

相场法模拟固体氧化物燃料电池阳极内 Ni-YSZ 界面处 YSZ 相变引发界面形貌演化

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摘 要: 固体氧化物燃料电池(SOFC)的电解质材料氧化钇稳定氧化锆(YSZ)在长期运行中会发生由立方晶向四方晶(c-t)相变所导致材料离子电导率下降与力学性能退化, 进而加剧全电池性能衰减。针对现有研究对 YSZ 相变动力学定量分析不足的问题, 本工作通过构建微弹性相场模型, 对 SOFC 阳极内部 Ni-YSZ 界面处的 YSZ 内部的 c-t 晶体相变过程进行了定量研究。模拟结果准确预测了实验过程中观察到的界面处 YSZ 形貌演化, 并解释了 Ni-YSZ 界面附近 YSZ 内部孔洞的生成机制。研究通过理论建模与实验的相互验证, 为提升 SOFC 阳极内部 Ni-YSZ 界面稳定性提供了理论支持。

关键词: 相场法; 固体氧化物燃料电池; 镍-氧化钇稳定氧化锆界面; 立方晶-四方晶相变; 形貌演化

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固体氧化物燃料电池(SOFC)因其能量转换效率高、燃料适应性强等优势, 成为新型能源技术的研究热点^[1]。作为 SOFC 传统电解质材料, 氧化钇稳定氧化锆(YSZ)凭借高温氧离子传导性和稳定的机械性能被广泛采用。有前期研究表明, YSZ 在还原环境下具有显著的热稳定性, 如 Wang 等^[2]通过原位纳米压痕实验证实 YSZ 力学性能在还原性气氛中几乎无衰减。Butz 等^[3]进一步揭示了 SOFC 中 Ni-YSZ 电极在烧结过程中由高温扩散导致的 Ni 渗入 YSZ, 能够导致 YSZ 的相变速率提高数十倍, 且离子电导率在 100 h 内下降 24%, 这一发现凸显了 SOFC 阳极制备工艺对电解质材料稳定性的深远影响。尽管 SOFC 技术在过去 30 年取得了显著进展, 但对于在长期运行过程中复杂高温工况所引发的电解质材料性能衰减仍然缺乏深入的研究, 并成为制约 SOFC 大规模应用的瓶颈问题。

现有研究大多聚焦于电极电化学性能的衰减^[4-7], 例如 Ni-YSZ 阳极中 Ni 的粗化与迁移已被证实为 SOFC 和固体氧化物电解池(SOEC)模式下性能衰减

的关键诱因^[8]。然而, 学界对于 YSZ 在长期运行过程中的材料稳定性, 如立方晶-四方晶(c-t)相变行为, 对 SOFC 性能的影响关注不足。YSZ 的 c-t 相变会直接导致离子电导率显著下降并伴随力学性能的劣化。在 Ni-YSZ 复合阳极中, 此类相变还可能通过改变界面特性直接影响局部的电化学活性。Hattori 等^[9]发现 8%(摩尔分数) Y_2O_3 掺杂 YSZ 在 800 °C 退火 1000 h 后, 其离子电导率由 $0.05 S \cdot cm^{-1}$ 降至 $0.04 S \cdot cm^{-1}$ 。拉曼光谱分析也显示四方相特征峰, 且原子力显微镜(AFM)表征也显示相变引发的马氏体表面结构演化。此外, Ni-YSZ 阳极制备过程中的 Ni 固溶(1%~2%)^[10]以及运行期间的 Ni 迁移^[11]均被证实会加速相变。同时, 除表面结构演化之外, 界面附近孔洞的形成也被证实是影响电解质离子导电率的诱因之一。Tietz 等^[12]对 SOEC 在 9000 h 运行后的样品分析表明, YSZ 晶界处孔洞的形成使欧姆电阻增加 50%。以上研究表明 YSZ 的相变行为不仅直接影响其离子电导率, 还可能通过局部孔洞的生成诱发应力集中和机械破坏^[13], 加速电池性能

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衰减或整体失效。

针对上述现象, 学界已从实验角度深入探究相变机制及其影响。Kishimoto 等^[14]在实际长期运行后的 SOFC 电堆样品中证实了 YSZ 相变的发生, 而 Deville 等^[15]通过微应变分析揭示了相变与微观裂纹形成过程的关联。Laguna-Bercero 等^[16]通过原位拉曼光谱表征证实 YSZ 的 c-t 相变与其电导率下降呈直接关联。然而, 目前传统实验表征手段难以定量解析高温下相变动力学过程。为此, 相场模型逐渐成为研究 YSZ c-t 相变的重要工具: Mamivand 等^[17]通过构建二维弹性相场模型, 成功模拟了应力场对氧化锆四方-单斜(t-m)相变的调控作用; Lei 等^[18]则通过多晶模型, 揭示了电极微观结构演化对电导性的影响。然而, 此类模拟多基于理想化结构, 无法真实反映实际材料的多尺度特征。Wilson 等^[19]开发的聚焦离子束扫描电子显微镜(FIB-SEM)介观三维重构技术虽能精确量化电极三相边界(TPB)等微观参数, 但结合真实结构的相场模型仍存在局限^[20–22], 尤其是模拟中未充分考虑 Ni-YSZ 界面处相变过程的动态工况耦合效应^[23]。

因此, 本工作提出构建基于 SOFC 阳极真实介观结构的三维微弹性相场模型, 通过模拟 YSZ c-t 相变过程中变体生长对 YSZ 表面形貌的影响, 揭示由 YSZ 相变所诱发的表面形貌演化及孔洞形成机制, 为优化 SOFC 电极提供理论支持。

1 相场模型的建立

在描述 c-t 相变的相场模型中, t 变体序参量被定义为 η_p , 其中, $p=1, 2, 3$ 对应母相 c 中沿坐标轴 3 个变体方向。基于非保守场的 Allen-Cahn 方程可得:

$$\frac{\partial \eta_p(\mathbf{r}, t)}{\partial t} = -L \frac{\delta F}{\delta \eta_p(\mathbf{r}, t)}, (p=1, 2, 3) \quad (1)$$

式中: L 为变体迁移系数; F 为体系的总自由能; $\mathbf{r}$ 为坐标向量。 η_p 的值定义在 0~1 变化, 其中, $\eta_p=1$ 对应 p 方向变体; $\eta_p=0$ 表示 p 方向变体以外的相。同时, 基于保守场的 Cahn-Hilliard 方程, 定义 YSZ 的体积分序参量为 C , 则控制方程为:

$$\frac{\partial C}{\partial t} = \nabla \cdot \left[M \left(\nabla \frac{\delta F}{\delta C} \right) \right] \quad (2)$$

式中: t 为时间。考虑到 YSZ 中 t 相变体在高温条件下生成后的相对稳定性^[24], 保守场序参量迁移率

定义为:

$$M = M_c \left[1 - 0.9 \times \sum_{p=1}^3 (\eta_p)^2 \right] \quad (3)$$

体系总自由能定义为:

$$F = \int_V dV \left[\Delta f \cdot f_0(C, \eta_p) + f_{\text{grad}} + f_{\text{el}} \right] \quad (4)$$

式中: Δf 为界面能系数, 代表四方相与母体立方相之间的自由能差; f_0 为由序参量定义的界面自由能密度, 且

$$f_0 = f_1 + f_2 + f_3 \quad (5)$$

式中:

$$f_1 = -\left(\frac{A}{2}\right)(C - C_m)^2 + \left(\frac{B}{4}\right)(C - C_m)^4 + \left(\frac{D}{4}\right)(C - C_0)^4 \quad (6)$$

$$f_2 = \left[\left(\frac{E}{2}\right) \sum_{p=1}^3 (\eta_p)^2 - \left(\frac{G}{3}\right) \sum_{p=1}^3 (\eta_p)^3 + \left(\frac{H}{4}\right) \left(\sum_{p=1}^3 (\eta_p)^2 \right)^2 \right] (C - C_m) \quad (7)$$

$$f_3 = -\sum_{p=1}^3 \left(\frac{J}{2} \right) (C - C_0)^2 (\eta_p)^2 \quad (8)$$

梯度能和弹性能密度定义为:

$$f_{\text{grad}} = \frac{\kappa_C}{2} (\nabla C)^2 + \sum_{p=1}^3 \frac{\kappa_\eta}{2} (\nabla \eta_p)^2 \quad (9)$$

$$f_{\text{el}} = \frac{1}{2} \mathbf{C}_{ijkl}(\mathbf{r}) \boldsymbol{\varepsilon}_{ij}^{\text{el}} \boldsymbol{\varepsilon}_{kl}^{\text{el}} \quad (10)$$

式中: κ_C 和 κ_η 为相应序参量对应的梯度能系数; $\mathbf{C}_{ijkl}(\mathbf{r})$ 为四阶弹性张量, 通过不同序参量的加权定义为

$$\mathbf{C}_{ijkl} = \sum_{p=1}^n P(\eta_p) \mathbf{C}_{ijkl}^t + \left[1 - \sum_{p=1}^n P(\eta_p) \right] \mathbf{C}_{ijkl}^c \quad (11)$$

式中: $\mathbf{C}_{ijkl}^c$ 和 $\mathbf{C}_{ijkl}^t$ 分别是 YSZ 立方和四方相的弹性张量矩阵, 且插值函数 $P(x) = x^3(6x^2 - 15x + 10)$ ^[17]。对于四方相的 3 个变体, 其固有应变与弹性常数矩阵在整体坐标系下各不相同, 因此, 在模拟中需要将变体的固有应变与弹性常数矩阵以特定角度参考全局坐标进行旋转得到局部坐标^[25]。 $\boldsymbol{\varepsilon}_{ij}^{\text{el}}$ 为二阶弹性应变张量, 且等于总应变 $\boldsymbol{\varepsilon}_{ij}$ 与相变变体本征应变张量 $\boldsymbol{\varepsilon}_{ij}^0$ 之差:

$$\boldsymbol{\varepsilon}_{ij}^{\text{el}} = \boldsymbol{\varepsilon}_{ij} - \boldsymbol{\varepsilon}_{ij}^0 \quad (12)$$

式中: $\boldsymbol{\varepsilon}_{ij}^0$ 定义为:

$$\varepsilon_{ij}^0 = \sum_{p=1}^3 \varepsilon_{ij}^{00}(p) \eta_p \quad (13)$$

$\varepsilon_{ij}^{00}(p)$ 是产生 t 相 p 方向变体所对应的无应力应变。

$$\begin{aligned} \varepsilon_{ij}^{00}(1) &= \begin{bmatrix} \varepsilon_1 & 0 & 0 \\ 0 & \varepsilon_3 & 0 \\ 0 & 0 & \varepsilon_3 \end{bmatrix} \\ \varepsilon_{ij}^{00}(2) &= \begin{bmatrix} \varepsilon_3 & 0 & 0 \\ 0 & \varepsilon_1 & 0 \\ 0 & 0 & \varepsilon_3 \end{bmatrix} \\ \varepsilon_{ij}^{00}(3) &= \begin{bmatrix} \varepsilon_3 & 0 & 0 \\ 0 & \varepsilon_3 & 0 \\ 0 & 0 & \varepsilon_1 \end{bmatrix} \end{aligned} \quad (14)$$

通过 c 与 t 相晶格参数计算可得 $\varepsilon_1 = -0.0086$, $\varepsilon_3 = 0.0078$ [25]。根据相场微弹性理论, 材料在纳米尺寸下一般表现为非均匀性, 而在宏观上呈现出均匀性, 此时总应变:

$$\varepsilon_{ij} = \bar{\varepsilon}_{ij} + \delta\varepsilon_{ij} \quad (15)$$

式中: $\bar{\varepsilon}_{ij}$ 和 $\delta\varepsilon_{ij}$ 分别为均匀应变和摄动应变, 且满足:

$$\int_V \delta\varepsilon_{ij} dV = 0 \quad (16)$$

因此, 位移可以表示为由均匀应变引起的位移 $\bar{\varepsilon}_{ij}x_j$ 和非均匀位移 $v(\mathbf{r})_i$ 之和:

$$u(\mathbf{r})_i = \bar{\varepsilon}_{ij}x_j + v(\mathbf{r})_i \quad (17)$$

式中: x_j 为 $\mathbf{r}$ 的笛卡尔坐标, 而摄动应变定义为:

$$\delta\varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial v_j}{\partial x_i} + \frac{\partial v_i}{\partial x_j} \right) \quad (18)$$

当 $\bar{\varepsilon}_{ij}$ 和 $v(\mathbf{r})_i$ 的变化使弹性能 $F_{el} = \int_V f_{el} dV$ 减小到最小值时, 达到力学平衡。此时通过下列关系可得到平均应变和摄动位移:

$$\frac{\partial F_{el}}{\partial \bar{\varepsilon}_{ij}} = 0 \quad (19)$$

$$\frac{\partial F_{el}}{\partial v_i} = 0 \quad (20)$$

本工作集中研究的是单晶 YSZ 结构在空间中的变体分布。通过构建 $64 \times 64 \times 64$ 的离散体素模型来定量描述初始三维结构。初始 YSZ 母相被设定为 $64 \times 64 \times 32$ 离散体素对应的单晶长方体结构。在计算过程中, 同时对控制式(1)和式(2)进行无量

纲化处理: $\nabla^* = l_0 \nabla$, $t^* = M_c t / l_0^2$, $\kappa_c^* = \kappa_c / l_0^2$, $\kappa_\eta^* = \kappa_\eta / l_0^2$, $L^* = L l_0^2 / M_c$, 式中: $l_0 = 41.2$ nm, 为体素的特征长度。这里采用傅里叶谱方法将高阶偏微分方程转换为傅里叶空间下的常微分方程进行求解。在时间迭代过程中, 选用半隐式迭代方案放宽对时间步长的限制, 同时保证计算稳定性和精度 [21, 25-28]。模拟时间步长设为 $t^* = 0.02$, L^* 取 0.1, $\Delta f = 2 \times 10^8$ J·m⁻³, 其他无量纲参数见表 1。模拟初期从随机分布的变体相形核开始, 且形核分布限制在 YSZ 表面, 这与 Kishimoto 等 [14] 通过原位拉曼光谱观测到的相变起始位置相似。控制方程在周期性边界条件下使用的傅里叶谱方法求解过程的细节可参考文献 [25]。

表 1 相场模型相关参数

Table 1 Parameters used in the phase-field model

Parameter	Value
A(-)	1.50
B(-)	6.00
D(-)	1.00
E(-)	0.14
G(-)	12.42
H(-)	12.28
J(-)	0.80
$C_m(-)$	0.50
$C_0(-)$	0.00
$\kappa_c^*(-)$	0.30
$\kappa_\eta^*(-)$	0.02

2 实验

以直径 24 mm、厚度 0.5 mm 的致密 YSZ 圆片为基底, 经机械抛光及丙酮-乙醇超声清洗后, 通过不锈钢掩模进行 2 次垂直磁控溅射形成厚度约 1 μ m 的连续 Ni 图案化薄膜阳极。阴极方面, 采用铂(Pt)浆料涂覆于 YSZ 基底另一侧。SOFC 放电实验采用自设计氧化铝反应腔体, 阳极通入加湿 97% (体积分数) H₂, 阴极通入纯 O₂, 气体流量均固定为 50 mL·min⁻¹。在 0.7 V 阳极-阴极端电压的极化条件下进行 100 h 放电。实验前后, 使用机械法剥离 Ni 薄膜, 选取样本表面 Ni 薄膜脱落的部分, 利用日本日立高新技术公司 TM4000 型 SEM 表征 YSZ 表面形貌, 如图 1 所示, 界面区域形成典型的马氏体浮雕结构, 并伴随亚微米级图案化脊结构 [29]。

3 结果与讨论

图 2~图 4 展示了模拟过程中 YSZ 内部 c-t 相变

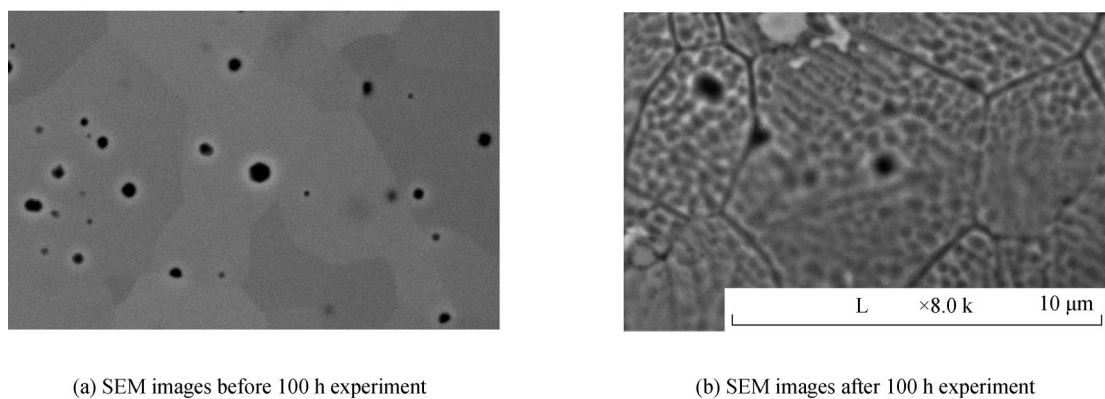


图 1 100 h 实验前后 Ni-YSZ 界面处 YSZ 表面形貌 SEM 照片

Fig. 1 SEM images of YSZ surface topography at the Ni-YSZ interface before and after the 100 h experiment

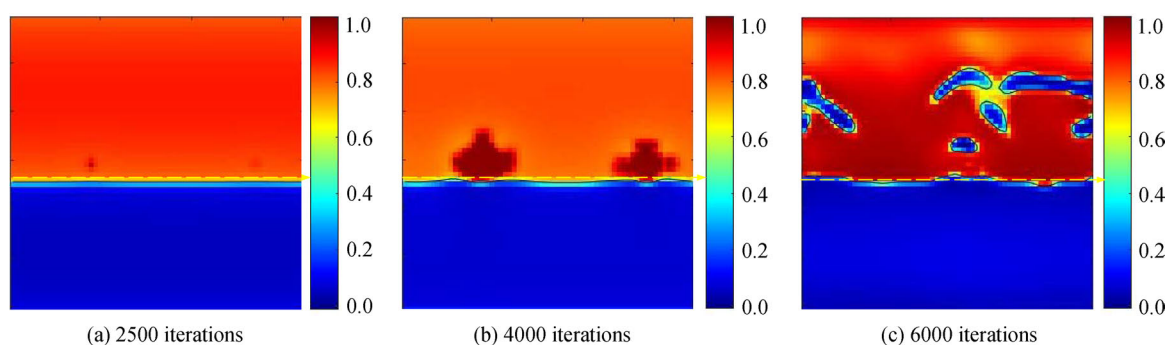
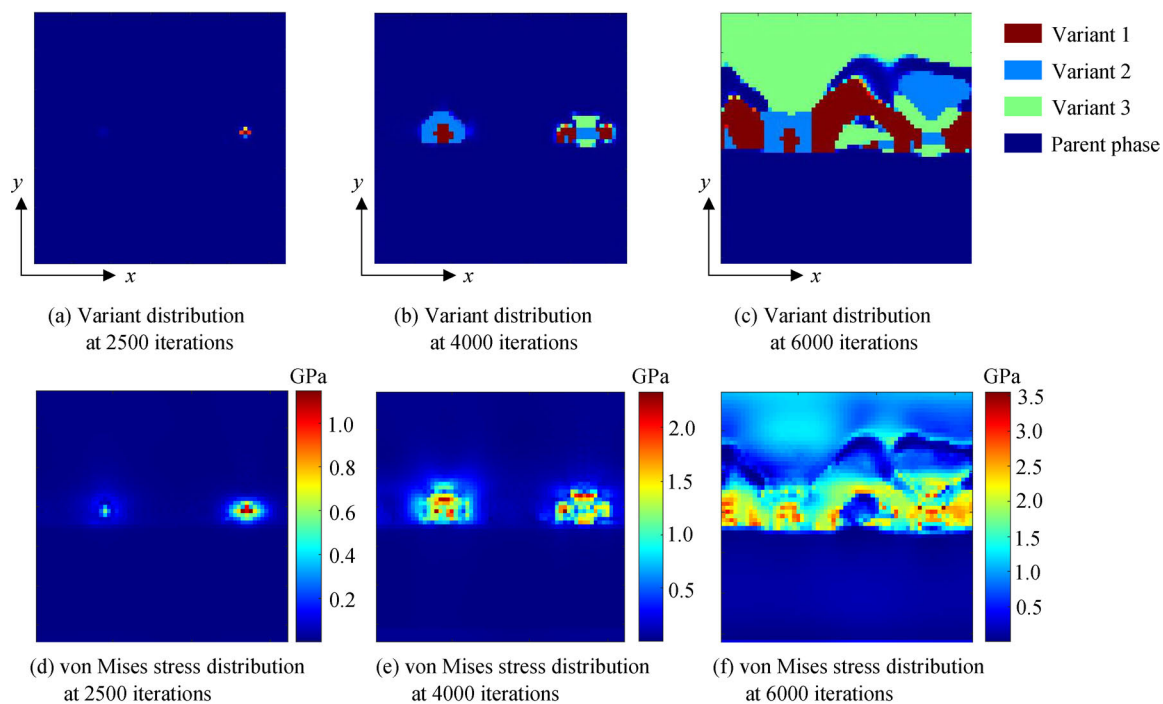


图 2 不同迭代次数后体积分数分布

Fig. 2 Distributions of volume fraction after different iterations

图 3 x - y 截面处不同迭代次数后变体分布及相应的米塞斯应力分布Fig. 3 Distributions of variant and corresponding von Mises stress at x - y sections after different iterations

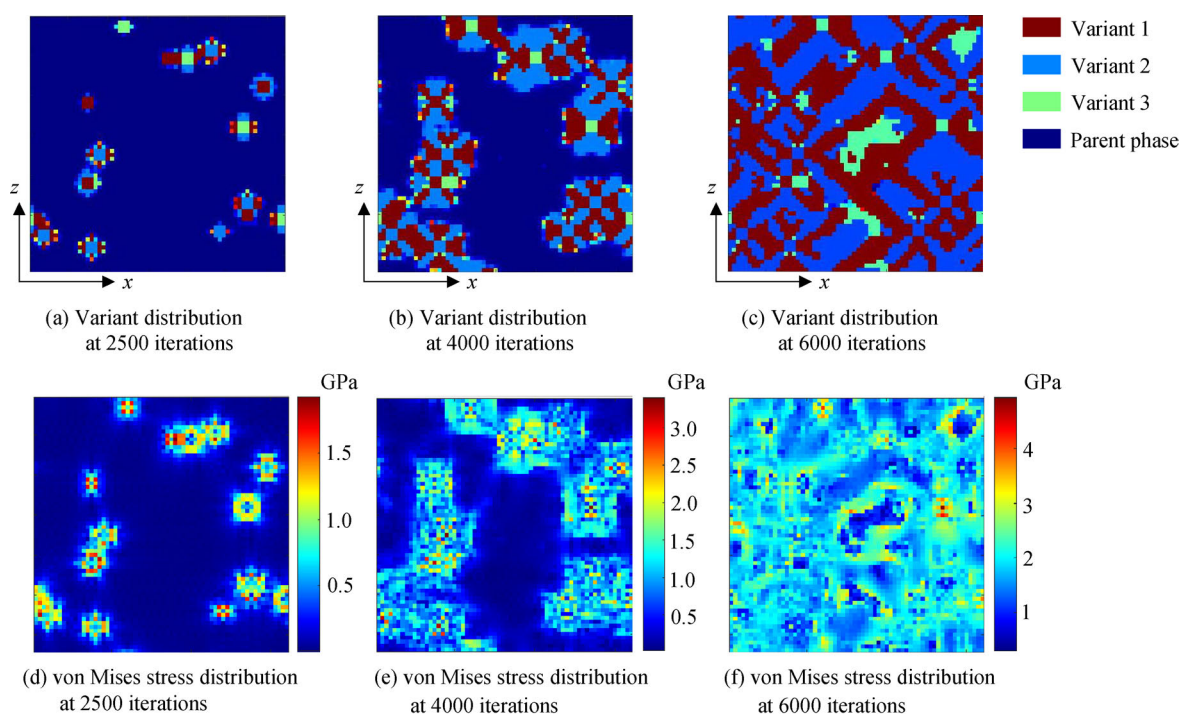
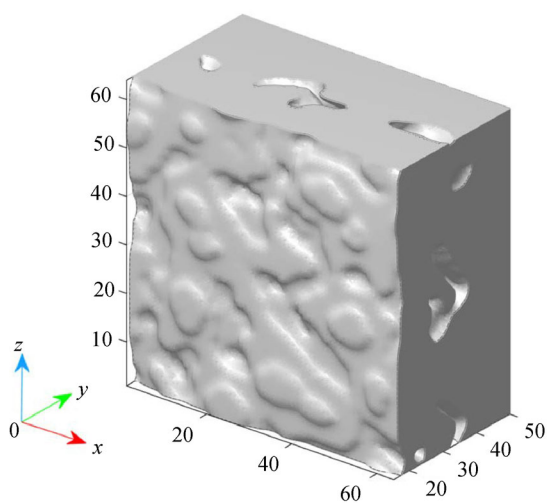
图 4 x - z 截面处不同迭代次数后变体分布及相应的米塞斯应力分布Fig. 4 Distributions of variant and corresponding von Mises stress at x - z sections after different iterations

图 5 YSZ 表面形貌 3D 模拟图

Fig. 5 3D simulation of YSZ surface topography

随时间的演化模拟结果。可以观察到, 2500 次迭代后变体优先在 YSZ 表面处沿初期形核开始生长。此时界面形貌还基本保持平整, 在生成变体周围可观察到应力集中现象。经过 4000 次迭代, 不同变体间可以观察到 2 GPa 以上的应力产生, 这是由于变体生长过程中相对于基底相本征应变弛豫过程所产生, 且弛豫过程使系统自由能降低^[30]。此时 t 变体呈放射状沿 YSZ 表面向固体内部生长。同时, 伴随材料在高温下迁移, 使 YSZ 表面形貌开始出现曲

率。6000 次迭代后, 变体生长扩展至 YSZ 整体, 原始平整表面发生明显形貌演化。基体内部由于物质迁移出现亚微米级孔洞。图 5 展示了迭代 6000 次后 YSZ 的三维结构。由图 5 可以看出, YSZ 表面呈现脊状起伏结构, 且侧面可观察到内部出现非均匀分布的孔洞。经过计算得出迭代后 YSZ 内部孔隙率为 10.87%。图 2~图 5 模拟结果与图 1b 实验后样品单一晶粒内部表面结构高度吻合, 验证了本单晶模型的有效性。变体演化过程中孔洞形成的位置并非大都位于表面以下。结合图 2~图 4 可知, c - t 相变诱发的高应力区多发于表面处, 而孔洞周围没有观察到 2 种及以上的变体出现, 且相应的 von Mises 应力显著低于临近区域。这是由于 c - t 相变引发的不同变体界面处产生的较高应力所致。由局部高应力所导致的高应力梯度能够导致较大的局部自由能梯度, 驱动物质向低应力区的迁移, 当本过程能够越过孔洞形核的临界能垒时, 会在 YSZ 表面下区域形成非均匀分布的孔洞, 这与 Tietz 等^[12]研究中观察到的 YSZ 表面以下内部孔洞形成的现象非常相似。相关 YSZ 内部孔洞形成机制能够通过本工作模拟所得到的结果进行定量解释。

本工作通过实验研究与数值模拟相结合, 基于相场法的数值模拟再现了拥有自由表面的单晶 YSZ 在 c - t 相变过程中的结构演化及内部孔洞的形成机

制。考虑到真实实验中样品为多晶多孔的复杂结构,在本工作基础上,后续研究将结合界面处 Ni 烧结、YSZ 表面缺陷以及多晶结构等,进一步探究 YSZ 相变过程对 SOFC 阳极内部 Ni-YSZ 界面及电极性能的影响。

4 结论

基于相场法通过理论框架构建及关键参数优化,通过数值模拟实现了对 SOFC 阳极内 Ni-YSZ 界面处 YSZ 在 c-t 相变过程影响下发生结构形态演化过程的精确模拟。研究表明,相变所诱导的结构演化微观机制表现为 t 相变体优先在 YSZ 表面处形成异质形核,并且在后续结构演化过程中影响 YSZ 表面形成三维脊状结构。与此同时,界面附近的 YSZ 内部会伴随变体生长演化出孔洞结构。该数值模拟结果与 SEM 观测到的实验样品表面结构高度吻合。由于当前模拟基于理想单晶假设,可能影响其在实际多晶多孔电极内的适用性,进一步考虑真实复杂工况与介观结构的研究工作将基于本工作所得到的结果在未来开展。本工作为优化 SOFC 电极内部异质界面的稳定性提供了理论支持,为进一步揭示复杂电化学过程中多物理场耦合条件下的界面的相变-形貌协同演化机制提供了重要参考与模型基础。

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Simulation of Evolution of Interface Morphology Induced by Yttria-Stabilized Zirconia (YSZ) Phase Transformation at Ni-YSZ Interface in Solid Oxide Fuel Cells Anode Using Phase Field Method

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Extended Abstract

Introduction Solid oxide fuel cells (SOFCs) are considered as a leading candidate for clean energy conversion due to their high efficiency and flexibility. Yttria-stabilized zirconia (YSZ) serves as an electrolyte material in SOFCs due to its high ionic conductivity and mechanical stability at a high operating temperature. However, the long-term stability of YSZ can be impaired via the cubic-tetragonal (c-t) phase transformation. This transformation leads to a decrease in ionic conductivity and mechanical integrity, which contributes to an overall degradation of SOFC performance. Despite its importance, most of the previous investigations primarily focused on electrochemical degradation mechanisms, while less attention was paid to the material stability of YSZ, especially at the Ni-YSZ interface. For instance, the atomic diffusion of Ni into YSZ during sintering can accelerate the phase transformation, leading to a significant decrease in ionic conductivity within 100 hours. Despite these findings, there is a lack of comprehensive quantitative analysis on the kinetics and morphological impacts of the c-t phase transformation at the Ni-YSZ interface. Moreover, the existing models often oversimplify an interplay between phase transformation and mechanical stress, restricting their ability to predict a long-term degradation behavior accurately. In this work, the phase field method was applied to simulate the c-t phase transformation in YSZ at the Ni-YSZ interface for elucidating its effect on the interface morphology and gaining insights into the SOFC degradation mechanisms.

Methods A 3D microelastic phase field model was proposed to investigate the c-t phase transformation in YSZ. The evolution of both conserved and nonconserved order parameters were governed by the Allen-Cahn and Cahn-Hilliard equations, respectively. The total free energy was constructed under multiphysics coupling. The elastic constants for cubic YSZ and tetragonal YSZ were defined based on their respective crystal structures, with the values assigned to reflect their distinct mechanical properties. The misfit strain was determined using the lattice parameters for the cubic and tetragonal phases. The simulations were performed on a 64×64×64 voxel grid representing a single-crystal YSZ. The governing equations could be solved by the Fourier spectral method and a semi-implicit time-stepping scheme. The shape of the nucleus distribution was restricted to the YSZ surface to ensure a realism under SOFC operating conditions.

In this work, a dense YSZ disk with a diameter of 24 mm and a thickness of 0.5 mm was served as a substrate. After mechanical polishing and ultrasonic cleaning in acetone and ethanol, a stainless-steel shadow mask was employed to perform two perpendicular magnetron-sputtering depositions, producing a continuous Ni patterned film anode with a thickness of approximately 1 μm. For the cathode, a Pt paste was screen-printed onto the opposite side of the YSZ substrate. The discharge tests of the SOFC were carried out in a custom-designed alumina reaction chamber. Humidified 97% H₂ was supplied to the anode and pure O₂ to the cathode, both at a fixed flow rate of 50 mL·min⁻¹. The cell was polarized at 0.7 V for 100 h. After testing, the Ni film was mechanically peeled off, regions where Ni detached were selected and the underlying YSZ surface morphology was examined by scanning electron microscopy (SEM).

Results and discussion The phase field simulations reveal that tetragonal variants preferentially nucleate at near the Ni-YSZ interface. High stresses appear at around the Ni-YSZ interfaces with the development of the t-variants. At certain iterations, high local stresses of exceeding 2 GPa can occur, leading to a radial growth of the variants into the bulk. A significant morphological evolution occurs, forming ridge structures along the YSZ surface and submicron pores in the interior at near the Ni-YSZ interface. The agreement between simulation data and experimental results confirms that the c-t phase transformation causes these morphological evolutions. The formation of pores is particularly detrimental as it disrupts the ion conduction pathways and weakens

mechanical stability of YSZ, which can be correlated to the degradation of the SOFC performance.

Conclusions In this work, a phase field modeling was used to simulate the c-t phase transformation in YSZ at the Ni-YSZ interface in SOFC anodes. The simulations accurately reproduced the morphological evolutions during long-term operation of SOFC, *i.e.*, the formation of surface ridges and internal submicron pores, providing important insights into the SOFC degradation mechanisms. The preferential nucleation of tetragonal variants at the surface and stress-driven void formation could highlight some key factors affecting interface stability. Although the simulations were conducted based on a single crystal, this work could lay a foundation for future research on polycrystalline and porous YSZ substrates. This work could indicate strategies for improving SOFC durability, such as optimizing material compositions or designing stress-relieving structures via identifying stress generation as a primary driver of degradation. The findings of this work could contribute to advancing SOFC technology towards sustainable and efficient energy solutions.

Keywords phase field method; solid oxide fuel cell; nickel-yttria-stabilized zirconia interface; cubic-tetragonal phase transformation; morphology evolution