

Experimental report

23/02/2021

Proposal: 7-03-156

Council: 10/2016

Title: Probing dynamics of water mass transfer in covalent triazine-based framework water-splitting materials by neutron spectroscopy

Research area: Materials

This proposal is a new proposal

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Samples: $\text{Na}_3\text{Sc}_x\text{Zr}_{2-x}(\text{SiO}_4)_2-x(\text{PO}_4)_{1+x}$ ($x=0, 0.25, 1$)
 $\text{Na}_2\text{Sc}_y\text{Zr}_{2-y}(\text{SiO}_4)_1-y(\text{PO}_4)_{2+y}$ ($y=0, 0.25, 1$)

Instrument	Requested days	Allocated days	From	To
IN16B	7	0		
IN5	7	3	12/07/2019	15/07/2019
IN6	7	0		

Abstract:

We propose to study diffusive dynamics in the sodium superionic conductor (NASICON) materials $\text{Na}_3\text{Sc}_x\text{Zr}_{2-x}(\text{SiO}_4)_2-x(\text{PO}_4)_{1+x}$ and $\text{Na}_2\text{Sc}_y\text{Zr}_{2-y}(\text{SiO}_4)_1-y(\text{PO}_4)_{2+y}$ by means of quasielastic neutron scattering (QENS). One of the advantages of the NASICON materials is the variety of compositions within the general formula $\text{Na}_x\text{M}_2(\text{SiO}_4)_z(\text{PO}_4)_{3-z}$. By substituting on the M site, the electrochemical and ion conduction properties can be tuned for specific applications. These materials have been used as electrodes and electrolyte, presenting homogeneous electrode/electrolyte interface and high stability.

Probing Dynamics of Water Mass Transfer in Organic Porous Photocatalyst Water-Splitting Materials by Neutron Spectroscopy

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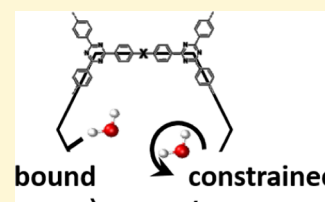


Article Recommendations



Supporting Information

ABSTRACT: The quest for efficient and economically accessible cleaner methods to develop sustainable carbon-free energy sources induced a keen interest in the production of hydrogen fuel. This can be achieved via the water-splitting process and by exploiting solar energy. However, the use of adequate photocatalysts is required to reach this goal. Covalent triazine-based frameworks (CTFs) are potential target photocatalysts for water splitting. Both electronic and structural characteristics of CTFs, particularly energy levels, optical band gaps, and porosities are directly relevant to water splitting and can be engineered through chemical design. Porosity can, in principle, be beneficial to water splitting by providing a larger surface area for the catalytic reactions to take place. However, porosity can also affect both charge transport within the photocatalyst and mass transfer of both reactants and products, thus impacting the overall kinetics of the reaction. Here, we focus on the link between chemical design and water (reactant) mass transfer, which plays a key role in the water uptake process and the subsequent hydrogen generation in practice. We use neutron spectroscopy to study the mass transfer of water in two porous CTFs, CTF-CN and CTF-2, that differ in the polarity of their struts. Quasi-elastic neutron scattering is used to quantify the amount of bound water and the translational diffusion of water. Inelastic neutron scattering measurements complement the quasi-elastic neutron scattering study and provide insights into the softness of the CTF structures and the changes in librational degrees of freedom of water in the porous CTFs. We show that two different types of interaction between water and CTFs take place in CTF-CN and CTF-2. CTF-CN exhibits a smaller surface area and lower water uptake due to its softer structure than CTF-2. However, the polar cyano group interacts locally with water leading to a large amount of bound water and a strong rearrangement of the water hydration monolayer, while water diffusion in CTF-2 is principally impacted by microporosity. The current study leads to new insights into the structure-dynamics–property relationship of CTF photocatalysts that pave the road for a better understanding of the guest–host interaction on the basis of water-splitting applications.



INTRODUCTION

Hydrogen has been suggested as the energy carrier of the future as it can be stored and does not emit greenhouse gases at the point of use.¹ However, most hydrogen is still produced using steam reforming processes emitting large amounts of carbon dioxide when produced. The generation of hydrogen using clean methods has, therefore, become an area of intense research. Photocatalytic water splitting has been of particular interest as it uses water and solar light, which are abundant on the Earth's surface.^{2–5}

In the process, a catalyst is used to generate charge carriers that facilitate water reduction and oxidation. The catalysts are typically inorganic semiconductors.^{2,3} Tremendous progress has been made in recent years in terms of improving photocatalysts and the overall systems.^{1,6} Nevertheless, organic materials have received significant attention in the past decade as they can be synthesized using many potential building blocks. Hence, the properties of the materials can be tuned by chemical design.^{4,7}

Particularly, carbon nitrides have been studied as organic photocatalysts. Carbon nitrides are usually made through high-

temperature condensation reactions and, exhibit, as a result, many defects including end groups.^{8,9}

Linear conjugated polymers,^{10–16} conjugated microporous polymers (CMPs),^{16–24} covalent triazine-based frameworks (CTFs),^{25–28} and covalent organic frameworks (COFs)^{29–33} have also been extensively studied in recent years allowing for fine-tuning of material properties. Several factors have been identified to be of a key importance for the activity of polymer photocatalysts, such as the ability of a photocatalyst to absorb light,^{13,21,23} the position of the redox potentials,¹³ exciton separation,¹⁴ crystallinity,²⁹ and wetting of the surface.^{15,17,20} Sufficient driving forces for both half-reactions (proton reduction and water/hole scavenger oxidation), the number of absorbed photons, and the dispersibility of the catalyst in the

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