Combination of Intercalation and Surface Modification in Layered Zirconium Phosphates: Investigation of Surface Stability and Reactivity

Eduardo Cruz Jr.[§], Edward J. Broker, Jr.[§], and Brian M. Mosby*

Department of Chemistry, Rollins College, Winter Park, FL 32789, United States

*Corresponding Author: Brian M. Mosby

[§] These authors contributed equally.

Address: 1000 Holt Ave. Box 2743 Winter Park, FL 32789

Email: <u>bmosby@rollins.edu</u>

ORCID ID: 0000-0002-9942-8327

Supporting information



SI Figure 1. TGA thermograms of a) fully exchanged ZrP and b) half exchanged ZrP prepared with various ions. Samples prepared with full exchange do not display condensation of the phosphate whereas half exchanged samples show a high temperature weight loss for partial condensation.



SI Figure 2. Typical FTIR spectra of ZrP before and after exchange with a monovalent ion. Successful exchange results in a slight shift in the peak position and intensity of the phosphates.

Sample	Interlayer Distance	Estimated Formulas
100% No+	0.50	7rH N ₂ (PO) • 27 H O
10070 INd	9.30	$2.11_{0.11}$ value (FO4)2 · 2.7 1120
50% Na ⁺	7.76	$ZrH_{0.8}Na_{1.2} (PO_4)_2 \bullet 1.5 H_2O$
100% K ⁺	7.66	ZrH _{0.1} K _{1.9} (PO ₄) ₂ • 0.98 H ₂ O
50% K ⁺	7.41	$ZrH_{0.9}K_{1.1}(PO_4)_2 \bullet 4.6 H_2O$
100% Li ⁺	8.56	$Zr(LiPO_4)_2 \bullet 3.9 H_2O$
82% Li ⁺	7.51	ZrH _{0.34} Li _{1.66} (PO ₄) ₂ • 4.2 H ₂ O
50% Li ⁺	7.78	ZrH _{1.0} Li _{1.0} (PO ₄) ₂ • 3.1 H ₂ O
100% Ca ²⁺	9.68	$Zr(Ca_{0.5}PO_4)_2 \bullet 4.1 H_2O$

SI Table 1. Interlayer distance and proposed formulas for materials prepared by ion-exchange of ZrP. Reported water content includes both interlayer and surface absorbed water.



SI Figure 3. FTIR of ZrP, dehydrated ZrP, and Surface modified and exchanged ZrP. Successful surface modification is primarily indicated by the alkyl stretching. Dehydrated ZrP displays a signal around 940 cm⁻¹ where phosphate ester formation was previously reported.

SI Table 2. Interlayer distance and loadings for 1,2 epoxyoctadecane modified samples based on powder XRD and XRF analysis.

Sample	Interlayer	Actual Loading (%)
	Distance	
	(Å)	
ZrP	7.6	
100% Na ⁺	8.31	95
50% Na+	9.85	60
100% K ⁺	7.41	100
50% K ⁺	7.47	70
100% Li ⁺	8.61	
82% Li ⁺	9.85	
50% Li ⁺	9.96	
100% Ca ²⁺	9.68	100



SI Figure 4. TGA thermogram of 1,2 epoxyoctadecane modified ZrP.



SI Figure 5. TGA thermograms of a) 1,2 epoxyoctadecane and b) fully functionalized ZrP prepared with 1,2 epoxyoctadecane.



SI Figure 6. a) FTIR spectra and b) TGA thermograms of heterofunctional prepared by the exchange of K^+ into ZrP surface modified with 1,2 epoxyhexane (black), 1,2 epoxydodecane (red), and 1,2 epoxyoctadecane (blue).



SI Figure 7. a) Titration curve showing the regeneration of the proton phase of ZrP by the treatment of exchanged and glycidol surface modified ZrP with 0.1 M HCl and b) FTIR spectra of the exchanged and surface modified sample before (black) and after (red) regeneration of the proton phase.