Supplementary Material (ESI) for Chemical Communications

Thin and defect-free Pd-based composite membrane without any interlayer and substrate penetration by an organic and inorganic combined process

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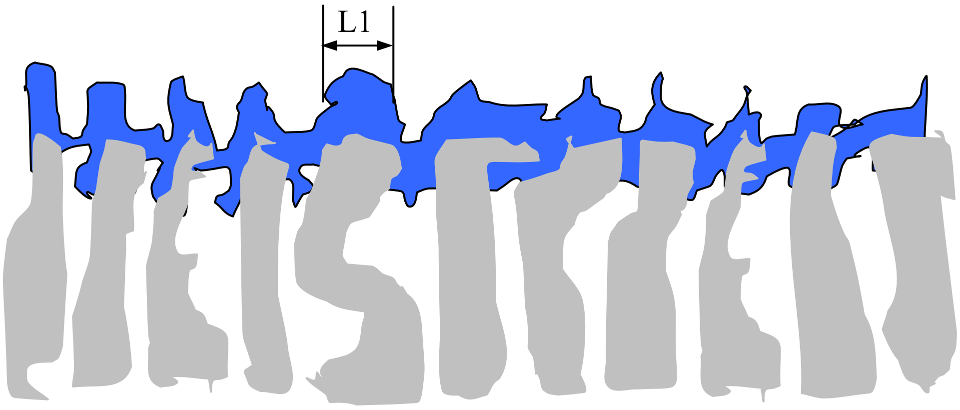
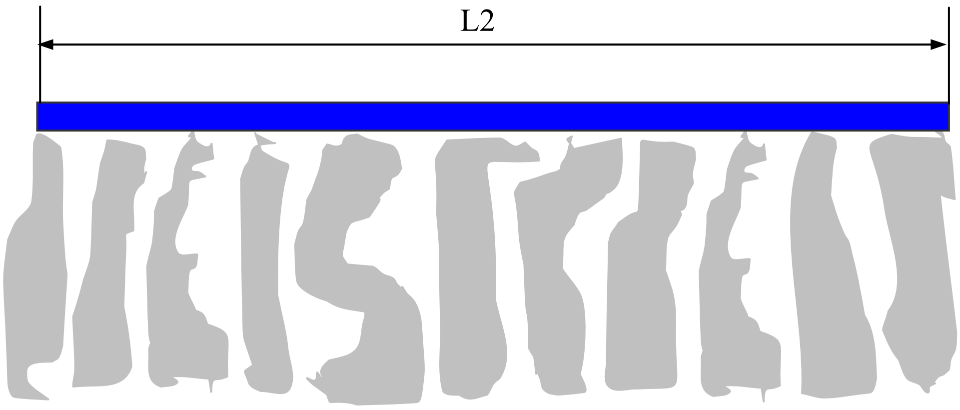
Theoretically analyzing the membrane stability

Figure (1a) shows that the Pd-based layer with preferential deposition on the substrate wall was deposited on porous substrate. Due to the existence of the substrate pore during the depositing process, the pinholes problem cannot be avoided for this kind of membrane configuration. Moreover, some Pd particles were anchored into the substrate pores, which decreased the effective Pd area greatly, increased the effective Pd thickness greatly, and decreased the active shear stress length largely (L1, about several mm). The smaller effective Pd area and the larger effective Pd thickness made the hydrogen permeation flux very low under certain experimental conditions. The small shear stress length was related to the large shear stress while enduring thermal cycles and hydrogen adsorption and desorption cycles, which is the key point for the poor membrane stability. **Figure 1(b)** shows that the thin and defect-free Pd-based layer with uniform thickness was covered on porous substrate by organic and inorganic combined process. There is not interlayer and substrate penetration between the Pd-based layer and the substrate layer. On the contrary, there existed a small interstice between the Pd layer and the substrate layer, which makes the shear stress length almost equal to the membrane tube length (L2, about two orders larger than L1).



(a)



(b)

Figure 1 Schematics of different Pd-based membrane configurations. (a) Membrane configuration from normal deposition method directly on porous substrate, (b) membrane configuration from organic and inorganic combined process.

Based on the literature published by S. Tosti et al. (Sputtered, electroless, and rolled palladium-ceramic membranes, Journal of Membrane Science, 2002, 196, 241-249), we can calculate the shear stress for both membrane configurations (**Figure 1(a)** and **Figure (b)**). The shear stress analysis schematic is shown in **Figure 2**. Under thermal cycling and hydrogen loading, at the interface of Pd-based layer and the ceramic substrate, shear stresses occur due to the differential elongation between the metal and the ceramic. It is obvious that the following equations can be obtained.

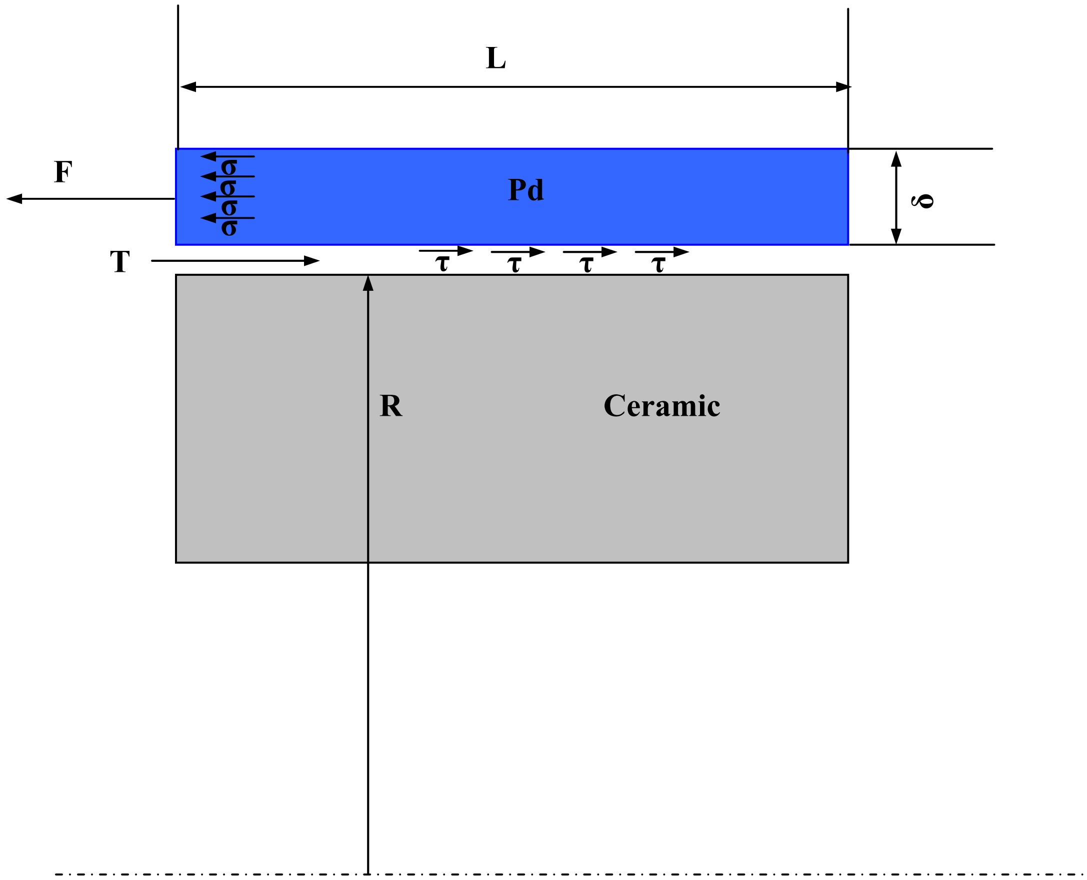


Figure 2 Schematic of force/stresses for Pd-ceramic composite membrane in the elongation of the Pd layer

(1) $F=\sigma 2\pi rs$

(2) $F=T=\tau 2\pi rL$ (L is a characteristic length in which shear stresses are active)

(3) $\tau=F/2\pi rL=E_{Pd}(\varepsilon_{H/Pd}-\varepsilon_{cer})s/L$

(4) $\tau 1=F/2\pi rL=E_{Pd}(\varepsilon_{H/Pd}-\varepsilon_{cer})s/L1$ (τ1 and L1 are the shear stress and the shear stress active length of normal membrane configuration respectively.)

(5) $\tau 2=F/2\pi rL=E_{Pd}(\varepsilon_{H/Pd}-\varepsilon_{cer})s/L2$ (τ2 and L2 are the shear stress and the shear stress active length of novel membrane configuration respectively.)

(6) $\tau 2/\tau 1=L2/L1\leq 10^{-2}$

Therefore, the shear stress for the novel membrane configuration from the organic and inorganic combined process is about two orders smaller than that for the normal membrane configuration from the normal deposition method.