

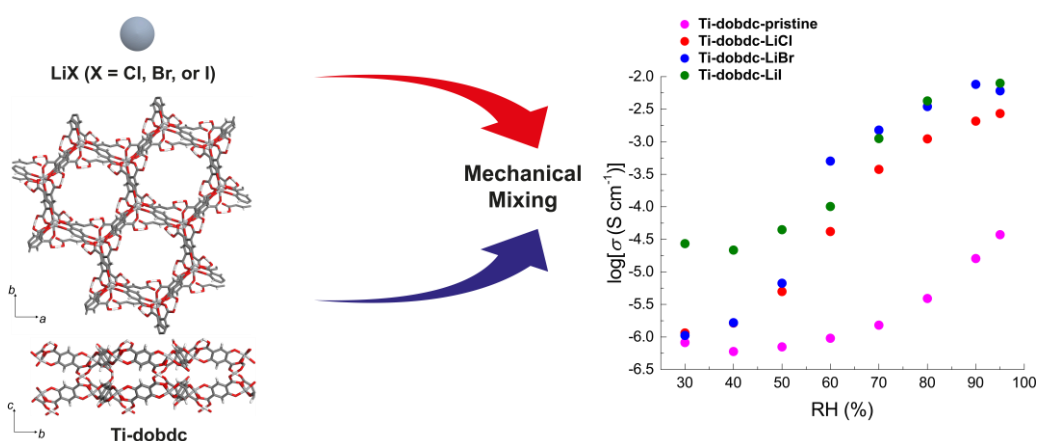
High Ionic Conductivity in 2D-layered Ti-MOF by Li Salts Mechanical Insertion

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Solid-state electrolyte is a key element for safety and high performance in fuel cell and battery systems. Recently, porous metal–organic frameworks (MOFs) have emerged as a platform of solid-state ionic conductors due to their designability and structural stability.¹ Typically, ionically conductive MOFs are achieved through the insertion of charge carriers by post-synthetic methods such as the dipping in charge carrier solution or the mechanical mixing. In particular, the mechanical mixing with charge carriers allows for precise *solvent-free* insertion of charge carriers.

Herein, we demonstrate the high ionic conductivity ($\sigma > 10^{-2} \text{ S cm}^{-1}$) in the 2D-layered Ti-dobdc framework ($\text{Ti}_2[(\text{Hdobdc})_2(\text{H}_2\text{dobdc})]$, H_4dobdc : 2,5-dihydroxyterephthalic acid) through the LiX salt (X = Cl, Br, or I) mechanical intercalation. The incorporation of LiX salts in the layered MOF (Ti-dobdc-LiX, X = Cl, Br, or I) improved the structural stability and boosted the H_2O adsorption property. At low humidity (RH = 30%), the Ti-dobdc-LiI shows a two-order of magnitude higher conductivity ($\sigma = 2.73 \times 10^{-5} \text{ S cm}^{-1}$) than the other samples, indicating that hydrophilicity and ionic/covalent character of LiX favor high ionic conductivity. Furthermore, at higher humidity (RH = 95%) all Ti-dobdc-LiX samples show superior ionic conductivity than the pristine sample by two-order magnitude. Further details are presented and discussed.



1) Thakur, A.K.; Majumder, M.; Patole, S.P.; Zaghib, K.; Reddy, M.V. *Mater. Adv.* **2021**, 2, 2457-2482.