Supporting Information

Rb intercalation enhanced the supercapacitive performance of layer-structured MoS$_2$ as a 2D model material

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Computational details

The capacitive behaviour of the electrode material (C_{total}) can be defined according to the following equation:

$$1/C_{total} = 1/C_Q + 1/C_{DL}$$

where C_Q is the quantum capacitance resulted as the electronic contribution of the material to the electrical double layer upon applying voltage. While, C_{DL} is the capacitance resulted from the adsorption/desorption process and is mainly dependent on the surface area. According to the previous equation, the C_{total} is limited by the lowest capacitance of (C_Q or C_{DL}). However, if both C_Q and C_{DL} are high, the C_{total} will be high and if only one of them is high, this will offer up to 100% use of the other. Therefore, even in low surface area, if the C_Q is high, the C_{DL} will be presented more effectively than in case the C_Q was low.

In experimental work, quantum capacitance is the capacitance measured from the impedance spectroscopy reflecting the electronic behavior of the electrode material. In short, quantum capacitance represents the effective part of the EDL capacitance, and it is important to tell if the large surface area will have an effect on the total capacitance or not.

In this study, the density functional theory (DFT)[1] was employed for total energy computations using Vienna Ab Initio Simulation Package (VASP)[2]. For the exchange-correlation,

the PBE-GGA[3] was implemented to treat the electron-electron interaction instead of the HSE06 hybrid functionals as Gao et al. [4] reported that PBE gave better results for MoS$_2$ in agreement with the experimental data. To account for the electron-ion interaction, the PAW pseudopotentials[5,6] were exploited. In this regard, PAW Rb_sv pseudopotential, where $4s^2 4p^6 5s^1$ electrons are treated as valence electrons, was used for accurate Rb intercalation calculations. For the expansion of Kohn-Sham wave functions, the kinetic energy cut-off was set to 600 eV within the plane-wave basis set framework. The three-layered-structures were adopted for the modelling of 1T, 2H, and 3R phase of MoS$_2$. A (2x2x1) supercell was constructed to accommodate for the octahedral binding site for the intercalated ions. To avoid the periodic image interactions, a 30 Å vacuum slab was introduced in the z-direction for the intercalated structures (Rb-MoS$_2$). The Monkhorst-pack scheme[7] was utilized to sample the k-points in the Brillouin zone and for the generation of the density of states (DOS) profile. The Monkhorst-pack meshes 25x25x1, 6x6x1, and 8x8x2 were constructed for the pristine bulk MoS$_2$, Rb-MoS$_2$ (2x2x1) supercell with a vacuum slab, and the DOS profiling of the intercalated structures, respectively. To remedy the under estimation of the non-local dispersion interactions, vDW-DF2 non-local correlation functional[8] was employed to describe the Van Der Waals forces between the MoS$_2$ layers. Concerning the smearing, Methfessel-Paxton scheme, with a broadening factor of 0.2 eV was applied in case of 1T-MoS$_2$ structures. While, Gaussian scheme, with a broadening factor of 0.05 eV was applied in case of 2H-MoS$_2$, and 3R-MoS$_2$ structures.

The quantum capacitance (C$_Q$) can be calculated according to **eq. 1 & 2**.[9]

$$C_Q = \frac{dQ}{dV} = e^2 \int_{-\infty}^{+\infty} DOS\, F_T(E - \mu)dE \tag{1}$$

$$F_T(E) = (4k_B T)^{-1} Sech^2(\frac{E}{2k_B T}) \tag{2}$$

where e is the electronic charge, K$_B$ is Boltzmann constant, T is the temperature (here 300 K), DOS is the density of states F$_T$(E) is the thermal broadening function, E is the relative energy with respect to the fermi level (potential of zero charge) and μ is the electrochemical potential.

The binding energy can be calculated according to the following equation per Rb ion:

$$E_{ad} = (E_{X-MoS_2} - E_{MoS_2} - nE_X)/2 \qquad (3)$$

where E_{X-MoS_2} is the total energy of the intercalated MoS_2, E_{MoS_2} is the total energy of the pare MoS_2, n is the number of intercalated ions, E_X is the energy of the intercalated atom in the BCC crystal, z is the valency number, and F is Faraday's constant.[9–11]

The formation energy of the intercalated MoS_2 can be calculated as following:

$$E_F = E_{X-MoS_2}/4 - E_{MoS_2}/4 - \frac{n}{4}E_X \qquad (4)$$

As 4 is the number of the MoS_2 formula units in the cell. For indicating the charge accumulation and charge transfer between the MoS_2 and the adsorbed ions, the charge density of adsorption (ρ_{ad}) was calculated according to **eq.5** using Bader analysis.[10]

$$\rho_{ad} = \rho_{X-MoS_2} - \rho_{MoS_2} - n\rho_X \qquad (5)$$

where ρ_{X-MoS_2} is the charge density of the intercalated MoS_2, ρ_{MoS_2} is the charge density of the pare MoS_2, n is the number of intercalated ions, ρ_X is the charge density of the intercalated atom.

Table 1S Comparative parameters of Rb intercalation and other alkali-metals.[12]

Phase	Structure	d'_{Mo-Mo} (Å)	E_{Tot} (eV)	E_b (eV)	E_f (eV)	q |e|
1T	Pristine	6.41	-162.80	----	----	----
	Li-MoS$_2$	6.45	-174.51	-5.80	-0.97	0.87
	Na-MoS$_2$	7.10	-171.43	-4.25	-0.71	0.81
	Rb-MoS$_2$	8.93	-169.44	-3.18	-0.53	0.84
2H	Pristine	6.81	-170.60	----	----	----
	Li-MoS$_2$	6.99	-176.99	-3.14	-0.52	0.87
	Na-MoS$_2$	7.54	-174.32	-1.79	-0.29	0.81

	Rb-MoS$_2$	10.04	-172.46	-0.79	-0.13	0.84
3R	Pristine	6.82	-170.60	----	----	----
	Li-MoS$_2$	7.76	-177.16	-3.22	-0.54	0.87
	Na-MoS$_2$	10.06	-174.39	-1.83	-0.30	0.81
	Rb-MoS2	9.97	-172.48	-0.80	-0.13	0.84

References

1   P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, B864.

2   G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15–50.

3   J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B*, 1992, **46**, 6671–6687.

4   B. Gao, J. R. Zhang, L. Chen, J. Guo, S. Shen, C. T. Au, S. F. Yin and M. Q. Cai, *Appl. Surf. Sci.*, 2019, **492**, 157–165.

5   P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953–17979.

6   D. Joubert, *Phys. Rev. B - Condens. Matter Mater. Phys.*, 1999, **59**, 1758–1775.

7   H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188–5192.

8   K. Lee, É. D. Murray, L. Kong, B. I. Lundqvist and D. C. Langreth, *Phys. Rev. B - Condens. Matter Mater. Phys.*, 2010, **82**, 081101.

9   B. A. Ali and N. K. Allam, *Phys. Chem. Chem. Phys.*, 2019, **21**, 17494–17511.

10   G. Barik and S. Pal, *J. Phys. Chem. C*, 2019, **123**, 21852–21865.

11   M. Mortazavi, C. Wang, J. Deng, V. B. Shenoy and N. V. Medhekar, *J. Power Sources*, 2014, **268**, 279–286.

12   A. H. Biby, B. A. Ali and N. K. Allam, *Mater. Today Energy*, 2021, **20**, 100677.