

OPERANDO TRACKING ION INTERCALATION INTO 2D MXENES IN AQUEOUS ELECTROLYTES

Qiang Gao^{1*}, Weiwei Sun¹, Poorandokht Ilani-Kashkouli², Paul R. C. Kent¹, Nadine Kabengi², Michael Naguib³, Stephen Jesse¹, Yury Gogotsi⁴, Nina Balke¹

¹*Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831, USA*

²*Department of Chemistry and Department of Geosciences, Georgia State University, Atlanta, USA*

³*Department of Physics & Engineering Physics, 2001 Percival Stern Hall, Tulane University, New Orleans, LA 70118, USA*

⁴*Department of Materials Science and Engineering & A.J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, PA 19104, USA*

*Presenting author's e-mail: gaoq@ornl.gov

Introduction

Supercapacitors have drawn considerable attention for portable electronics, grid and transportation systems due to their rapid power delivery and almost unlimited cycle life. To enhance the energy stored, the intensive efforts have been devoted to exploring new electrode materials, new electrolytes, and novel cell configurations. In search for new electrode materials, 2D transition metal carbides-MXenes, are of particular interest owing to their excellent electrical conductivity and high volumetric capacitance^{1,2}. Various aqueous cations can be electrochemically intercalated into Ti_3C_2 , resulting in very high volumetric capacitance outperforming a variety of carbons. The mechanism for high capacitance was essentially described as intercalation pseudo-capacitance arising from redox reactions of the Ti atoms. Similar to graphite or other electrode materials, MXene also show a significant change in volume during intercalation. This electro-chemo-mechanical coupling can be used to get unprecedented insight into ion intercalation pathways with lateral resolution of 10's of nm using Scanning Probe Microscopy (SPM) techniques. Herein, we introduce contact resonance (CR) SPM to extract mechanical properties and its changes under electrochemical control^{3,4}. It is of great importance to explore the different intercalation contributions with varying aqueous cations to the mechanical property's variations of material itself, which is required to evaluate the electrochemical long-term stability of electrode materials. Of special interest to boost energy storage is the intercalation of multivalent ions suffering from sluggish intercalation and transport kinetics due to its ion size. By combining electrochemical dilatometry and CR SPM, the synergetic effects of smaller ion size cation and larger ion size cation are demonstrated to improve charge storage to maximize the utilization of electrode volume, as well as tune mechanical and actuation properties of Ti_3C_2 MXene^{4,5}. Our results have important implications for quantitatively understanding the charge storage processes in intercalation compounds and provide a new path for studying the mechanical evolution for electroactive materials.

Materials and Methods

MXene was synthesized by etching Al from Ti_3AlC_2 using a mixture of LiF and HCl as reported by Ghidui

et al².

Results and Discussion

The development of scanning probe microscopy (SPM) to quantify interfacial fluid-solid interactions. It involved the development of technology to detect aqueous single and dual cation interactions with MXene. The major obstacle of quantitative SPM in liquid is correctly accounting for the environmental damping and added mass effects for cantilever dynamics. We overcame those issues by employing photothermal cantilever excitation in multiple resonance modes and a predictive model for the hydrodynamic effects. To measure and reconstruct the hydrodynamic function for a given electrolyte, lots of efforts have been put into the investigation of cantilever dynamics in air and a variety of aqueous solutions including Li_2SO_4 , Na_2SO_4 , K_2SO_4 , Cs_2SO_4 , MgSO_4 , and DI H_2O . It has been achieved a reliable model to extract the fluid background for given electrolytes via computational programming. We looked into single cation interaction with MXene, which involved the collaborations with computational modelling and in situ flow microcalorimetry. It provided the novel insights into the difference of cation hydration and resulting mechanical loss parameter-Quality factor of sample (Q_{sample}). Q_{sample} from SPM, the heat changes for ion absorptions obtained with calorimetry, and radial distribution functions of the interaction between H_2O -O with aqueous cations follows the linear trend, indicating the linear correlations.

Conclusions

For the first time, it is to expand the capability of SPM to detect ion-materials interaction quantitatively by providing the energy related parameter. It shed the light on the ion hydration chemistry plays the central role in ion intercalations into materials.

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