chemosensors

MDPI

Article

Additive Manufacturing as a Means of Gas Sensor Development for Battery Health Monitoring

Oleg Lupan [1,2,3,*], Helge Krüger [1], Leonard Siebert [1], Nicolai Ababii [2,3], Niklas Kohlmann [4], Artur Buzdugan [3,5], Mani Teja Bodduluri [6], Nicolae Magariu [2,3], Maik-Ivo Terasa [1], Thomas Strunskus [7], Lorenz Kienle [4], Rainer Adelung [1,*] and Sandra Hansen [1,*]

1 Institute for Materials Science—Functional Nanomaterials, Faculty of Engineering, Kiel University, Kaiser Str. 2, 24143 Kiel, Germany; hkr@tf.uni-kiel.de (H.K.); lesi@tf.uni-kiel.de (L.S.); mate@tf.uni-kiel.de (M.-I.T.)
2 Center for Nanotechnology and Nanosensors, Technical University of Moldova, 168 Stefan cel Mare Av., MD-2004 Chisinau, Moldova; nicolai.ababii@mib.utm.md (N.A.); nicolae.magariu@mib.utm.md (N.M.)
3 Department of Microelectronics and Biomedical Engineering, Faculty of Computers, Informatics and Microelectronics, Technical University of Moldova, 168 Stefan cel Mare Av., MD-2004 Chisinau, Moldova; artur.buzdugan@mib.utm.md
4 Synthesis and Real Structure, Institute for Materials Science, Kiel University, Kaiser Str. 2, 24143 Kiel, Germany; niko@tf.uni-kiel.de (N.K.); lk@tf.uni-kiel.de (L.K.)
5 National Nuclear Security Support Centre, Technical University of Moldova, 168 Stefan cel Mare Av., MD-2004 Chisinau, Moldova
6 Fraunhofer Institute for Silicon Technology (ISIT), Fraunhoferstrasse 1, 25524 Itzehoe, Germany; mtb@tf.uni-kiel.de
7 Multicomponent Materials, Faculty of Engineering, Christian-Albrechts Universität zu Kiel, Kaiser Str. 2, 24143 Kiel, Germany; ts@tf.uni-kiel.de
* Correspondence: ollu@tf.uni-kiel.de or oleg.lupan@mib.utm.md (O.L.); ra@tf.uni-kiel.de (R.A.); sn@tf.uni-kiel.de (S.H.)

Citation: Lupan, O.; Krüger, H.; Siebert, L.; Ababii, N.; Kohlmann, N.; Buzdugan, A.; Bodduluri, M.T.; Magariu, N.; Terasa, M.-I.; Strunskus, T.; et al. Additive Manufacturing as a Means of Gas Sensor Development for Battery Health Monitoring. *Chemosensors* **2021**, *9*, 252. https://doi.org/10.3390/chemosensors9090252

Academic Editor: Yoon-Bo Shim

Received: 2 July 2021
Accepted: 30 August 2021
Published: 6 September 2021

Abstract: Lithium-ion batteries (LIBs) still need continuous safety monitoring based on their intrinsic properties, as well as due to the increase in their sizes and device requirements. The main causes of fires and explosions in LIBs are heat leakage and the presence of highly inflammable components. Therefore, it is necessary to improve the safety of the batteries by preventing the generation of these gases and/or their early detection with sensors. The improvement of such safety sensors requires new approaches in their manufacturing. There is a growing role for research of nanostructured sensor's durability in the field of ionizing radiation that also can induce structural changes in the LIB's component materials, thus contributing to the elucidation of fundamental physicochemical processes; catalytic reactions or inhibitions of the chemical reactions on which the work of the sensors is based. A current method widely used in various fields, Direct Ink Writing (DIW), has been used to manufacture heterostructures of Al_2O_3/CuO and CuO:Fe_2O_3, followed by an additional ALD and thermal annealing step. The detection properties of these 3D-DIW printed heterostructures showed responses to 1,3-dioxolan (DOL), 1,2-dimethoxyethane (DME) vapors, as well as to typically used LIB electrolytes containing LiTFSI and $LiNO_3$ salts in a mixture of DOL:DME, as well also to $LiPF_6$ salts in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) at operating temperatures of 200 °C–350 °C with relatively high responses. The combination of the possibility to detect electrolyte vapors used in LIBs and size control by the 3D-DIW printing method makes these heterostructures extremely attractive in controlling the safety of batteries.

Keywords: heterostructures; 3D printing; DIW; battery safety

1. Introduction

The development of solid-state sensors and sensor arrays with low costs and efficiency is a growing goal of the sensor community. Detecting potential hazards in mixtures or ionizing radiation is a challenging task that requires the determination of specific individual components positively and sensitively. For this purpose, the development of sensor arrays with a wide range of varying materials and performances/possibilities is necessary. Whereas many approaches are based on various synthesis steps, the automatic combination of many complex materials can easily be realized by e.g., additive manufacturing or three-dimensional (3D) printing [1]. A large variety of 3D printed sensors have been developed and manufactured recently in the field of biotechnology e.g., for detection of glucose [2], selected medicament [3], trace elements [4], neurotransmitters [5], nucleic acids [6] and/or proteins [7].

Sharafeldin et al. [1] pointed out that 3D printing is very promising even for the detection of cancer and other diseases, because these complex diagnostic devices could be simply connected to portable devices like smartphones with batteries [1]. Also the fabrication of strain sensors by 3D printing has been demonstrated by Liu et al. [8] using various printing methods, such as Digital Light Processing (DLP) and Direct Ink Writing (DIW) [8]. Han et al. [9] presented an overview of the challenges of current biomedical sensors [9]. The authors hint at some possible limitations, one of which is related to the biocompatibility of printed materials [9]. Another concern is related to their recyclability and reuse on the stability of the signal determination [9]. It is proposed that one of the solutions to improving this problem is the association of dynamic thresholds of Flexiforce Sensor [10]. Another idea is to increase the use of other materials to develop 3D printed sensors based on nanocomposites with optimized characteristics [9].

Not only biotechnology can profit from the rapid developments enabled by the 3D printing of sensors. Another rapidly growing field is the safety monitoring in Lithium-ion batteries (LIBs) [11,12], attributable to highly reactive components inside this type of battery. Regarding this type of battery, safety is a significant concern and it must be monitored carefully and reliably. Battery safety requires sensors for the detection of many different volatile compounds (e.g., $C_4H_{10}O_2$, $C_3H_6O_3$, 1,2-dimethoxyethane, dimethyl carbonate, $C_4H_8O_3$) [13] that could be formed upon battery failure. Especially due to their use in portable electronics, such as computers or smartphones [14,15], or in electric or hybrid vehicles, safety monitoring is even more important and therefore, there is a need of suitable sensors that fit the requirements for the possible application [16]. Further, with the increase in LIB's performance in terms of energy density and power density, the safety guarantee has not yet been fully addressed [17], thus the main causes of fires and battery explosions being the heat leakage and the presence of inflammable components [15,17,18]. One of the solutions proposed by Chen et al. [17] to secure the batteries against thermal and mechanical harm is the improvement of the outer casing [17]. Another solution is to mount the batteries in the parts of auto vehicles that are least affected during an accident [17] and to prevent the thermal runaway before sensors are indispensable.

For safer batteries related to their heating protection, Chen et al. [18] have developed a class of ultra-fast and thermo-responsive reversible polymer switching (TRPS) material, which consists of the use of graphene-coated, nano-spiked Ni particles on polymer composite films, thus demonstrating good battery characteristics at ambient temperatures and their rapid disconnection under abnormal regimes, such as overheating and short circuiting [18]. The generation of heat and its accumulation inside the batteries is often accompanied by the generation of flammable gas due to various parasitic reactions, therefore it is necessary to improve the safety of the batteries by preventing the generation of these gases. [15,17,19].

In particular, the generation of heat and its accumulation inside the batteries is often accompanied by the generation of inflammable gases, such as CO, H_2, CH_4, C_2H_4, C_2H_6, and C_3H_8 due to various parasitic reactions depending on temperature, electrolysis, electrolytes and the appearance of thermal leakage [13,20]. Therefore, it is necessary to improve the safety of the batteries by preventing the generation of these gases and/or by the implementation of suitable sensors for early hazard detection and rapid disconnection of the battery. Essl et al. [13] investigated, tested, and proposed the use of various gas sensing structures as early detectors of battery deterioration. Here, it is shown that sensing