FLUORESCENT OPTICAL SENSORS FOR CARBON DIOXIDE USING THE QUENCHING EFFECT OF 4-NITROPHENOL

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The sensing chemistry of carbon dioxide is mainly based on the measurement of the internal pH change of the sensing membrane. All-solid-state fluorescent optical sensors have been introduced by replacing the Severinghaus-type aqueous buffer by a polymer soluble one, using large alkyl chain quaternary ammonium hydroxide (QA-OH) as additive. It converts the indicator into its deprotonated form, and, by using it in large excess, also acts as a buffer. In the presence of CO_2, carbonic acid is formed and due to its dissociation the pH of the buffer system and, hence, the optical property of the indicator, will be changed.

In our work p-nitrophenol (pNP) and its polymer derivatives are introduced as a buffer system for optical carbon dioxide sensor. pNP has a pKa ~ 7.2, turns its color from colorless to yellow, and these properties make it suitable as an indicator for CO_2 sensing. However the molecule is readily soluble in water, therefore it was considered to synthesize i) a phenol-formaldehyde (novolak type) polymer and to nitrate it partly in a second step making it pH-sensitive in the proper range; ii) to synthesize p-NP-formaldehyde resin (PPNP) directly, where all of the segments of the polymer are pH sensitive, theoretically.

Instead of using pNP and its polymer derivatives directly as colorimetric CO_2 sensor, luminescent sensors were developed by dissolving cationic indicators, such as rhodamine B (zwitterionic form), Al-morin complex and carbocyanine indicator (D282) into the polymeric cocktails. The cocktail contained p-NP or one of the polymers, an indicator, Tecoflex hydrogel, DDMA-OH as additive. Microscope cover glasses were spincoated by the cocktail and subsequently coated by a proton impermeable thin silicone layer after drying.

The wide variety of luminescent indicators covers a broad spectral and also a broad life-time range. The polymers were converted to their anionic form by using quaternary ammonium compounds. In the presence of the deprotonated nitrophyenol groups the luminescence of the indicators are almost totally quenched, because the cationic indicators form ion-pair with the negatively charged polymer. In the presence of CO2 the nitrophenol groups becomes partly protonated, this way the quencher ions (originally located in close vicinity of the indicators) are replaced partly by hydrogen carbonate anions, and as a result the luminescence signal (both the intensity and the lifetime) increases.

The optical signal change is a complex function of the CO_2 concentration, because it is influenced both by the protonated and deprotonated p-NP units, that results in two different quenching constants. Moreover, in some cases (e.g. Al-morin) the absorption band of the polymer and of the luminescent indicator overlaps, causing an inner filter effect. Analytical parameters of the sensors, such as response time, dynamic range, detection limit, drift, etc. were measured; the effect of the composition of the sensing chemistry (namely the dye/quencher ratio and the dye/acceptor ratio) on the relative signal change and on the sensitivity will be also discussed.

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