1. Effects of $H_2O$ in Hydrogen Oxidation Reaction on the Perovskite Surfaces

The electrochemical performances of perovskite materials Sr$_x$Fe$_{1-x}$Mo$_y$O$_{3+y}$ (SF1.5M) and the Pr- and La-substituted series for the hydrogen oxidation reaction (HOR: $H_2(g) + O_2(g) = H_2O(g) + V_{2H} + 2e^-$) in dry and humidified $H_2$ are investigated by Density Functional Theory (DFT) based thermodynamic modeling, electrical conductivity relaxation (ECR), and electrochemical impedance spectroscopy (EIS) techniques [1].

Both ECR and EIS measurement results indicated a promoted electrochemical performance on tested SF1.5M material in humidified $H_2$.

DFT-based thermodynamic modeling revealed nonstoichiometry of SF1.5 (001) slab models significantly alters the HOR energy landscape.

DFT energy analysis showed enhanced interaction of surface H species with the hydrated SF1.5M surface.

Acknowledgements

[1] Qi and Lee et al., ACS Catal. 2020, 10, 5567−5578

2. Hydrogen and Cation Diffusion in Bulk Tetragonal Zirconia

Density functional theory based thermokinetic modeling was performed to determine the effect of $H_2O$ and $O_2$ gas pressure on the defect chemistry, hydrogen solubility and diffusivity, and on cation transport in tetragonal bulk ZrO$_2$ [2].

The DFT based defect thermodynamic modeling results provide information related to the stable defect complexes and hydrogen-related defect species relevant to bulk cation transport kinetics at different gas pressure and $T$ conditions.

**Summary**
- Most of the stable hydrogen defect species in tetragonal bulk ZrO$_2$ is $H_2O(-3)$, and its concentration is 4-6 orders magnitude higher than that of $H$ interstitial ($H_{int}$). Nonetheless, the most active hydrogen transport occurs via $H_{int}(+1)$ with migration barriers 0.2-0.4 eV than through the stable $H_2O(-3)$ defect which has a larger migration barrier of 1.6 eV.
- The calculated diffusion coefficients reveal that cation diffusion in tetragonal bulk ZrO$_2$ will transit from the $V_{2H}(-4)$ mechanism at high temperatures to the $H_2O(-3)$ mechanism upon lowering the operating temperature and/or increasing the humidity content.
- The model further predicts another transition in the bulk cation transport mechanisms, $V_{2H} \to$ fully- or partially-bound Schottky defects above $T=1573$ K (attributed to enhanced gas entropic stabilization) [2,3].
- Formation of $V_{2H}(-4)$, $Zr_{int}+O_2(+4)+V_{2H}(-4)+Zr_{int}(−4)$-$H^+$ involves the $O_2$ gas phase (or $H_2O$ - $H_2$) on the reactant side, which destabilizes the reaction with increasing temperature; this gas effect was further balanced in the Schottky defect formation.

**Dependence of Modeled $D_{H2}$ and $D_{O2}$ on 1/T**

**Cation migration barriers ($V_{2H}$ vs $H_{int}$)**
- $V_{2H}(-2)$ $V_{2H}(-4)$
- $H_{int}(+1)$ $H_{int}(-4)$

**H migration barriers ($H_{2O}$ vs $H_{int}$)**
- $H_{int}(+1)$ $H_{int}(-4)$

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