Evaluating Zeolite-Modified Sensors: towards a faster set of chemical sensors

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Abstract. The response of zeolite-modified sensors, prepared by screen printing layers of chromium titanium oxide (CTO), were compared to unmodified tin oxide sensors using amplitude and transient responses. For transient responses we used a family of features, derived from the exponential moving average (EMA), to characterize chemo-resistive responses. All sensors were tested simultaneously against 20 individual volatile compounds from four chemical groups. The responses of the two types of sensors showed some independence. The zeolite-modified CTO sensors discriminated compounds better using either amplitude response or EMA features and CTO-modified sensors also responded three times faster.

Keywords: Zeolite-modified CTO gas sensors, e-nose, transient response, signal processing.
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INTRODUCTION

Chemo-sensing applications would greatly benefit from highly selective and sensitive, fast responsive, and no drifting gas sensors. Unfortunately, such ideal gas sensors are largely unrealizable today. Real sensors normally show a trade-off between sensitivity, selectivity, response time, and reversibility. Accordingly, when approaching a new sensing problem, a very reasonable, yet arguable, question arises: given the existence of the vast number and diversity of chemical sensors available, how does one select the best combination of sensors for a fast and reliable discrimination of chemical species? Undoubtedly, providing a general answer to this question is difficult, if possible at all, but a conceivable way to address this issue is to compromise, and hence to use a number of sensors that show only partial specificity to some of the target species of the application at hand. In view of this, in this paper we explore, for the first time, the possibility of creating an orthogonal gas sensor array. In doing so, we characterize Zeolite modified chromium titanium oxide (CTO) gas sensors[1] and compare them with it unmodified SnO_2 sensing technology.

MATERIALS AND RESULTS

We evaluated two sensor arrays, one comprising six standard, doped tin dioxide gas sensors the other comprising six doped chromium titanium oxide sensors with a

TABLE 1. Metal oxide based gas sensors: (top row) zeolite-modified chromium titanium oxide (CTO) and (bottom row) tin dioxide.

CTO sensors	**CTO**	**CTO -HZSM-5**	**CTO+ NaZSM-5**	**CTO+ HLTA**	**CTO+ MCM41**	**CTO+ HZSM-22**
τ_{min} (s)	9.5	8.0	6.5	8.5	7.0	6.5
τ_{max} (s)	13	11.5	10.5	13.5	10.5	9.5
SnO_2 sensors	T30/1	P10/1	P10/2	P40/1	T70/2	PA/2
τ_{min} (s)	16.0	17.5	20.0	15.5	23.0	19.5
τ_{max} (s)	25.0	24.5	31.0	23.5	34.0	28.5

zeolite-modified (CTO) coating (Table 1)[1]. The sensors were exposed to 20 volatile compounds at a single concentration per chemical group (Table 2).

We compared the sensitivities of the two arrays using the ratio of the maximal resistance change to the baseline (R/R_0). This feature of the sensor responses is recognized as one of the most informative. However, R/R_0 omits useful information that may be contained in the transient phases of the sensor responses. Therefore, we analyzed the transient responses of the sensor, which are the aggregate of a number of dynamic processes that take place at the sensing surface. We focused on a family of features, contained in the exponential moving average (EMA), to characterize chemo-resistivity under tightly-controlled flow conditions[2]. The raw response and EMA transforms for one zeolite-modified CTO sensor responding to pentanol are shown in Fig. 1 panel (a).

TABLE 2. Analyte type and family name comprised in the dataset.

Family	**Alcohol 1.22E^{-5}M**	**Aldehyde 8.03E^{-5}M**	**Ester 3.70E^{-5}M**	**Ketone 3.79^{-5}M**
Chemical compound	Pentanol	Acetaldehyde	Ethylhexanoate	Acetone
	Hexanol	Butanal	Ethylacetate	2-butanone
	2-hexenol	Hexanal	Isopentylacetate	2-pentanone
	Octenol	2-hexenal	Methylacetate	2-heptanone
	Methylbutanol	Furfural	Ethylbutyrate	2-3-butanedione

Figure 1 ((b) through (d)) displays the loadings of a principal components analysis (PCA) computed for the features of two EMA conditions (α=0.001 and 0.005) for the entire dataset. When either the CTO or SnO_2 sensor arrays are considered in isolation,

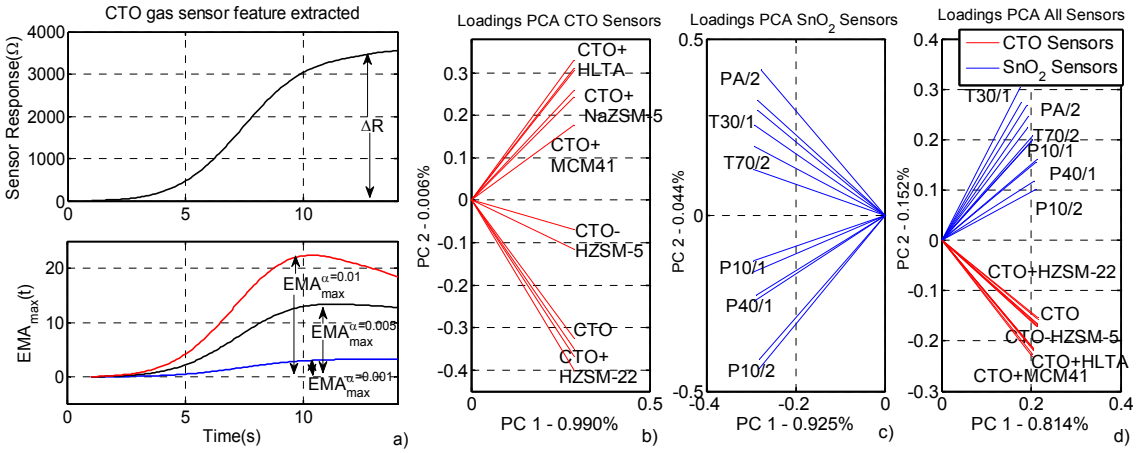

FIGURE 1. A raw CTO sensor response (with offset removed) to pentanol (top row (a)) and its ema$_\alpha$ transforms for α=0.001, 0.005, 0.01 (bottom row (a)). Loadings of the main two PCs for each sensor technology (panels (b) and (c)) and both together (c). The PCA was calculated on the transient response of the sensor (features: emaα=0.001 + emaα=0.005).

the loadings span only one dimension (99% and 92% of the variance in the first principal component respectively). In contrast, PCA calculated on the EMAs extracted from both sets of sensors (rightmost plot of Figure 1) spans two dimensions (PC1 explains 81% and PC 2 15% of the variance). Thus, the responses of the two types of sensors are not completely correlated, meeting one of the requirements for improved electronic nose performance[3].

We also compared the discrimination capability of the two sensor arrays using a well-known classifier, the linear support vector machine (SVM). Results of "leave-one-out" cross validation are shown in Table 3. The two sensor arrays yielded similar performance for all the classification tasks except for the discrimination of ketones, where the CTO sensors performed significantly better using either R/R_0 or EMA features. Using R/R_0, CTO sensors also performed better than standard SnO_2 sensors in classifying all 20 analytes in the dataset. In addition, zeolite-modified CTO sensors responded to analytes up to three times faster than standard sensors (see Table 1), which potentially makes them more suitable for a number of time-sensitive applications such as gas distribution mapping or gas plume tracking with a robotic platform.

TABLE 3. Odor classification success rate. The second column describes the family type. Columns 3-5 provide the odor classification (in %) for each sensing technology respectively.

Feature	Family Group	CTO sensors	SnO_2 sensor	Combined
R/Ro	Alcohols	100 %	100%	100%
	Aldehyde	98%	100%	100%
	Ester	96%	94%	94%
	Ketone	96%	82%	98%
	all	92%	86.5%	97%
Dynamic: $EMA_{\alpha=0.001}$ + $EMA_{\alpha=0.005}$	Alcohols	100%	96%	98%
	Aldehyde	100%	98%	98%
	Ester	96%	96%	96%
	Ketone	100%	92%	94%
	all	97%	95%	96.5%

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