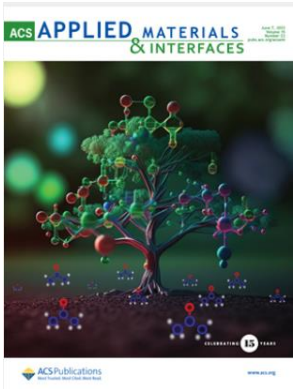

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Development of 2-in-1 Sensors for the Safety Assessment of Lithium-Ion Batteries via Early Detection of Vapors Produced by Electrolyte Solvents

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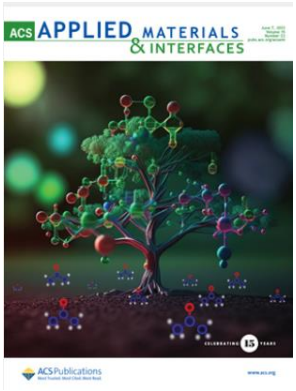
https://doi.org/10.1021/acsami.3c03564

Abstract

Batteries play a critical role in achieving zeroemission goals and in the transition toward a more circular economy. Ensuring battery safety is a top priority for manufacturers and consumers alike, and hence is an active topic of research. Metal-oxide nanostructures have unique properties that make them highly promising for gas sensing in battery safety applications. In this study, we investigate the gas-sensing capabilities of semiconducting metal oxides for detecting vapors produced by common battery components, such as solvents, salts, or their degassing products. Our main objective is to develop sensors capable of early detection of common vapors produced by malfunctioning batteries to prevent explosions and further safety hazards. Typical electrolyte components and degassing products for the Li-ion, Li–S, or solid-state batteries that were investigated in this study include 1,3-dioxololane ($C_3H_6O_2$_DOL), 1,2-dimethoxyethane ($C_4H_{10}O_2$_DME), ethylene carbonate ($C_3H_4O_3$_EC), dimethyl carbonate ($C_4H_{10}O_2$_DMC), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium nitrate ($LiNO_3$) salts in a mixture of DOL and DME, lithium hexafluorophosphate ($LiPF_6$), nitrogen dioxide (NO2), and phosphorous pentafluoride (PF_5). Our sensing platform was based on ternary and binary heterostructures consisting of TiO_2(111)/CuO($\bar{1}$11)/Cu_2O(111) and CuO($\bar{1}$11)/Cu_2O(111), respectively, with various CuO layer thicknesses (10, 30, and 50 nm). We have analyzed these structures using scanning electron microscopy (SEM), energy-



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dispersive X-ray spectroscopy (EDX), micro-Raman spectroscopy, and ultraviolet–visible (UV–vis) spectroscopy. We found that the sensors reliably detected DME $C_4H_{10}O_2$ vapors up to a concentration of 1000 ppm with a gas response of 136%, and concentrations as low as 1, 5, and 10 ppm with response values of approximately 7, 23, and 30%, respectively. Our devices can serve as 2-in-1 sensors, functioning as a temperature sensor at low operating temperatures and as a gas sensor at temperatures above 200 °C. Density functional theory calculations were also employed to study the adsorption of the vapors produced by battery solvents or their degassing products, as well as water, to investigate the impact of humidity. PF5 and $C_4H_{10}O_2$ showed the most exothermic molecular interactions, which are consistent with our gas response investigations. Our results indicate that humidity does not impact the performance of the sensors, which is crucial for the early detection of thermal runaway under harsh conditions in Li-ion batteries. We show that our semiconducting metal-oxide sensors can detect the vapors produced by battery solvents and degassing products with high accuracy and can serve as high-performance battery safety sensors to prevent explosions in malfunctioning Li-ion batteries. Despite the fact that the sensors work independently of the type of battery, the work presented here is of particular interest for the monitoring of solid-state batteries, since DOL is a solvent typically used in this type of batteries.

Keywords: copper oxide, titanium dioxide, heterostructures, gas sensor, battery safety, 2-in-1 sensors

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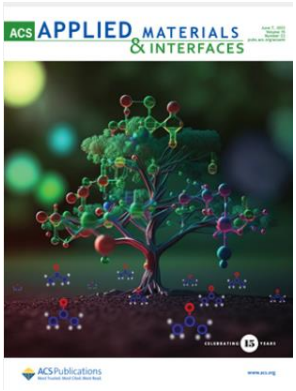

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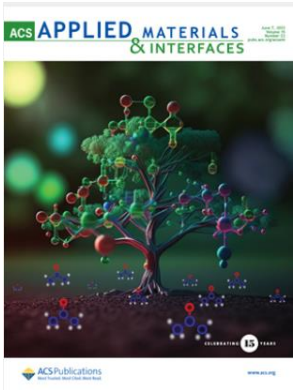

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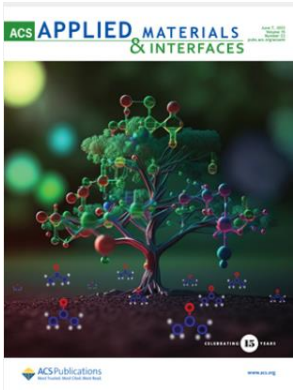

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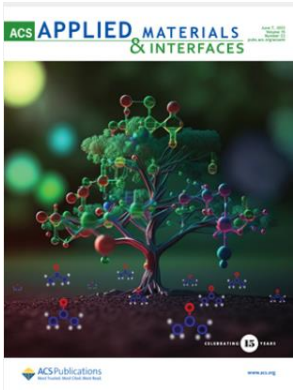

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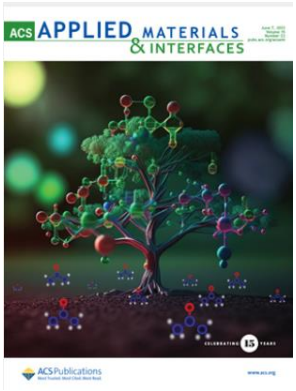

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