Unraveling the Role of Lithium in Enhancing the Hydrogen Evolution Activity of MoS$_2$: Intercalation versus Adsorption

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ABSTRACT: Molybdenum disulfide (MoS$_2$) is a highly promising catalyst for the hydrogen evolution reaction (HER) to realize large-scale artificial photosynthesis. The metallic 1T'–MoS$_2$ phase, which is stabilized via the adsorption or intercalation of small molecules or cations such as Li, shows exceptionally high HER activity, comparable to that of noble metals, but the effect of cation adsorption on HER performance has not yet been resolved. Here we investigate in detail the effect of Li adsorption and intercalation on the proton reduction properties of MoS$_2$. By combining spectroscopy methods (infrared of adsorbed NO, 7Li solid-state nuclear magnetic resonance, and X-ray photoemission and absorption) with catalytic activity measurements and theoretical modeling, we infer that the enhanced HER performance of Li$_x$MoS$_2$ is predominantly due to the catalytic promotion of edge sites by Li.

Molybdenum disulfide (MoS$_2$) has demonstrated significant potential to replace noble-metal-based catalysts in electrochemical hydrogen production. Like other transition-metal dichalcogenides (TMDs), MoS$_2$ can exist in different polymorphs, that is, the 2H (trigonal prismatic $D_{3h}$), 1T’ (octahedral $O_h$), and 3R (rhombohedral $C_{3h}$) phases.1 By tuning the arrangement of the S atoms, MoS$_2$ can convert from the semiconducting 2H to the metallic 1T’ phase. Such a rearrangement of S atoms is typically caused by interlayer atomic plane gliding induced by electron donation or the intercalation of small molecules or cations.2–6 Alkali metal cations, especially Li, are typically used to intercalate between the MoS$_2$ layers to induce the 2H to 1T’ phase conversion.7–9 Despite many years of study of lithium-intercalated MoS$_2$ (1T’–Li$_x$MoS$_2$), the 1T’ phase is metastable and can easily change to the 2H phase.7–9 Furthermore, the quick hydration of Li in aqueous solution makes the stable operation of 1T’–MoS$_2$ under HER conditions challenging.8,10–13 Upon Li intercalation, the crystal structure of MoS$_2$ is modified, shown by the emergence of broad diffraction peaks and a distinct red shift of Raman modes.14 However, previous works have mostly only assumed a 2H to 1T’ phase conversion upon the adequate intercalation of Li ions without paying further attention to the behavior of adsorbed Li.14,15

Even though there are several theoretical works in the literature investigating the structural transitions in MoS$_2$ monolayers induced by Li adsorption,16–18 a systematic experimental study on the effect of Li adsorption is still lacking. Whereas, for instance, trace metal impurities are known to play an active role in determining the electrocatalytic properties of graphene,19,20 the role of adsorbed Li in the MoS$_2$-catalyzed HER remains ambiguous.

Since the discovery of 1T’–MoS$_2$, it has emerged as a promising candidate for a broad range of applications, including photocatalysis, supercapacitors, and, in particular, as an electrocatalyst for the hydrogen evolution reaction (HER).8,10–22 Bulk 2H-MoS$_2$ is a poor HER catalyst because the reaction is limited by the density of active sites, which are concentrated at the layer edges or edge-like defect sites on the (0001) basal planes.23 Significant research efforts have been...
devoted to synthesis strategies that can expose more active (edge) sites to enhance the overall HER performance, for example, nanoparticulate MoS2, nanstructured MoS2 or MoS2 basal planes with sulfur vacancies.24−26 In contrast with its 2H counterpart, the significant catalytic improvement toward HER of 1T′-MoS2 has been ascribed to the intrinsic activity of its basal planes.3 Numerous studies have reported the structural change (extensive layer displacement or bond distortion) of 2H-MoS2 to 1T′-MoS2 after Li intercalation, and density functional theory (DFT) modeling suggests that the catalytic improvement of Li-intercalated MoS2 can be attributed to octahedral and distorted MoS2 phases.13,27−31 Nonetheless, a more direct role of the Li ions, which are inevitably present in 1T′-MoS2 in HER catalysis has never been shown. In most cases, excessive amounts of Li are used to induce the 2H-1T′ structural transformation.11,13,32 However, considering that the local surface chemistry governs the catalytic performance, both excess Li and Li adsorbed on the catalysts may play a vital role during the catalytic reaction as well.

Here we report a study of the role of Li in the MoS2-catalyzed HER. The influence of Li adsorption on the MoS2 2H-to-1T′ phase transformation was systematically investigated by X-ray photoelectron spectroscopy (XPS) and extended X-ray absorption fine structure (EXAFS) spectroscopies. With the assistance of in-situ IR spectroscopy with NO as a probe molecule as well as 7Li MAS nuclear magnetic resonance (NMR) spectra, we were able to identify the interaction between Li ions and MoS2. Interestingly, Li-adsorbed 2H-LiMoS2 (0 < x < 0.5) presents much higher activity than 1T′-Li0.52MoS2 (x ≈ 1 or 2), which sheds new light on understanding the intrinsic activity of lithiated TMDs. This systematic investigation on the adsorption and promotion effects of Li on MoS2 in the electrocatalytic HER will provide a new platform for designing effective TMD-based catalysts.

We adopt a typical impregnation method to prepare a series of carbon-supported LiMoS2 catalysts with a precisely controlled Li content (Figure S1). As indicated in Figure 1a, Li is expected to preferentially adsorb on the surface of MoS2 at low concentrations, whereas at high Li concentrations, the structure undergoes a transformation from 2H- to 1T′-MoS2.3−5 HR-TEM images (Figure 1b,c and Figure S2) show that the molybdenum sulﬁde phase is well distributed across the carbon support, and the inﬂuence of particle dispersion upon Li addition on HER activity could be ruled out. Because the catalytic activity of MoS2 is known to be signiﬁcantly enhanced by edge-terminated surfaces,24,33,34 we predict here through ﬁrst-principles (DFT) calculations the surface formation energy of a (0001) monolayer of 1T′-MoS2 with a pristine Mo edge and how it is stabilized through adsorbed Li atoms in increasing concentration (LixMoS2). As shown in Figures S3 and S4, Li adsorption on the Mo-edge surface is found to have a stabilizing effect on the monolayer, as refected in the monotonic decrease in the surface formation energies with increasing adsorbed Li concentration. The stabilization of the Mo-edge monolayers can be rationalized by considering the fact that the adsorption acts to coordinate the Li to the under-coordinated Mo ions, thus providing a closer match to the bulk coordination of the edge species. Moreover, we characterized the electronic structure of Li0.52MoS2 by means of X-ray photoelectron spectroscopy (XPS) (Figure 1d,e, Figures S5 and S6, and Tables S4 and S5). The Mo 3d core-level spectra present a shift to lower binding energy for Li0.06MoS2 and Li1.06MoS2 as compared with samples with lower Li loading, indicating the formation of 1T′-MoS2.35,36 Because the S 2p binding energy of 1T′-phase sulfur overlaps with that of

Figure 1. (a) Schematic model of 1T′-LiMoS2 preparation via Li intercalation. The slab model is periodic in a and b directions and nonperiodic in c direction. (b,c) HR-TEM images of pure MoS2 (b) and Li0.29MoS2 (c) loaded on activated carbon. Yellow arrows indicate MoS2 nanosheets. (d,e) XP spectra of Mo 3d (d) and S 2p (e) for Li0.52MoS2/C catalysts with various Li contents.
The absence of cross-peaks indicates that Li ions at different sites are not in close vicinity. Figure 2d,e and Figures S9−S11 display the scheme of NO adsorption on Li$_x$MoS$_2$. A gradual red shift of the IR bands at $\sim 1782$ cm$^{-1}$ (coupled mononitrosyl or dinitrosyl, symmetric stretch, $\nu_s$) and $\sim 1687$ cm$^{-1}$ (coupled mononitrosyl or dinitrosyl, asymmetric stretch, $\nu_{as}$) (Figure 2e and Figure S10) is observed upon the introduction of Li ions.

X-ray absorption spectroscopy (XAS) was conducted to investigate the atomic structural change of Li$_x$MoS$_2$ upon interaction with Li (Figures S12 and S13). The Fourier transforms of the Mo K-edge extended X-ray absorption fine structures (EXAFS) in R-space are shown in Figure 3. The distinct downshift of the Mo−Mo bond from 3.16 to 2.80 Å (Table 2) in Li$_{1.00}$MoS$_2$ and Li$_{2.06}$MoS$_2$ reflects the characteristic length of the Mo−Mo bond in 1T’-MoS$_2$. Upon Li adsorption or intercalation, Li atoms donate electron density to the d band of 2H-MoS$_2$, thereby transforming it into 1T’-MoS$_2$ with octahedrally coordinated Mo atoms. Further insight into the charge transfer of MoS$_2$ after Li adsorption was gained through a Bader charge and differential charge density analysis of monolayer 1T’-MoS$_2$ with different concentrations of adsorbed Li. The calculated Bader charges of S and Mo atoms before and after the adsorption of Li ions (Table S6) indicate that the adsorption process is characterized by a charge transfer from the Li atoms to the S and Mo atoms. Consistently, from the differential charge density isosurface plots in Figure 3g, where the pink and cyan blue contours indicate an electron density increase and decrease by 0.02 e$^{-}$ Å$^{-3}$, respectively, it is obvious that the electron densities of the Li atoms (cyan contours) were transferred to the S-2p and Mo-3d orbitals (pink contours) in the process of Li adsorption. The electron transfer from the Li atoms to the S and Mo atoms is responsible for the observed distortions in the Mo−S and Mo−Mo bonds of the Li$_x$MoS$_2$ monolayers, as obtained from EXAFS fitting (Table 2) and confirmed by DFT results (Table S7).

The HER performance of different Li$_x$MoS$_2$ catalysts on glassy carbon was evaluated using a standard three-electrode
electrochemical configuration in 0.1 M H2SO4 deaerated with Ar (Figures S14 and S15). The polarization curves (Figure 4a) show that a small amount of Li adsorption (Li0.14MoS2 and Li0.29MoS2) greatly decreases the onset overpotential and improves the current density for HER as compared with pure MoS2. Interestingly, the cathodic current was lower in the case of Li0.48MoS2 and decreased sharply for Li1.00MoS2 and Li2.06MoS2. Tafel slopes in Figure 4b reveal the same trend, that is, that an optimum amount of Li loading dramatically improves the HER activity (lower Tafel slope and higher cathodic current density), whereas an excess of Li hinders the electrocatalytic reaction. To quantify the catalytic activity, we measured the actual number of active sites using the IR NO titration method (for further details see the experimental section of the SI). On the basis of this method, we have determined the number of active sites to be \( \sim 3.0 \times 10^{15} \) sites cm\(^{-2}\) (based on geometric electrode area; Table S8 and Figures S16 and S17). The turnover frequency (TOF) (s\(^{-1}\)) of the hydrogen evolution was calculated, as shown in Figure 4c. Among the compared catalysts, Li0.14MoS2 and Li0.29MoS2 show the highest TOF, which is three times larger than that of bare MoS2 at a cathodic overpotential of 300 mV. It is worth noting that despite the presence of the 1T phase in Li1.00MoS2 and Li2.06MoS2, the relatively lower catalytic activity of these samples compared with that of Li0.29MoS2 (entirely 2H phase) indicates that next to Li intercalation, Li adsorption plays a key role in describing the high HER activity of Li\(_x\)MoS2 electrocatalysts.28,41–43

Table 2. Mo K-Edge EXAFS Fitting Results of Molybdenum Sulfide Loaded on Carbon Support

| sample         | Mo–S        | Mo–Mo       | Mo–Mo (short) | \( \Delta E_0 \) (eV) | R factor |
|----------------|-------------|-------------|--------------|-----------------------|----------|
| CN            | R (Å)       | \( \sigma^2 \) | CN            | R (Å)       | \( \sigma^2 \) | CN            | R (Å)       | \( \sigma^2 \) | \( \Delta E_0 \) (eV) | R factor |
| MoS2          | 5.46 ± 0.48 | 2.405 ± 0.006 | 0.003        | 1.93       | 3.157 ± 0.013 | 0.002        | 3.157 ± 0.013 | 0.002 | 3.42 | 0.011 |
| Li0.14MoS2    | 4.94 ± 0.54 | 2.408 ± 0.008 | 0.003        | 1.60       | 3.158 ± 0.016 | 0.001        | 3.158 ± 0.016 | 0.001 | 1.64 | 0.015 |
| Li0.29MoS2    | 4.80 ± 0.55 | 2.409 ± 0.008 | 0.003        | 1.48       | 3.158 ± 0.017 | 0.001        | 3.158 ± 0.017 | 0.001 | 1.00 | 0.017 |
| Li0.48MoS2    | 5.78 ± 0.79 | 2.397 ± 0.010 | 0.004        | 2.35       | 3.152 ± 0.019 | 0.003        | 3.152 ± 0.019 | 0.003 | 2.93 | 0.017 |
| Li1.00MoS2    | 5.52 ± 0.44 | 2.408 ± 0.006 | 0.005        | 1.43       | 3.166 ± 0.017 | 0.003        | 3.166 ± 0.017 | 0.003 | 2.35 | 0.005 |
| Li2.06MoS2    | 4.80 ± 1.01 | 2.422 ± 0.016 | 0.006        | 0.99       | 3.176 ± 0.030 | 0.003        | 3.176 ± 0.030 | 0.003 | 1.33 | 0.012 |

Figure 3. (a–f) Mo K-edge EXAFS spectra plotted as the magnitude of the Fourier transform of MoS2 (a), Li0.14MoS2 (b), Li0.29MoS2 (c), Li0.48MoS2 (d), Li1.00MoS2 (e), and Li2.06MoS2 (f). Open black circles represent experimental data, and red curves are fitted spectra. (g) Electron density difference isosurface contours of MoS2 upon Li adsorption, where the pink and cyan contours indicate an electron density increase and decrease by 0.02 e Å\(^{-3}\), respectively. (Gray, yellow, and green correspond to Mo, S, and Li atoms, respectively.) i–vi correspond to Li0.13MoS2, Li0.25MoS2, Li0.31MoS2, Li0.50MoS2, Li1.00MoS2, and Li2.00MoS2 respectively.

Table 2. Mo K-Edge EXAFS Fitting Results of Molybdenum Sulfide Loaded on Carbon Support
To gain further insight into the synergistic effect of Li adsorption on the MoS_2-catalyzed HER, we have calculated the Gibbs free energy of hydrogen adsorption (ΔG_H*) on Li_{x}MoS_2 monolayers, as shown in Figure 4d. The adsorption structures of hydrogen on the Li_{x}MoS_2 monolayers are shown in Figures S19–S22. The value of ΔG_H* must be close to zero, indicating that the free energy of adsorbed H is close to that of the reactant or product. Among the various Li_{x}MoS_2 samples studied,
Li$_{0.29}$MoS$_2$ and Li$_{0.31}$MoS$_2$ compositions show the smallest $|\Delta G_{\text{ads}}|$ value of 0.11 and 0.12 eV, respectively, both of which are similar to the $\Delta G_{\text{ads}}$ value for the well-known and highly efficient Pt catalyst, that is, $\Delta G_{\text{ads}}^{\text{Pt}}$ $\approx 0.09$ eV. Similarly, the $|\Delta G_{\text{ads}}|$ for the Li$_{0.13}$MoS$_2$ composition was calculated to be 0.16 eV compared with 0.29 eV in MoS$_2$ without Li adsorption. Largely negative $\Delta G_{\text{ads}}$ values of $-0.60$, $-0.84$, and $-1.09$ eV were calculated for the Li$_{0.30}$MoS$_2$, Li$_{0.25}$MoS$_2$, and Li$_{0.20}$MoS$_2$ monolayers, respectively, indicating that the chemical adsorption of H* on their Mo edges is too strong, which makes them less active in the HER. We have also considered H adsorption on the S edge of the Li$_2$MoS$_2$ with increasing Li concentration. As can be seen Figures S21–27, the $\Delta G_{\text{ads}}$ values at the pure, Li$_{0.13}$MoS$_2$, Li$_{0.25}$MoS$_2$, Li$_{0.31}$MoS$_2$, Li$_{0.50}$MoS$_2$, Li$_{1.00}$MoS$_2$, and Li$_{2.00}$MoS$_2$ S edges are $-0.43$, $-0.32$, $-0.34$, $-0.30$, $-0.77$, $-0.92$, and $-1.32$ eV, respectively. Similar to the results obtained at the Mo edge, the stronger chemical adsorption of H* on the S edges with increased Li concentration suggests that higher Li compositions will be less active in HER. However, the more optimum $\Delta G_{\text{ads}}$ values predicted at lower Li concentrations at the Mo edge compared with the S edge demonstrate a superior HER activity of the Mo edges. This is consistent with previous theoretical predictions that showed the Mo edges to be more active for HER than S edges. Further insights into the adsorption of H on the Mo edge of the Li$_2$MoS$_2$ materials were gained through a Bader charge and electron density difference isosurface analyses. Consistent with the higher $\Delta G_{\text{ads}}$, Bader population analyses revealed that the adsorbed H atom on the Mo edge draws larger amounts of charge from the Li$_{0.13}$MoS$_2$, Li$_{0.25}$MoS$_2$, and Li$_{0.31}$MoS$_2$ monolayers, calculated at 0.52, 0.63, and 0.82 e$^-$ respectively, compared with 0.29, 0.39, 0.35, and 0.36 e$^-$ drawn from the pure MoS$_2$, Li$_{0.13}$MoS$_2$, Li$_{0.25}$MoS$_2$, and Li$_{0.31}$MoS$_2$ monolayers. The analysis of the electron density difference isosurfaces (Figure S24) of H adsorbed at pure and Li$_2$MoS$_2$ Mo edge reveals electron density accumulation (pink contours) around the centers of the newly formed H–Mo bonds, indicating ionic bonding. The smaller amount of charge gained by adsorbed H atoms from the Li$_{0.13}$MoS$_2$, Li$_{0.25}$MoS$_2$, and Li$_{0.31}$MoS$_2$ monolayers suggests that their hydrogen–surface bonds are neither too strong nor too weak (i.e., $\Delta G_{\text{ads}}$ $\approx 0$) to limit the recombination of the adsorbed H atoms to evolve molecular hydrogen via a Volmer–Tafel or Volmer–Heyrovsky mechanism, therefore resulting in the observed increase in HER activity.

As Li can easily hydrolyze in H$_2$O, we have employed $^7$Li MAS NMR spectroscopy to probe the local coordination environments of Li in the presence of H$_2$O. As shown in Figure 4e, a small portion of Li migrates to the carbon support (chemical shift: around $-1$ ppm) for Li$_{2.00}$MoS$_2$ once in contact with H$_2$O, whereas most Li remains adsorbed on MoS$_2$ (chemical shift: $\sim 7$ ppm). Additionally, and in contrast with MoS$_2$ and Li$_{2.00}$MoS$_2$, Li$_{0.20}$MoS$_2$ exhibits outstanding long-term electrochemical stability at $-23$ mA/cm$^2$ with an increase in overpotential of only 10 mV after 24 h (Figure 4f and Figures S18 and S19). The spent Li$_{2.00}$MoS$_2$ catalyst after 24 h of stability testing was further subjected to an NMR analysis. As shown in Figure 4g, the presence of Li species for Li$_{2.00}$MoS$_2$ after long-term HER measurements indicates the strong interaction between Li and MoS$_2$, further illustrating the promotion effects of Li adsorption on MoS$_2$-catalyzed HER.

In conclusion, we have systematically employed a suite of complementary experimental and computational techniques to investigate the effect of Li adsorption on the phase conversion and HER activity of MoS$_2$ catalysts. The promoting effect of Li adsorption on 2H-MoS$_2$ in enhancing the electrocatalytic hydrogen evolution was shown for the first time. With the assistance of IR spectroscopy using NO as a probe molecule, we experimentally determined the number of active sites for Li$_x$MoS$_2$ catalysts, which allowed us to determine the TOF of the catalysts. Both experimental and theoretical results indicate that, next to Li intercalation, Li adsorption plays a key role in describing the high HER activity of Li$_x$MoS$_2$ electrocatalysts. Whereas Li intercalation causes a phase transition from 2H- to 1T’-MoS$_2$ and, with that, impacts on electronic properties such as conductivity, Li adsorption leads to a promotion of the HER active edge sites by changing $\Delta G_{\text{ads}}$ in a favorable direction. Thus the overall influence of Li in the MoS$_2$-catalyzed HER appears to be more complex than initially reported. Following these results, we believe that an appropriate amount of adsorbed Li or other alkali cations on TMDs would change their corresponding electron density, resulting in a beneficial tuning of the activity in electrocatalytic reactions involving proton adsorption and reduction.

### ASSOCIATED CONTENT

#### Supporting Information

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Experimental and theoretical details as well as supplementary figures and discussions (PDF)

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**Notes**

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