Interlayer structures of birnessite: A first principle molecular dynamics study

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Birnessite is a layered manganese oxide characterized by large surface areas and the presence of cation vacancy sites. Natural birnessite plays an important role in many geochemical processes, such as transportation and adsorption of metal elements, oxidaton of variable valency metal ions like As or Co and process related to water-splitting and photosynthesis due to its unique surface charge, cation-exchange and redox properties. Therefore, the properties ofinterlayer species are essential for better understanding the interfacial processes of birnessite.

First principles molecular dynamics (FPMD) are performed in this study to investigate birnessite containing K/Na/Mg/Ca cations. Interlayer structures and adsorption mechanisims are revealed from these simulations. The results suggest that these cations can form a tridentate inner-sphere complex above the vacancy site while bridge oxygen and ditrigonal cavities can also act as adsorption sites. Moreover, constrained molecular dynamics are employed to examine the stabilities of different adsorption sites over outer-sphere complexes. stabilities of coordination shells and dynamic properties like diffusion coefficients will also be discussed.