Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

SUPPORTING INFORMATION

S1: Calculation details of ϕ functions given in Table 3

From the mechanism described in Table 2, the ϕ functions, specific for each step, can be calculated by considering one rate-determining step and all the other at the equilibrium. The ϕ functions are obtained by resolution of an equations system given in Table S1- 1.
The used notations are k_i ($1 \leq i \leq 8$) for the rate constants, K_i ($1 \leq i \leq 3$ and $5 \leq i \leq 8$) for the equilibrium constants, where i corresponds to each step of the mechanism, D for the diffusion coefficients and θ for the ZnS surface site fractions. Equations (1) to (3) and (6) to (8) represent the expressions of the equilibrium constants of the corresponding steps. Equations (4) and (5) correspond respectively to the equality of the zinc vacancies and oxygen atoms concentrations at interstitial sites at both interfaces when one diffusion step is at the equilibrium (flow conservation). Equation (9) represents the electro-neutrality equation at the external interface for which two Brouwer cases can be considered. The electro-neutrality in the ZnO phase is represented by equation (10). Equation (11) and (12) are the conservation equations of the surface ZnS sites. In order to obtain the ϕ function expressions, by considering each step as a rate-determining step and all the other at the equilibrium, each equation system to resolve is different. Indeed, the equilibrium constant of the step considered as rate-determining is not taken into account, since this step is not at the equilibrium. In particular, if a diffusion step is considered as rate-determining, the equations of concentration equality at the interfaces are not valid.

Table S1- 1. Equations system for the calculation of the ϕ functions for each step considered as a rate-determining step.

Equations	Unknown variables
(1) $K_1 = \frac{\theta_{H-s}^{\ 2}\,\theta_{S-s'}}{P_{H_2S}\,\theta_s^{\ 2}\,\theta_{s'}}$	$[O''_{i\,\mathrm{int}}]$
(2) $K_2 = \frac{P(H_2O)\theta_s^{\ 2}}{\theta_{H-s}^{\ 2}[O''_{iext}][h^{\circ}_{ext}]^2}$	$[O''_{i\,ext}]$
(3) $K_3 = \frac{\theta_{s'}[V''_{Zn\,ext}][h^{\circ}_{ext}]^2}{\theta_{S-s'}}$	$[V''_{Zn\,\mathrm{int}}]$
(4) $[V''_{Zn\,\mathrm{int}}] = [V''_{Znext}]$	$[V''_{Zn\,ext}]$
(5) $[O''_{i\,\mathrm{int}}] = [O''_{i\,ext}]$	$[h^{\circ}_{ext}]$
(6) $K_6 = [V^{\circ\circ}_{O(ZnO)}][O''_{i\,\mathrm{int}}]$	$[V^{\circ\circ}_{O(ZnO)}]$
(7) $K_7 = \frac{[V''_{Zn(ZnO)}]}{[V''_{Zn\,\mathrm{int}}]}$	$[V''_{Zn(ZnO)}]$
(8) $K_8 = \frac{1}{[V''_{Zn(ZnO]}][V^{\circ\circ}_{O(ZnO)}]}$	θ_s
(9) $2[V''_{Zn\,ext}] + 2[O''_{i\,ext}] = [h^{\circ}_{ext}]$	θ_{H-s}
(9 a) $2[V''_{Zn\,ext}] = [h^{\circ}_{ext}]$	$\theta_{s'}$
(9 b) $2[O''_{i\,ext}] = [h^{\circ}_{ext}]$	$\theta_{S-s'}$
(10) $[V^{\circ\circ}_{O(ZnO)}] = [V''_{Zn(ZnO)}]$	
(11) $\theta_s + \theta_{H-s} = 1$	
(12) $\theta_{s'} + \theta_{S-s'} = 1$	

1. Zhang, H. Z.; Banfield, J. F. *Journal of Physical Chemistry C* **2009**, *113* (22), 9681-9687