



**Livia Giordano, Ph.D.**

University of Milano-Bicocca, Milan, Italy  
and Electrochemical Energy Laboratory, Massachusetts Institute of  
Technology, Cambridge, USA

**Electrode-Electrolyte Reactivity Descriptors at the  
Positive Electrodes in Li-ion Batteries**

**ABSTRACT:** Understanding the (electro)chemical reactions at the interface between the positive electrode and the organic electrolyte is crucial for the rational design of Li-ion batteries with improved capacity retention and cycle life. Commonly used positive electrodes, such as layered intercalation transition metal oxides, exhibit different degrees of chemical reactivity with carbonate-based electrolytes, yet a comprehensive understanding of the reaction mechanisms and the parameters governing the interfacial reactivity is still lacking. In this talk, we analyze the reaction mechanism and reactivity trends for organic solvents at the surface of layered oxides by combining density functional theory calculations, spectroscopic measurements and electrochemical testing. We demonstrate that solvent dehydrogenation, accompanied by an interfacial charge transfer, occurs for organic carbonate at the surface of  $\text{Li}_x\text{MO}_2$ . The driving force for this reaction increases on oxide surfaces with transition metal ions from left to right in the periodic table and by increasing transition metal oxidation state in the oxide upon delithiation, where greater solvent reactivity was found as the oxide Fermi level was lowered into the oxide O  $2p$  band [1]. The predicted trends can explain the reactivity and the interfacial compositions observed experimentally for  $\text{LiCoO}_2$ ,  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (NMC111) and Ni-rich NMC. These findings were used to identify a design principle for the screening of coating materials which can prevent the dissociation of organic carbonates [2], and for more stable organic electrolytes [3].

[1] Giordano *et al.*, *J. Phys. Chem. Lett.*, 8, 3881 (2017).

[2] Giordano *et al.*, *Chem. Mater.* 31, 5464 (2019).

[3] Giordano *et al.*, in preparation.

**BIO:** Livia Giordano is an Associate Professor at the University of Milano-Bicocca in Italy. From 2013-2021 she worked at the Massachusetts Institute of Technology, where she led the computational chemistry research in the Electrochemical Energy Laboratory at the Department of Mechanical Engineering, and in 2019-2021 she also served as program manager of the Low Carbon Energy Center for Energy Storage for the MIT Energy Initiative. She obtained her PhD in Material Science from the University of Milano-Bicocca in Italy, and joined the faculty there in 2007. Her research applies fundamental understanding in reaction mechanisms and reactivity trends to design new materials for energy storage and conversion, with a focus on electrode/electrolytes interfaces in Li-ion batteries, novel electrolytes, and oxygen electrocatalysis. Livia's work has contributed to the discovery of new electrolytes for Li-air batteries and new catalysts for the oxygen evolution reaction.