</sub> molecule and the calculated entropy is 214.419 J (mol<sup>-1</sup> K<sup>-1</sup>), which is comparable with the standard molar entropy of 213.79 J (mol<sup>-1</sup> K<sup>-1</sup>). In this study, we proposed two pathways to intercalate CO<sub>2</sub> into MoS<sub>2</sub>, directly intercalating CO<sub>2</sub> molecules into one bilayer MoS<sub>2</sub> (P1) or two monolayers (P2) one by one as shown in Fig. S6a.† Under the condition of  $P = 0$  atm, we calculated the CO<sub>2</sub> intercalated stacking Gibbs free energies, and the results are shown in Fig. S6b.† In comparison, using two monolayers (P2) may easily realize the CO<sub>2</sub> intercalated MoS<sub>2</sub>. As shown in Fig. S6b,† the stacking Gibbs free energy of one CO<sub>2</sub> intercalated MoS<sub>2</sub> is 3.48 eV using the P1 pathway and dramatically decreases to -3.50 eV. When the CO<sub>2</sub> coverage increases to 3/4 and 1 ML, the stacking Gibbs free energies of the CO<sub>2</sub> intercalated MoS<sub>2</sub> are 0.36 and 0.26 eV using the P1 pathway, much higher than those of -0.16 eV and -0.13 eV

using the P2 pathway, respectively. Based on the definition of the stacking Gibbs free energy, the negative value denotes that the final product of the CO<sub>2</sub> intercalated MoS<sub>2</sub> is thermodynamically stable, and the reaction is exothermic. It should be noted that the calculated stacking Gibbs free energies of the CO<sub>2</sub> intercalated MoS<sub>2</sub> are based on  $P = 0$  atm. Based on eqn (1), we may estimate the pressure needed to realize 3/4 ML CO<sub>2</sub> intercalation when the Gibbs free energy is zero using the P1 process. The estimated pressure is 107 atm (0.0108 GPa) to stabilize CO<sub>2</sub> molecule (3/4 ML) intercalating in bilayer MoS<sub>2</sub>. Furthermore, intercalating one CO<sub>2</sub> molecule may require higher pressure ( $P = 961$  atm). Based on the results shown in Fig. S6b,† it can be seen that the intercalated structure appears unstable at a low coverage and becomes more stable at a high coverage, which reveals a substantial kinetic barrier in realizing the CO<sub>2</sub> molecules intercalated structure. Not surprisingly, the calculated CO<sub>2</sub> diffusion barriers of 0.209 and 0.394 eV shown in Fig. 1b can be considered the kinetic barrier for realizing a stable structure at a high coverage. The diffusion barriers also reveal that the intercalating CO<sub>2</sub> would be kinetically stable in the bilayer MoS<sub>2</sub> since the diffusion barriers are much higher than 0.0256 eV (room temperature). Also, we performed *ab initio* molecular dynamics (AIMD) for one CO<sub>2</sub> molecule intercalated MoS<sub>2</sub> and bilayer MoS<sub>2</sub> with a CO<sub>2</sub> coverage of 1 ML at 300 K within 1000 fs. Fig. S7† shows intercalated CO<sub>2</sub> molecules stabilized in the bilayer MoS<sub>2</sub>, maintaining the 2H structural symmetry. The optimized models obtained from AIMD simulations also confirm the thermodynamical stability. Therefore, the CO<sub>2</sub> intercalated MoS<sub>2</sub> is thermodynamically stable and feasible. The diffusion barrier also indicates that intercalating CO<sub>2</sub> molecules can easily form a uniform distribution in bilayer MoS<sub>2</sub>. The relative energy results also reveal that intercalating CO<sub>2</sub> molecules prefer to separate rather than cluster in the bilayer MoS<sub>2</sub>.

To expand the interlayer spacing and reduce the interlayer coupling further, more CO<sub>2</sub> molecules were intercalated into the bilayer MoS<sub>2</sub>. The CO<sub>2</sub> coverage-dependent intercalation energy  $E_f$  was computed based on the definition of  $E_f = E_{(\text{MoS}_2+n\text{CO}_2)} - E_{(\text{MoS}_2+(n-1)\text{CO}_2)} - E_{\text{CO}_2}$ , where  $E_{(\text{MoS}_2+n\text{CO}_2)}$ ,  $E_{(\text{MoS}_2+(n-1)\text{CO}_2)}$  and  $E_{\text{CO}_2}$  are the energies of  $n\text{CO}_2$  intercalating into MoS<sub>2</sub>,  $(n-1)\text{CO}_2$  intercalating into MoS<sub>2</sub> and an isolated CO<sub>2</sub> molecule. In this study, we only consider the CO<sub>2</sub> coverage of 1/8 ML, 1/4 ML, 1/2 ML, 3/4 ML and 1 ML (24 CO<sub>2</sub> molecules) using big rectangle supercells composed of 96 Mo and 192 S atoms, and the optimized models are shown in Fig. S5.† The calculated CO<sub>2</sub> molecule coverage-dependent intercalation energies and the corresponding layer spacings are shown in Fig. 1c and d. The simulation results show that the intercalation energy decreases with the increase in coverage, and the 3/4 ML coverage of the CO<sub>2</sub> molecules results in the lowest intercalation energy of -0.615 eV, and the intercalation energy is increased when the CO<sub>2</sub> coverage further increases. Not surprisingly, the interlayer spacing increases with the increase in coverage, resulting in the largest layer spacing of 9.384 Å among five considered coverages. A further increase in coverage (1 ML) makes the interlayer spacing decrease when the CO<sub>2</sub> coverage is higher than 3/4 ML. Based on the results shown in Fig. S5,† the



CO<sub>2</sub> intercalated MoS<sub>2</sub> keeps the structural stability with increased coverage even at the coverage of 1 ML. The calculated AA' stacking formation energy of bilayer MoS<sub>2</sub> with a CO<sub>2</sub> molecule coverage of 3/4 ML increases to -28.01 meV per atom, which is higher than that in pristine MoS<sub>2</sub> of -34.33 meV per atom. A comparison of these results reveals that the intercalation of CO<sub>2</sub> weakens the layer coupling. The calculated interlayer spacing of the bilayer MoS<sub>2</sub> with 3/4 ML coverage is 9.384 Å, slightly higher than that with a 1 ML coverage of 9.356 Å. It should be noted that the interlayer spacing is the average distance between two Mo atoms in the different layers. Based on the results shown in Fig. 1d, we may consider that the expanded interlayer spacing is converged when the CO<sub>2</sub> coverage is more than 3/4 ML. Therefore, we adopted the optimized bilayer MoS<sub>2</sub> models with a CO<sub>2</sub> coverage of 3/4 ML to investigate the diffusion of metal ions.

In this study, we investigated the diffusion barriers of three metal ions (Zn, Mg, and Li) in bilayer MoS<sub>2</sub>. Based on the structure and 2H symmetry of the bilayer MoS<sub>2</sub>, we proposed two possible embedding sites (tetrahedral *T<sub>h</sub>* and octahedral *O<sub>h</sub>*), as shown in Fig. S3† Considering the Zn ion as a representative, we calculated the relative energies of two possible embedding sites, and the results are shown in Fig. S4† and proposed the possible diffusion pathway of metal ions as (b) → (c) → (d), as shown in Fig. S4.† The diffusion barriers of Zn, Mg and Li ions in the pristine bilayer MoS<sub>2</sub> were calculated, and the results are shown in Fig. 2a. The calculated diffusion barriers of Zn, Mg and Li ions in the pristine bilayer MoS<sub>2</sub> are 0.785, 0.942 and 0.356 eV, respectively. The temperature-dependent ion diffusivity of the three metal ions was predicted based on the computed diffusion barriers considering thermal corrections (ESI†), and the results are shown in Fig. 2b. The calculated ion diffusivities are  $4.18 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ ,  $1.01 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$  and  $6.90 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  at room temperature, corresponding to the Zn, Mg, and Li ions, respectively. These calculation results indicate that the pristine bilayer MoS<sub>2</sub> is a cathode material with limited performance for metal ion batteries. Clearly, new

strategies are highly demanded to reduce the ion diffusion barrier for high-performance batteries.

We further demonstrated a feasible and effective strategy to reduce the ion diffusion barrier by using intercalating CO<sub>2</sub> molecules to expand the MoS<sub>2</sub> interlayer spacing. With a high coverage of 3/4 ML CO<sub>2</sub>, the interlayer spacing of MoS<sub>2</sub> is expanded to 9.383 Å. Compared with the interlayer spacing of 6.369 Å obtained from the pristine bilayer MoS<sub>2</sub>, a bigger interlayer spacing results in a weak interaction between layers and lower diffusion barriers of metal Li, Zn and Mg ions. With the intercalating CO<sub>2</sub> molecules, the results shown in Fig. 2c and d reveal that the diffusion barriers of Zn and Mg were dramatically reduced to 0.026 and 0.064 eV, significantly boosting the Zn and Mg ion diffusion by 12 and 14 orders of magnitude at room temperature, while only by one order of magnitude for Li ions. Our comprehensive DFT results reveal that the CO<sub>2</sub> intercalated MoS<sub>2</sub> is a promising cathode material for realizing rapidly chargeable Zn and Mg metal ion batteries. Compared with previously reported results shown in Table 1, the calculated diffusivity of Zn in the bilayer MoS<sub>2</sub> is much smaller than the experimental one in the bulk MoS<sub>2</sub>,<sup>51</sup> and Mg has a higher diffusivity in the bilayer MoS<sub>2</sub> than in the bulk MoS<sub>2</sub>. As for Li ions, they have nearly the same diffusivity in the bilayer MoS<sub>2</sub> as in the bulk MoS<sub>2</sub>. It should be noted that the diffusivities of three ions are very low, showing that the pristine bilayer and bulk MoS<sub>2</sub> are not suitable for metal ion batteries. Comparing the experimental values shown in Table 1 and our theoretical values reveal that the CO<sub>2</sub> intercalated MoS<sub>2</sub> has significant potential for metal ion batteries. However, Zn and Mg ions have much higher diffusivity in the CO<sub>2</sub> intercalated MoS<sub>2</sub> than in O-modified<sup>51</sup> and MoS<sub>2</sub>/graphene hetero-junctions.<sup>52</sup> Not surprisingly, no significant improvement in Li ion diffusivity was found in our study compared with W and Mo alloyed MoS<sub>2</sub>.<sup>53</sup>

Beyond the metal ion diffusion barrier and diffusivity, another challenge is to improve the storage capacity of AMMIBs, mainly determined by the embedding concentration of ions. Meanwhile the ion concentration or solubility in cathode materials is governed by the intercalation energy of metal ions.<sup>49</sup> Consequently, we calculated the intercalation energy of embedded metal ions in the pristine and the intercalating CO<sub>2</sub> bilayer MoS<sub>2</sub> (ESI†). The results are shown in Fig. 3a reveal that the intercalation energy of Zn ion significantly decreases to 0.411 eV from 1.279 eV in the pristine bilayer MoS<sub>2</sub>, and the intercalation energy of Li dramatically decreases to 0.204 eV from 0.898 eV. However, the intercalation energy of Mg slightly decreases to 0.463 eV from 0.613 eV. Based on the calculated intercalation energies of metal ions in the pristine and CO<sub>2</sub>

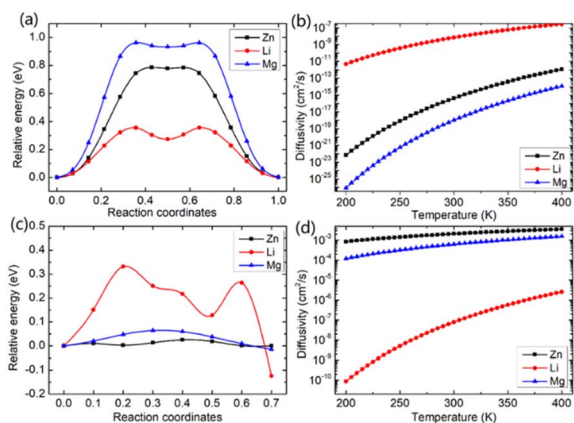


Fig. 2 The computed diffusion barriers (a) and (c) and diffusivities (b) and (d) of metal Zn, Li, and Mg ions in pristine bilayer MoS<sub>2</sub> and in bilayer MoS<sub>2</sub> with an intercalating CO<sub>2</sub> coverage of 3/4 ML, respectively.

Table 1 The comparison between the computed ion diffusivity ( $\text{cm}^2 \text{ s}^{-1}$ ) with reported experimental values shown in brackets

Ions	Bilayer MoS <sub>2</sub>	Bulk MoS <sub>2</sub>	CO <sub>2</sub> -MoS <sub>2</sub>	Modified MoS <sub>2</sub>
Zn	$4.18 \times 10^{-16}$	$(8 \times 10^{-12})$	$2.08 \times 10^{-3}$	$(9 \times 10^{-8} \text{ to } 10^{-9})$ <sup>51</sup>
Mg	$1.01 \times 10^{-18}$	$(1 \times 10^{-20})$	$6.26 \times 10^{-4}$	$(3.24 \times 10^{-9})$ <sup>52</sup>
Li	$6.90 \times 10^{-9}$	$(3.78 \times 10^{-9})$	$7.84 \times 10^{-8}$	$(1.2 \times 10^{-8})$ <sup>53</sup>



embedded bilayer MoS<sub>2</sub>, we computed the temperature-dependent intercalation ion concentration (ESI<sup>+</sup>), and the results are shown in Fig. 3b. The Zn ion embedding concentration is enhanced by 7 orders of magnitude to  $3.63 \times 10^{11} \text{ cm}^{-2}$ , and the Li ion embedding concentration is enhanced by 5 orders of magnitude to  $1.98 \times 10^{13} \text{ cm}^{-2}$  at 300 K. However, the Mg ion embedding concentration is slightly boosted by just one order of magnitude to  $1.25 \times 10^{11} \text{ cm}^{-2}$ . In contrast, the intercalating CO<sub>2</sub> molecules have significant contributions to the enhancement of the embedding concentration of Zn and Li ions but have a feeble effect on Mg ions. Hence, we consider that the intercalation of CO<sub>2</sub> molecules significantly promotes bilayer MoS<sub>2</sub> to be a promising cathode material for high-capacity Zn and Li ion batteries, but only slightly for Mg ion batteries.

To gain an in-depth understanding of the diffusion barrier decrease originating from the intercalating CO<sub>2</sub> and the possible chemical reaction between CO<sub>2</sub> and embedding metal ions, we analyzed the charge difference between embedding metal ions and bilayer MoS<sub>2</sub>. As a benchmark, the charge differences of metal ions in the pristine bilayer MoS<sub>2</sub> were evaluated as well. We calculate the charge density difference between the embedding ions and CO<sub>2</sub> molecule intercalated bilayer MoS<sub>2</sub> systems by using the formula of  $\Delta\rho = \rho_{(\text{host}+\text{M})} - (\rho_{\text{host}} + \rho_{\text{M}})$ , where  $\rho_{(\text{host}+\text{M})}$ ,  $\rho_{\text{host}}$  and  $\rho_{\text{M}}$  represent the charge density of the ion embedded MoS<sub>2</sub>, the pristine MoS<sub>2</sub> and the isolated metal ion, respectively. The simulation results are shown in Fig. 4, in which the purple color corresponds to the charge accumulation forming bonding states, and the green color represents the charge depletion forming anti-bonding states. Fewer bonding states and more anti-bonding states make the interaction stronger between embedded ions and their host systems. For the Zn ion embedding system as shown in Fig. 4a and d, the intercalating CO<sub>2</sub> molecules result in more charge depletion than in the pristine MoS<sub>2</sub>, resulting in a decrease of the Zn ion intercalation energy. A similar tendency is also found in the Li ion embedding system shown in Fig. 4c and f. However, no significant change can be seen in the Mg ion embedding system shown in Fig. 4b and e. The results shown in Fig. 4 indicate that the intercalation of CO<sub>2</sub> molecules has a great contribution to the intercalation energy of Zn and Li ions only, consistent with the calculated intercalation energies of metal ions as shown in Fig. 3a. Also, we found no electron

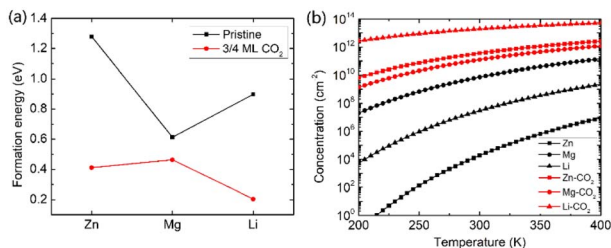


Fig. 3 The intercalation energies (a) and temperature-dependent concentration (b) of metal ions of Zn, Mg and Li in the pristine and modulated bilayer MoS<sub>2</sub> with an intercalating CO<sub>2</sub> coverage of 3/4 ML.

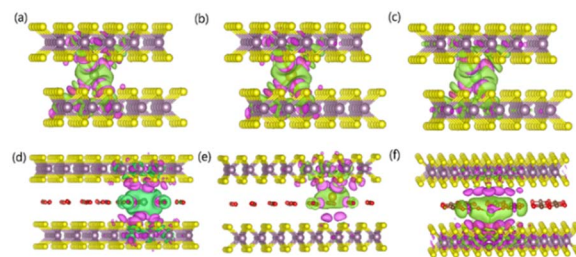


Fig. 4 Charge density difference isosurfaces for (a) Zn, (b) Mg and (c) Li interacting with pristine MoS<sub>2</sub> and the charge density difference isosurfaces for (d) Zn, (e) Mg and (f) Li interacting with CO<sub>2</sub> embedded MoS<sub>2</sub>. The purple (green) color corresponds to charge accumulation (depletion). The isosurface is taken as  $6 \times 10^{-5} \text{ e}/\text{\AA}$ .

transfer and bond formation between intercalating CO<sub>2</sub> and embedded Zn and Mg ions, except for the Li-ion system. We also calculated the projected density of states (PDOS) of the pristine and intercalated CO<sub>2</sub> (3/4 ML) MoS<sub>2</sub> as shown in Fig. 5a and b, respectively. It can be seen that O-p orbitals have strong interaction with Mo-d orbitals. The results reveal that CO<sub>2</sub> can be stabilized in the bilayer MoS<sub>2</sub>. We also computed d-band centers of Mo from the intercalated CO<sub>2</sub> (3/4 ML) and pristine MoS<sub>2</sub>, and the results are shown in Fig. 5c. Intercalated CO<sub>2</sub> molecules push the d-band of Mo to a higher energy state and result in a lower d-band center than in the pristine MoS<sub>2</sub>, and further enhance the metal ion solubility in intercalating CO<sub>2</sub> bilayer MoS<sub>2</sub>. Bader charge<sup>54</sup> provides the definition of the chemical bond for charge analysis, which is based on the

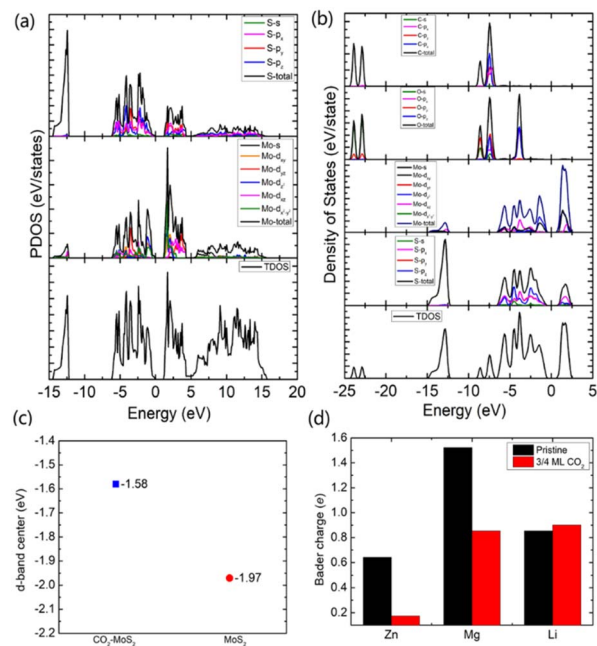


Fig. 5 The calculated projected density of states (PDOS) of the pristine MoS<sub>2</sub> (a) and CO<sub>2</sub> intercalated MoS<sub>2</sub> (b). (c) The calculated Mo d-band center with respect to the Fermi level (set to zero) of CO<sub>2</sub> intercalated and pristine MoS<sub>2</sub>. (d) The calculated Bader charge of metal ions in the pristine and CO<sub>2</sub> intercalated (3/4 ML) MoS<sub>2</sub>.



electronic charge density. In Fig. 5d, the Bader charges for Zn and Mg are significantly decreased but there is a little increase for Li ions with CO<sub>2</sub> embedding. The result reveal that intercalating CO<sub>2</sub> molecules weaken the ion interaction of Zn and Mg with host elements, while the slightly increased Bader charge of Li ions reveals that Li ions have strong chemical interaction with CO<sub>2</sub> as shown in Fig. 4f, which well explains the multi-saddle points in Li NEB results shown in Fig. 2c. We consider that those embedding CO<sub>2</sub> molecules would not react with Zn and Mg and may form chemical bonds with Li ions. Therefore, we believe that it is feasible to use CO<sub>2</sub> intercalation for improving the performance of MoS<sub>2</sub>-based Zn and Mg ion batteries.

To gain an in-depth understanding of the location of CO<sub>2</sub> insertion at active sites, we computed the work function of pristine and CO<sub>2</sub> with/without metal ion intercalation bilayer MoS<sub>2</sub>. The work function  $\Phi$  is defined as the vacuum energy respective to the Fermi level ( $\Phi = E_{\text{vac}} - E_{\text{F}}$ ). The work function of bilayer MoS<sub>2</sub> highly depends on the crystal orientation, the presence of impurities, defects, and doping. The calculated local potentials along the z-direction are shown in Fig. S8a.† It should be noted that the results shown in Fig. S8a† are simply plotted in one figure without considering the common alignment reference. Based on the calculated local potential along the z-direction shown in Fig. S8a,† we computed the work functions of selected five cases and the results are shown in Fig. S8b.† It can be seen that the calculated work function of the pristine bilayer MoS<sub>2</sub> is 6.02 eV, and the same as that of 3/4 ML CO<sub>2</sub> embedded MoS<sub>2</sub>. The results reveal that intercalated CO<sub>2</sub> molecules do not affect the work function. Therefore, we considered that CO<sub>2</sub> is a promising material to expand the interlayer spacing of layered MoS<sub>2</sub>. With metallic ion (Zn, Mg and Li) insertion, the work function decreases to 5.65 eV in Zn intercalated 3/4 ML CO<sub>2</sub> embedded MoS<sub>2</sub>, further decreases to 4.78 eV in Mg intercalated 3/4 ML CO<sub>2</sub> embedded MoS<sub>2</sub>, and further decreases to 4.53 eV in Li intercalated 3/4 ML CO<sub>2</sub> embedded MoS<sub>2</sub>.

## Conclusions

In conclusion, we developed a simple and effective strategy by tuning the interlayer spacing of MoS<sub>2</sub> and the intercalation energy of Zn, Mg and Li ions for cathode materials of rapidly chargeable batteries. Employing DFT simulations, we demonstrate that the intercalation of CO<sub>2</sub> molecules with a 3/4 ML coverage effectively expands the interlayer spacing, reduces layer coupling of bilayer MoS<sub>2</sub>, and significantly reduces the diffusion barrier and intercalation energies of metal ions, achieving high performance metal ion batteries. As a result, the diffusivities of Zn and Li increase by 12 and 13 orders of magnitude, and the intercalating ion concentration or the storage capacities of Zn and Li ion batteries are boosted by 7 and 5 orders of magnitude. Our simulation result demonstrated that intercalated CO<sub>2</sub> molecules significantly contribute to both diffusivity and embedding concentration of Zn ions but they contribute to only the diffusivity of Mg and the embedding concentration of Li ions. Therefore, we demonstrate that CO<sub>2</sub>

molecule intercalated bilayer MoS<sub>2</sub> is a promising cathode material for high-capacity and rapid-charging ZIBs. The strategy of expanding interlayer spacing and reducing intercalation energy developed in this study can be generally applied to increase the ion storage capability in layered structure-based electrode materials and sheds light on the development of advanced materials for next-generation high-performance energy storage.

## Author contributions

Xuefei Han: methodology, investigation, writing – original draft, and writing – review & editing. Jing Yang: writing – review & editing. Yong-Wei Zhang: conceptualization and writing – review & editing. Zhi Gen Yu: conceptualization, methodology, writing – review & editing, and supervision.

## Conflicts of interest

There are no conflicts to declare.

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