Lightweight, Room-Temperature CO₂ Gas Sensor Based on Rare-Earth Metal-Free Composites—An Impedance Study

Christoph Willa, †,‡ Alexander Schmid, † Danick Briand, § Jiayin Yuan, # and Dorota Koziej* †,‡, §, #

†Laboratory for Multifunctional Materials, ETH Zurich, Vladimir-Prelog-Weg 5, 8093 Zurich, Switzerland
‡Center for Hybrid Nanostructures and Institute of Nanostructure and Solid State Physics, University of Hamburg, Luruper Chaussee 149, 22607 Hamburg, Germany
§Ecole Polytechnique Fédérale de Lausanne, LMTS, Rue de la Maladière 71b, 2002 Neuchâtel, Switzerland
#Department of Chemistry and Biomolecular Science and Center for Advanced Materials Processing, Clarkson University, Potsdam, New York 13699, United States

Supporting Information

ABSTRACT: We report a light, flexible, and low-power poly(ionic liquid)/alumina composite CO₂ sensor. We monitor the direct-current resistance changes as a function of CO₂ concentration and relative humidity and demonstrate fast and reversible sensing kinetics. Moreover, on the basis of the alternating-current impedance measurements we propose a sensing mechanism related to proton conduction and gas diffusion. The findings presented herein will promote the development of organic/inorganic composite CO₂ gas sensors. In the future, such sensors will be useful for numerous practical applications ranging from indoor air quality control to the monitoring of manufacturing processes.

KEYWORDS: CO₂ sensing, poly(ionic liquid), nanocomposite, flexible substrate, impedance

INTRODUCTION

The steadily increasing concentration of pollutant gases in the atmosphere is a major concern of modern society. For the first time, in 2016, the CO₂ level measured at the Mauna Loa observatory on Hawaii did not undercut 400 ppm during a full year. As a consequence, measuring, capturing, and reducing CO₂ are steadily gaining in importance and triggering interest in new technological solution for CO₂ monitoring. To date, atmospheric CO₂ concentration is generally measured using nondispersive infrared (NDIR) sensors due to their high selectivity and sensitivity. However, the NDIR technology has limited miniaturization potential, impeding its use in small and portable electronic devices. Furthermore, high power consumption, typically several hundreds of microwatts, hampers its use in battery-driven devices. As a consequence, efforts are devoted to developing alternative or improved techniques for the detection of CO₂. For example, a recent study presents a new sensor concept aiming at reducing the light path length in NDIR sensors. Furthermore, various simplified, small-sized CO₂ sensors taking advantage of changes in electrical response of the active material have been proposed. Yet, issues related to high power consumption remain unsolved. To reduce the power required to operate metal-oxide gas sensors at high temperatures, attempts using pulsed heating or MEMS microheaters were made. Alternatively, nanostructured materials can be used to enable room-temperature (RT) operability of gas sensors or to enhance reactivity toward CO₂. An orthogonal approach is the utilization of polymeric active materials featuring high tunability of electrical, chemical, and structural properties, and which simplify sensor fabrication. Previously, we developed a poly(ionic liquid) (PIL)-rare earth oxycarbonate composite showing sensitivity to CO₂ even at RT. In particular, we used a composite of poly[(p-vinylbenzyl)-trimethylammonium hexafluorophosphate] [P[VBTMA]-[PF₆]] and La₂O₂CO₃ as a sensing layer, which at RT and
upon exposure to 2400 ppm of CO₂ shows almost 12% of resistance changes but response and recovery times as long as 5 and >120 min, respectively. We observed that the interface between the organic and inorganic part determines the CO₂ sensing behavior. Originally, we used rare earth oxycarbonate particles due to their ability to detect CO₂ at elevated temperatures. This unique property is attributed to selective adsorption of CO₂ at La sites, which leads to changes of the oxygen coordination of La. However, the industrial-scale production of lanthanum-based sensors would inevitably lead to cost, recyclability, and environmental issues. As a consequence, the question arises whether the intrinsic sensitivity of La₂O₂CO₃ particles toward CO₂ is needed, or if they can be exchanged for another type of ceramic material. One possible substitute is alumina, which is chemically inert and abundantly available at low cost.

Here, we focus on replacing La₂O₂CO₃ by Al₂O₃ nanoparticles in the P[VBTMA][PF₆]/nanoparticle composite and subsequently on their application as CO₂ sensor at room temperature and under humid conditions. Direct-current (DC) resistance and alternating-current (AC) impedance measurements reveal that the intrinsic bulk properties of inorganic constituents do not play a role in the CO₂ sensing mechanism. Instead, it seems that the surface of the inorganic filler has a strong impact on the mobility of the charge carriers and diffusivity of CO₂. Sensors show similar sensing performance independent if they are spin- or spray-coated on the polyimide (PI) substrates. The fabrication procedure is robust, and utilization of the lightweight, flexible PI substrates increases sensors’ portability and brings a promise of potential up-scaling.

### EXPERIMENTAL SECTION

#### Chemicals

Vinylbenzyl trimethylammonium chloride ([VBTMA][Cl]) was synthesized via quaternization reaction of 4-vinylbenzyl chloride (31 g) with trimethylamine in ethanol (23.6 g, 0.4 M) in an ice bath and subsequent precipitation in diethyl ether. The presence of δ and γ phase was confirmed by powder X-ray diffraction (PXRD) analysis as shown in Figure S1 (Supporting Information).

#### Synthesis of P[VBTMA][PF₆]

The synthesis of P[VBTMA][PF₆] is performed in three steps: (1) Synthesis of (p-vinylbenzyl)-trimethylammonium chloride ([VBTMA][Cl]) via quaternization reaction of 4-vinylbenzyl chloride (31 g) with trimethylamine in ethanol (23.6 g, 0.4 M) in an ice bath and subsequent precipitation in diethyl ether. (2) Preparation of theionic liquid monomer, (PI) substrates. The fabrication procedure is robust, and utilization of the lightweight, flexible PI substrates increases sensors’ portability and brings a promise of potential up-scaling.

### Patterning of Electrodes on Polyimide Substrate

The deposition of the interdigitated electrodes (IDE) was adapted from previous studies. A 50 μm thick, flexible PI foil (Uplex-S05, UBE Industries Ltd., Yamaguchi, Japan) was used as a substrate. Before the deposition of the electrodes, the substrate was cleaned by successive rinsing with acetone, isopropanol, and deionized water. Next, the substrate was dried in a lab furnace for 1 h at 120 °C. E-beam evaporation and lift-off technique were used to deposit the IDEs. The transducer consists of a 130 nm platinum layer deposited onto a 20 nm titanium adhesion layer. A schematic of the transducer is shown in Figure S2 (Supporting Information). Three different designs, denoted as type A, B, and C, were tested. Their geometric parameters are summarized in Table 1, where N is the total number of fingers, L is their length, s is the interelectrode space, w is the finger width, A is the sensor area, and κ is the geometric cell constant. κ is the proportionality factor between specific and measured resistance of the composite material.

#### Deposition of the Composite

First, 50 mg of P[VBTMA][PF₆] was dissolved in 2 mL of acetonitrile, and 50 mg of Al₂O₃ nanoparticles was added. The dispersion was sonicated for 30 min and stored under vigorous stirring. Composite films were deposited onto the Pt-IDEs by spin- or spray-coating. For spin-coating, the electrodes were fixed onto a Menzel glass slide using Kapton tape. They were then coated four times with the PIL/nanoparticle dispersion within an interval of 5 min, while rotating at 700 rpm under nitrogen flush. A spin-coater (WS-400—6NPP-LITE, Laurell, North Wales, PA, USA) was used for that purpose. Alternatively, as a proof of concept, spray-coating was performed using a conventional airbrush pistol. The dispersion was sprayed at 1.5 bar of air pressure from a distance of 20 cm onto vertically mounted electrodes.

#### Characterization Techniques

Scanning electron microscopy (SEM) images were taken on a LEO 1530 Gemini microscope operating at 3 kV of acceleration voltage. For cross-sectional SEM, films were deposited on fluorine-doped tin oxide (FTO) substrates and in a second step broken in two. Powder X-ray diffraction (PXRD) data were acquired with a PANalytical Empyrean powder diffractometer in reflection mode using Cu Kα radiation and operating at 45 kV and 40 mA. The CO₂ sensing performance of the composites was tested by inserting the samples into a custom continuous-flow chamber. A computer-controlled gas mixing setup based on Bronkhorst gas flow controllers was used to deliver a constant gas flow of 200 mL/min with tunable humidity and CO₂ concentration in synthetic air (20/80 vol % O₂/N₂) as carrier gas. We calibrated each of the Bronkhorst gas-flow controllers at flow rates between 25 and 100% of their maximal gas flow and adjusted the measurement program accordingly. Furthermore, we used a CO₂-insensitive reference sensor (TGS 2600, Figaro Inc., Arlington Heights, IL, USA) for ensuring that the measured resistance changes were truly related to changes in CO₂. The analyte gas 1/19.8/79.2 vol % CO₂/O₂/N₂ was obtained from PanGas. DC resistance was monitored using a programmable electrometer (Model 617, Keithley, Solon, OH, USA). From these data we retrieved the sensor signal as well as response and recovery time. The sensor signal for a given CO₂ concentration was given by the ratio $R / R_{\text{CO}_2}$, where $R_{\text{CO}_2}$ is the baseline resistance before the pulse and $R_{\text{CO}_2}$ is the resistance measured at the end of a given pulse. For multiple series of pulses, the average sensor signal and standard deviation were calculated for each CO₂ concentration. The response ($t_{\text{on}}$) and recovery ($t_{\text{off}}$) times are defined as the times needed for the sensor to reach 90% of the resistance change during and after a pulse, respectively. AC impedance spectra were acquired in the frequency range from 100 mHz to 2.5 MHz using an impedance spectroscope (HP4192, Zurich Instruments, Switzerland) in combination with a transimpedance amplifier (HE27A, Zurich Instruments, Switzerland). Because of relatively large impedance values, the amplitude of the signal was set to 200 mV to obtain a stable output signal. Fitting of the impedance data to the equivalent circuit was performed using complex nonlinear least-squares.

### Table 1. Parameters of the IDEs Used Within This Study

| Type | N  | L [mm] | s [μm] | w [μm] | A [mm²] | κ [cm⁻¹] |
|------|----|--------|--------|--------|---------|---------|
| A    | 70 | 6.30   | 50     | 50     | 44.10   | 0.046   |
| B    | 70 | 2.50   | 20     | 20     | 7.00    | 0.116   |
| C    | 70 | 1.25   | 10     | 10     | 1.75    | 0.231   |

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algorithm implemented in a commercial software package (ZView, Scribner Associates Inc., Southern Pines, NC, USA).

**RESULTS AND DISCUSSION**

We investigate the role of Al$_2$O$_3$ nanoparticles on CO$_2$ sensing properties of a P[VBTMA][PF$_6$] matrix by subjecting both pristine polymer (see Figure S3) and P[VBTMA][PF$_6$]/Al$_2$O$_3$ composites to a series of gas pulses. We observe that the pristine polymer is sensitive toward CO$_2$; however, the addition of Al$_2$O$_3$ nanoparticles decreases the overall resistance of the films and reduces the response and recovery times by at least a factor of 7. We explain this by the fact that Al$_2$O$_3$ nanoparticles interact with the polymer matrix leading to an increase of the concentration of free counteranions in the vicinity of the polymer/nanoparticle interface. It was shown that such a behavior can lead to enhanced ionic conductivity and gas permeability. A similar observation was made in the field of Li-ion diffusion, where inorganic filler particles could be used to increase ion dissociation. Interestingly, an increase of gas permeability is in contrast with Maxwell’s model for conventional filled systems, stating that filler particles obstruct molecular transport. However, the inclusion of nanoparticles affects the conformation of polymer chains at the polymer/nanoparticle interface, and segmental motion is reduced, thus explaining the permeability increase and the discrepancy with Maxwell’s filler model. This observation points toward the importance of gas permeability and diffusion processes in composite sensing materials. As a consequence, inherent CO$_2$ sensitivity of the inorganic nanoparticles is not a prerequisite for sensitivity of the composite. This will be discussed in detail in the following sections.

We investigate the morphology of spin- and spray-coated films with SEM as shown in Figure 1. We observe that spin-coating results in rough films ~600 nm thick, whereas spray-coating typically yields homogeneous but thicker films up to a few micrometers. We note that the reproducibility of the spray-coating is lower due to inaccuracy of spraying time and nozzle—substrate gap given by manual spray-brush operation; however, we anticipate that this could be easily overcome in the automated system. Figure 2a,b shows that the baseline resistance of Al$_2$O$_3$—PIL films do not notably differ independently on the fabrication method and are slightly lower than for previously reported La$_2$O$_2$CO$_3$—PIL sensors. We hypothesize that for the thick spray-coated film a large dead volume, through which no significant portion of the measuring current passes, exists. The baseline resistance is independent of the inorganic constituents and can only be diminished to a certain extent by increasing film thickness. Furthermore, in both cases, the shape of the resistance changes indicates that the CO$_2$ absorption is fully reversible. This is in line with CO$_2$ absorption and desorption characteristics of tetraalkylammonium-based PILs. The sample prepared by spin-coating shows slightly higher sensor signal at all concentrations tested as shown in Figures S4–S5. We attribute this observation to its lower film thickness and thus absence of dead volume. In what follows, we will thus focus only on spin-coated samples.

The response time is ~1 order of magnitude shorter than the recovery time indicating that absorption kinetics is faster than desorption kinetics, an observation that is in accordance with literature. Also, both response and recovery time decrease with increasing CO$_2$ concentration as shown in Figure S6. Despite the fact that the baseline resistance decreases monotonically upon increase of humidity from 30 to 70% relative humidity (RH), we measure the highest CO$_2$ sensor signal at 50% RH as shown in Figure 3. The sensor signal versus CO$_2$ concentration for all curves is plotted in Figure S7.

The fit of the AC impedance data with a Randles equivalent circuit enables studying the role of the individual constituents of the composites in the CO$_2$ sensing mechanism. The Randles equivalent circuit consists of an ohmic resistor ($R_s$), a double-
layer constant phase element (CPE$_{dl}$), and the faradaic impedance ($R_{ct} - W_{oc}$) as shown in the inset of Figure 4a. A generalized open-circuit Warburg element ($W_{oc}$) models finite-length linear diffusion of charged species and is generally used to characterize ion transport as observed, for example, in conductive polymers deposited on metallic contacts$^{36}$ or in membranes inside which mobile electroactive ions are confined.$^{37,38}$ Figure 4a shows the impedance data of a P[VBTMA][PF$_6$]/Al$_2$O$_3$ composite at 0, 1000, 2000, and 4000 ppm of CO$_2$ in a Nyquist plot. We identify three distinct regions. At high frequencies, a semicircle resulting from the parallel combination of charge transfer resistance ($R_{ct}$) and CPE$_{dl}$ is observed. In the intermediate frequency region, a straight line at 45° results from concentration fluctuations of diffusion limited to the zone close to the electrode. At low frequencies, the penetration length of charged species becomes larger than the electrode–electrode distance resulting in a capacitive behavior.$^{36}$ The finite slope of the high-frequency tail indicates nonideal capacitive behavior of the generalized $W_{oc}$. This suggests that there is a distribution of diffusion path lengths ($\Phi_W$), which in the ideal case is equal to 1, and in our case is equal to 0.88 for all curves. Such behavior is typically assigned to inhomogeneous film thickness or ionic charge adsorption in the film.$^{39}$ We evaluate the frequency at which the transition between diffusion governed region and capacitive tail occurs from the Warburg plot shown in Figure 4b. This frequency lies at $\sim 2$–3 Hz, corresponding to a characteristic time scale $\tau$ of 0.3–0.5 s. This value can be attributed to the time needed for the ionic species involved in diffusion to fully diffuse from one electrode to the other. Such a time scale points toward the diffusion of protons ($3.62 \times 10^{-3}$ Vs/cm$^2$), present due to humidity in the film, via proton hopping, so-called Grotthus mechanism.$^{40–42}$ PF$_6^-$, the other ionic species present in the composite, have much smaller mobility due to their large size and therefore can only diffuse as a whole. We thus conclude that, unlike initially assumed for La$_2$O$_2$CO$_3$–PIL composites,$^{19}$ protons and not PF$_6^-$ are the main charge carrier during CO$_2$ sensing. Furthermore, the slope of the curve at intermediate frequencies corresponds to the Warburg coefficient and is inversely proportional to the square root of the diffusion coefficient and directly proportional to CO$_2$ concentration (see Table S1 in Supporting Information).
We deduce that proton diffusion is diminished by CO₂. The Warburg parameters varying in the presence of CO₂ are of major interest, since they depend on concentration of electroactive species. Figure 4a shows the relative changes of fitting parameters as a function of CO₂. The original data are given in Table S2. We observe that only the faradaic branch \( R_{ct}, W_{oc}, R \), and \( W_{oc}, T \) are increased by 34.2%, 39.2%, and 50.0%, with respect to CO₂ free atmosphere. This implies that CO₂ increases the charge-transfer resistance of the composite films. Also, since \( W_{oc}, T \) is inversely proportional to the diffusion constant, the presence of CO₂ leads to a decreased diffusion coefficient. On the contrary, \( R_s \) and CPE \( \alpha \) are not affected by CO₂. Bode plots of all curves are shown in Figure S8.

In the composite, both protons and \([PF_6]^-\) species from the polymer are present. Since diffusion of the latter is hindered by its relatively large size, it is important to further investigate the role of water vapor leading to proton conductivity. The Nyquist plots in Figure 5a illustrate that the impedance is strongly affected by RH. The fitting parameters are given in Table S3. We find that RH influences the same circuit elements of the equivalent circuit as CO₂ (Figure 5b), namely, \( R_{ct}, W_{oc}, R \), and \( W_{oc}, T \), but with opposite sign. On the basis of this observation, we propose that the absorption of CO₂ molecules leads to disruption of the hopping chains necessary for the Grotthus mechanism and therefore hinders proton transport, which in turn leads to increased charge transfer resistance and reduced proton diffusion coefficient.

**CONCLUSIONS**

Here, we demonstrate a \( P[VBMTA][PF_6]/Al_2O_3 \) composite material that can be used for CO₂ sensing in humid air. The inclusion of alumina nanoparticles modifies permeation properties of films and thus influences the mobility of diffusing charge carriers and small molecules such as CO₂. Since alumina particles do not interact with CO₂, the chemical nature of the particles plays a secondary role in the sensing process. Therefore, alternatives to rare-earth-based CO₂ sensitive inorganic particles can be used in the future. On the basis of AC impedance studies it appears that CO₂ affects only the faradaic branch composed of a charge transfer resistance and a Warburg diffusion process. The strong humidity dependence of impedance indicates that variations in proton conduction are contributing to the sensitivity. As CO₂ hampers proton diffusion by blocking Grotthus pathways in the composite, inverse effects relative to humidity are observed. Furthermore, we demonstrate that the composites show CO₂ sensitivity over a large range of humidity, from 30 to 70%. The results presented herein are relevant to the development of new CO₂ sensors being potentially competitive with the NDIR technology. For the application in air quality monitoring the CO₂ sensor can be combined with already commercially available capacitive humidity sensors. Moreover, the compatibility of the composite films with light and flexible PI substrates is a first step toward utilizing cost-effective and large-area manufacturing methods, such as digital and roll-to-roll (R2R) printing for next-generation electronics.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b07379.

- PXRD pattern, electrode design, resistance measurements, sensor signal at various RH, tabulated impedance fitting results, and Bode plots of impedance (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: dorota.koziej@uni-hamburg.de.*

**ORCID**

Jiayin Yuan: 0000-0003-1016-5135

Dorota Koziej: 0000-0002-9064-2642

**Notes**

The authors declare no competing financial interest.

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