

## Sensing of n-Butanol Vapours with Oxygen Vacancy-Enriched Zn<sub>2</sub>SnO<sub>4</sub>-SnO<sub>2</sub> Hybrid-composite

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### Scheme S1: Detailed derivation of the fitting equation of the conductance transients

As discussed earlier, when the sensor is exposed to butanol, it oxidised by the pre-adsorbed oxygen species (Eqn. 3) forming RO<sub>ad</sub>. Assuming the monolayer adsorption of ethanol on the sensor surface at constant temperature, T, the conductance transients can be modelled with the Langmuir- Hinshelwood adsorption mechanism. Since the Eqn. 3 is a rate-limiting step, the rate of the RO<sub>ad</sub> formation can be written as:

$$\frac{d[RO_{ad}]}{dt} = k_a[R_g][O_{ad}^-] - k_d[RO_{ad}] \quad (i)$$

If it is assumed that at time, t, the fraction of the surface is occupied by chemisorbed oxidised vapours (RO<sub>ad</sub>) is  $\theta$ . The remaining unoccupied sites,  $(1 - \theta)$ , are filled by the excess oxyanion ( $O_{ad}^-$ ) and concentration of the injected reducing gas such as acetone and ethanol is C<sub>g</sub>, we may write from Eqn. (i):

$$\frac{d\theta}{dt} = k_a(1 - \theta)Cg - k_d\theta \quad (ii)$$

Where,  $k_a$  and  $k_d$  represents the adsorption and desorption constants.

$$k_a = \frac{SN_0K_0}{(2\pi MRT)^{1/2}} \exp\left(-\frac{E_a}{RT}\right) \quad (iii)$$

where, S denotes the surface area of the sensor where VOC adsorbed,  $K_0$  is the condensation coefficient,  $E_a$  represents the activation energy for adsorption,  $N_0$  and R are the Avogadro's number, and universal gas constant respectively.

Eqn. (ii) can be rearranged as;

$$\frac{d\theta}{dt} = k_a Cg - (k_a Cg - K_d)\theta \quad (iv)$$

Assuming  $(k_a Cg - K_d) = k_1$ , Eqn. (iv) can be rewrite as;

$$\frac{d\theta}{dt} = k_a Cg - k_1\theta \quad (v)$$

$$\frac{d\theta}{dt} + k_1\theta = k_a Cg \quad (vi)$$

Multiplying both side of Eqn. (vi) with the integrating factor,  $\exp(k_1t)$ ;

$$\exp(k_1t)\frac{d\theta}{dt} + k_1\theta\exp(k_1t) = k_a Cg \exp(k_1t) \quad (vii)$$

Left hand side is the derivative of;

$$\frac{d}{dt}(\theta \exp(k_1 t)) = k_a C g \exp(k_1 t) \quad (viii)$$

Integrate both side with respect to time, t;

$$\theta \exp(k_1 t) = k_a C g \int \exp(k_1 t) dt \quad (ix)$$

$$\theta \exp(k_1 t) = \frac{k_a C g}{k_1} \exp(k_1 t) + C \quad (x)$$

C is integration constant here. The Eqn. (x) can be rewrite as;

$$\theta = \frac{k_a C g}{k_1} + C \exp(-k_1 t) \quad (xi)$$

Assuming at t=0, the surface coverage,  $\theta = 0$ ;

$$C = -\frac{k_a C g}{k_1} \quad (xii)$$

Replacing C in Eqn. (xi) and rewriting it;

$$\theta = \frac{k_a C g}{k_1} (1 - \exp(-k_1 t)) \quad (xiii)$$

when  $t \rightarrow \infty$ ,  $\theta = \theta_0 = \frac{k_a C g}{k_1}$ , Eqn. (xiii) can be rewritten as,

$$\theta(t) = \theta_0 \{ 1 - \exp[-k_1 t] \} \quad (xiv)$$

When,

$$k_1 \sim \frac{1}{\tau_{1(res)}} = (k_a C g - k_d) \quad (xv)$$

$$\theta(t) = \theta_0 \left\{ 1 - \exp \left[ -\frac{t}{\tau_{1(res)}} \right] \right\} \quad (xvi)$$

In gas sensors, the conductance  $G(t)$  of the sensor is typically related to the surface coverage  $\theta(t)$  of adsorbed molecules. Assuming the linear functional dependency between  $\theta(t)$  and  $G(t)$  and the single adsorption site present on  $Zn_2SnO_4-SnO_2$  chemiresistor, the conductance variation of the response cycle  $G_A(t)$  can be written as:

$$G_A(t) = G_o + G_1 \left\{ 1 - \exp \left[ -\frac{t}{\tau_{1(res)}} \right] \right\} \quad (xvii)$$

where  $G_0$  is the base conductance of the sensing material,  $\tau_1$  is the response time constant.

In case of desorption cycle, the rate of change of surface coverage is written as;

$$\frac{d\theta}{dt} = -k_d \theta \quad (xviii)$$

Assuming at  $t=0$  (when desorption started), the surface coverage,  $\theta=\theta_0$  and at time  $t$ ,  $\theta$  would be  $\theta_d$  integrating the Eqn. (xviii) from both sides,

$$\int_{\theta_0}^{\theta_d} \frac{d\theta}{\theta} = -k_d \int_0^t dt \quad (xix)$$

$$\ln \left( \frac{\theta_d}{\theta_0} \right) = -k_d t \quad (xx)$$

Taking exponential both side;

$$\theta_d(t) = \theta_0 \exp(-k_d t) \quad (xxi)$$

The Eqn. (xxi) can be expressed as;

$$G_d(t) = G_o + G_2 \left\{ \exp \left[ -\frac{t}{\tau_{2(rec)}} \right] \right\} \quad (xxii)$$

Where  $k_d = \frac{1}{\tau_{2(rec)}}$ ,  $G_2$  is the change in conductance due to desorption and  $G_o$  is the baseline conductance.

From Eqn. (xvii) & Eqn. (xxii), we can write;

$$G(t) = G_o + G_1 \left\{ 1 - \exp \left[ -\frac{t}{\tau_{1(res)}} \right] \right\} + G_2 \left\{ \exp \left[ -\frac{t}{\tau_{2(rec)}} \right] \right\} \quad (xxiii)$$

Now assuming  $k_d \ll k_a C_g$ ,  $(k_a C_g - k_d) = k_1$  can be rewritten as,

$$k_1 = k_a C_g \quad (xiv)$$

From Eqn. (iii), we can deduce

$$k_a = A \exp \left( -\frac{E_a}{KT} \right) \quad (xv)$$

Where, A is pre-exponential constant and K is Boltzmann constant.

From Eqn. (xv), (xxiv) and (xxv), one can write

$$\tau_1 C_g = A^{-1} \exp \left( \frac{E_a}{KT} \right) \quad (xvi)$$

$$\tau_1 = \tau_0 \exp \left( \frac{E_a}{KT} \right) \quad (xxvii)$$

Where,  $\tau_0$  is a constant. At constant concentration of the ethanol and acetone ( $C_g = \text{constant}$ ),

taking logarithm of both side in Eqn. (xxvii)

$$\ln(\tau_1) = \text{const} + \frac{E_a}{RT} \quad (xxviii)$$

From the slope of the linear fitting of  $\ln(\tau_1)$  vs  $1/T$  plot using Eqn. (xxviii), the activation energy can be calculated.

**Table S1: The characteristics kinetic fitting parameters of conductance transients at different operating temperature and concentration of butanol**

<b>Temp.</b>	<b>Conc. (ppm)</b>	<b>G<sub>0</sub> (S)</b>	<b>G<sub>1</sub> (S)</b>	<b>G<sub>2</sub>(S)</b>	<b>τ<sub>1</sub> (s)</b>	<b>τ<sub>2</sub> (s)</b>
<b>275 °C</b>	100	5.102E-8	1.884E-7	-	30.46	-
	250	2.973E-8	3.049E-7	-	35.11	-
	500	4.202E-8	3.666E-7	-	47.98	-
	1000	1.026E-7	6.065E-7	-	80.26	-
<b>300 °C</b>	100	8.462E-8	3.614E-7	-	74.68	-
	250	5.882E-8	1.039E-6	-	83.06	-
	500	1.942E-7	1.438E-6	-	95.15	-
	1000	7.534E-8	2.129E-6	-	139.47	-
<b>325 °C</b>	100	4.158E-8	7.882E-7	-3.391E-8	32.48	13.60
	250	2.403E-7	1.743E-6	-2.053E-7	39.67	909.09
	500	2.623E-7	3.043E-6	-1.241E-7	53.28	192.30
	1000	2.454E-7	5.669E-6	-1.903E-7	100.00	833.33
<b>350 °C</b>	100	1.332E-7	1.187E-6	-2.260E-7	27.55	769.23
	250	1.219E-7	2.294E-6	-2.464E-7	34.32	344.82
	500	1.234E-7	4.971E-6	-1.432E-8	39.97	112.36
	1000	1.244E-7	1.099E-5	-3.680E-7	70.17	344.82