Functionalization of a layered oxide with organic moieties: towards hybrid proton conductors

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The design of innovative proton conductors for intermediate-temperature fuel cells, closing the gap between PEMFC and SOFC, is a forefront research theme in materials chemistry. [1] Layered perovskites with the Dion-Jacobson structure ($ALaNb_2O_7$) have bidimensional lanthanum niobate sheets, separated by a layer of A^+ cations. These can be substituted by a variety of molecules with soft chemistry, to yield inorganic-organic hybrids. In particular, the intercalation of amines, alcohols, carboxylic or phosphonic acids, and their covalent binding to the sheets has been demonstrated recently. [2-4]–We present preliminary results on the intercalation and covalent bonding of different organic molecules, in order to develop hybrid proton conductors for use in intermediate temperature fuel cells. Smaller molecules (such as alcohols) are intercalated to expand the interlayer space, to form intermediates for the further binding of proton carriers such as imidazoles or sulfonates.–The intercalation process is investigated by XRD (to measure the interlayer distance) and TGA (to determine the weight loss upon thermal decomposition). NMR is applied to confirm the covalent bonding between the organic and oxide parts. The intercalation behavior of different functional groups is explained in terms of van der Waals and/or hydrogen bonding between organic chains. The interplay of theory (*ab initio* and periodic DFT) and experiment allowed us to elucidate the ^1H and ^{13}C-NMR spectra, and to investigate the nature of interaction (i.e. ionic or covalent bond) of the organic chains with the interlayer surface.

[1] Laberty-Robert et al., *Chem. Soc. Rev.* **2011**, 40, 961.
[2] Suzuki et al. *Chem. Mater.* **2003**, *15*, 636.
[3] Shimada et al. *Chem. Mater.* **2009**, *21*, 4155.
[4] Takeda et al. *Mater. Res. Bull.* **2006**, *41*, 834.