Mechanistic study of sulfur-poisoning and removal reactions of barium zirconate-based anodes: An ab initio atomistic calculation

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In the present study, we investigated the mechanism of sulfur-poisoning and removal reactions on the Y and Yb doped barium zirconate ($BaZrO_3$), the perovskite ceramic widely employed for solid oxide fuel cell (SOFC) application, by ab initio atomistic calculation. The computational result found that sulfur-poisoning reaction corresponds to SO_4^{2-} formation in the bulk phase, $H_2S_{(g)} + 6O^{2-}_{(b)} \rightarrow SO_4^{2-}_{(b)} + 2OH^-_{(b)} + 8e^-$. This oxidation reaction is a kinetically fast, with the highest activation barrier of 0.58 eV, and thermodynamically favorable process with the overall exothermicity of -17.21 eV, showing the vulnerability of $BaZrO_3$-based anodes. The poisoned SO_4^{2-} can be removed by the assistance of steam, in which SO_4^{2-} is oxidized to SO_2, $SO_4^{2-}_{(b)} + 2H_2O_{(g)} + 2e^- \rightarrow SO_{2(g)} + 4OH^-_{(b)}$. This reduction reaction is somewhat energetically unfavorable with the highest barrier of 1.81 eV and overall endothermicity of 0.79 eV. Additionally, we utilized the thermodynamic corrections on the energetic result to examine the effects of partial pressures of gas-phase species and applied voltage in the practical SOFC operation. Our result found that the poisoning reaction is unavoidable as the nonspontaneity occurs at rather high electric bias of -2.07 V or low H_2S contamination of 100 ppm. On the other hand, the removal reaction is feasible at the bias voltage of -0.31 V or sufficient steam partial pressure of 0.03 torr. The computationally resolved mechanisms provide the new insights for better design anodic materials in SOFC application and have been further confirmed by *operando* surface enhanced Raman spectroscopy (SERS).