质子交换膜燃料电池的模拟
ANSYS-Fluent

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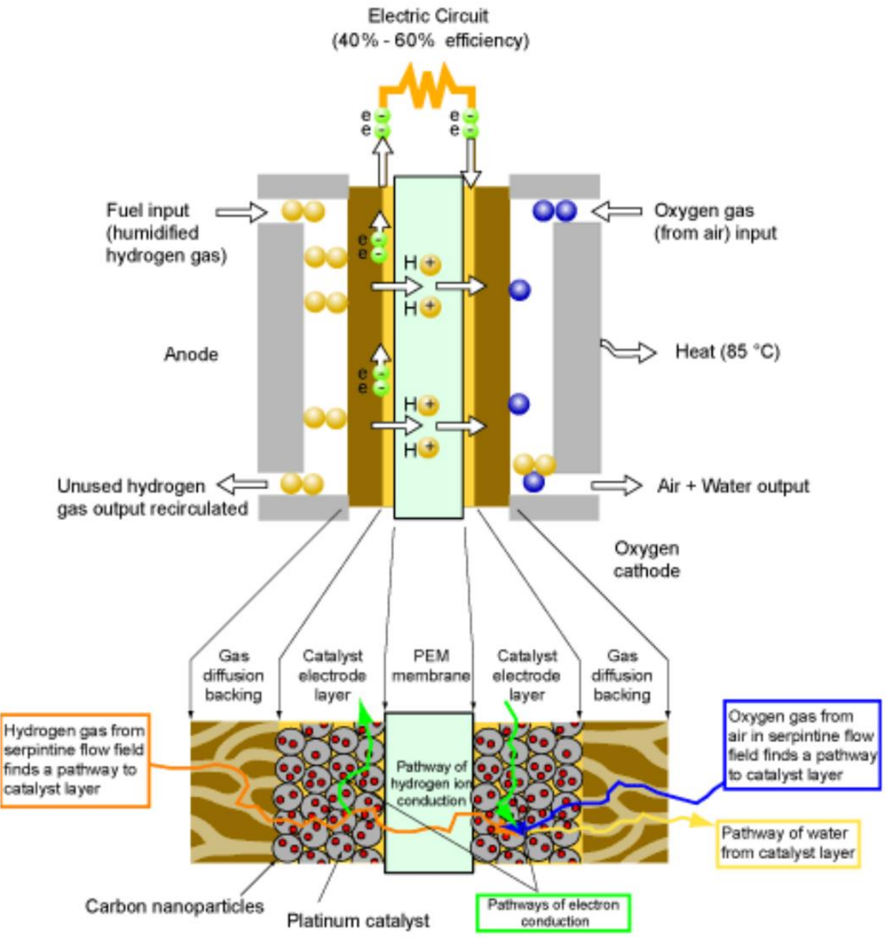
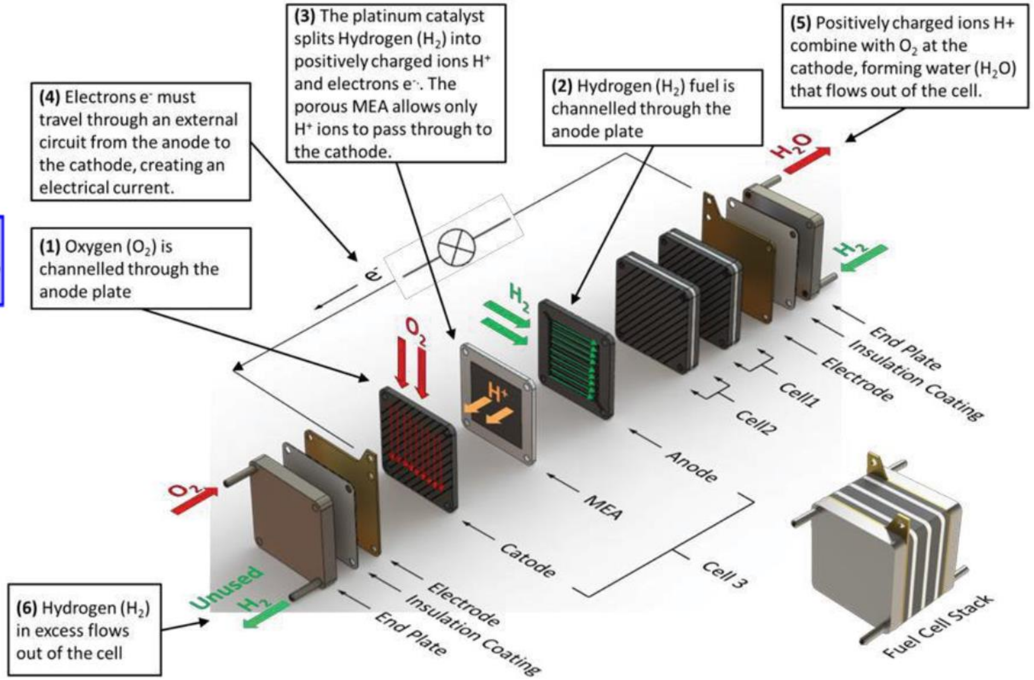
内容简介

燃料电池原理 - PEMFC



- 燃料电池种类
  - PEMFC，Proton Exchange Membrane Fuel Cells
  - DMFC，Direct Methanol Fuel Cell
  - PAFC，Phosphoric Acid Fuel Cell
  - AFC，Alkaline Fuel Cell
  - SOFC，Solid Oxide Fuel Cell
  - MCFC，Molten Carbonate Fuel Cell


(4) Electrons e^- must travel through an external circuit from the anode to the cathode, creating an electrical current.

(3) The platinum catalyst splits Hydrogen (H_2) into positively charged ions H^+ and electrons e^-. The porous MEA allows only H^+ ions to pass through to the cathode.

(2) Hydrogen (H_2) fuel is channelled through the anode plate

(5) Positively charged ions H+ combine with O_2 at the cathode, forming water (H_2O) that flows out of the cell.

(1) Oxygen (O_2) is channelled through the anode plate

(6) Hydrogen (H_2) in excess flows out of the cell

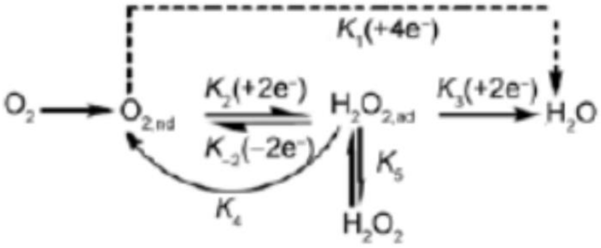
PEMFC的性能 – 重要因素

- 热管理（燃料电池的散热、温度）
- 水管理（反应气的湿度，燃料电池内的水分布）
- 流动分布
- 化学配比
- 电流密度
- 极化曲线

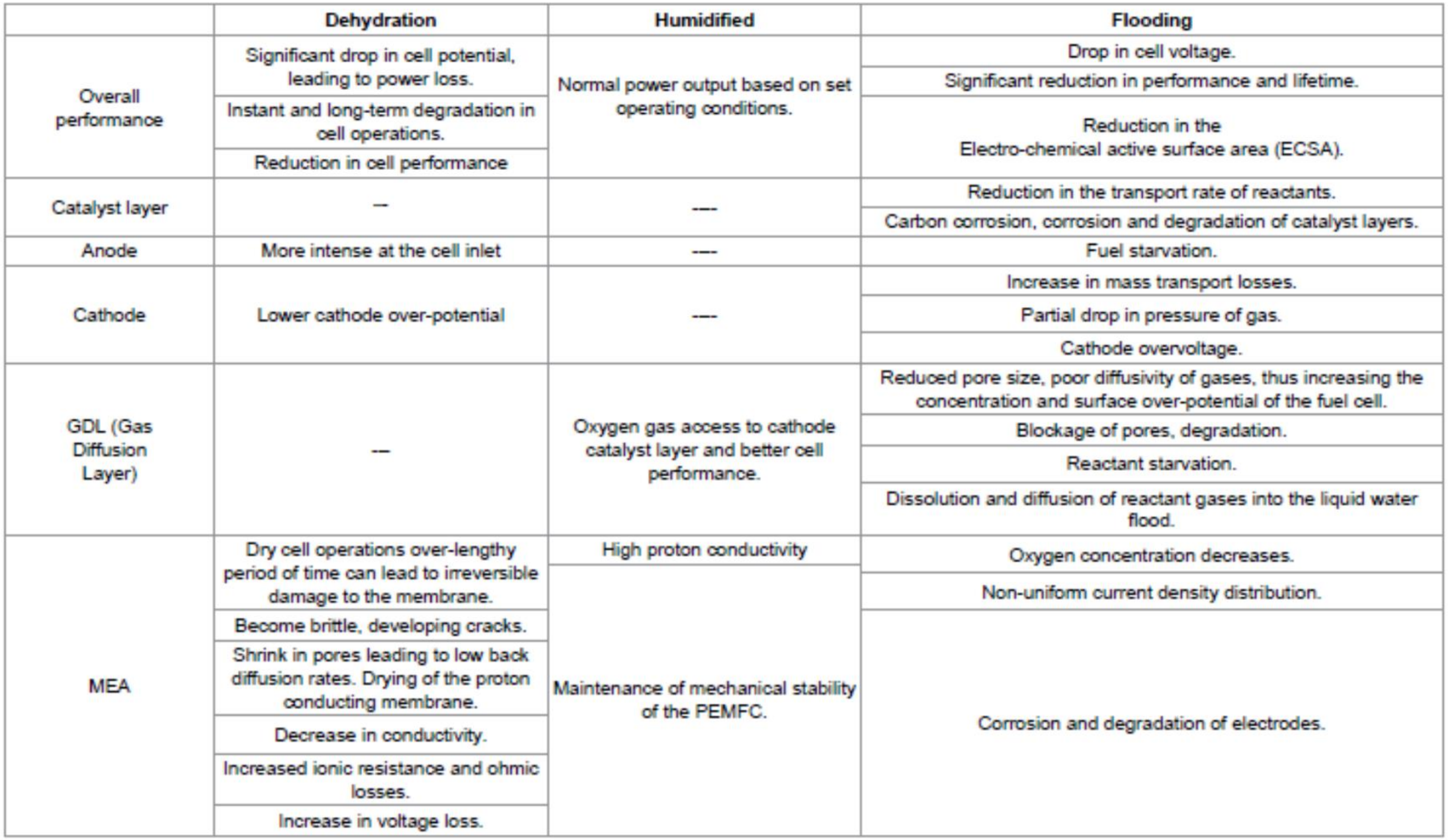
水管理

- 在相当大的程度上，燃料电池的性能取决于膜的湿化（**Hydration of the polymer membrane**）状况
  - 水淹电极
    - 当电流密度超过一定的阈值时，
      - 在电渗作用下，被水合的质子携带由阳极向阴极运动的水
      - 阴极的氧还原反应（**ORR**）生成的水
      - 二者超过了离开阴极催化层的水
    - 水淹电极发生，输运到阴极的氧气减少
    - 阴极过电势急剧上升
    - 燃料电池的输出急剧降低
  - 脱水
    - 质子交换膜电阻增加，高电流密度时产生较大的欧姆电阻
      - 保证交换膜处于良好的水合状态，保持其质子导电率
    - 催化层的活性下降
    - 膜破裂

ORR可能路径， Wroblowa



水管理



	Dehydration	Humidified	Flooding
Overall performance	Significant drop in cell potential, leading to power loss. Instant and long-term degradation in cell operations. Reduction in cell performance	Normal power output based on set operating conditions.	Drop in cell voltage. Significant reduction in performance and lifetime. Reduction in the Electro-chemical active surface area (ECSA).
Catalyst layer	--	----	Reduction in the transport rate of reactants. Carbon corrosion, corrosion and degradation of catalyst layers.
Anode	More intense at the cell inlet	----	Fuel starvation.
Cathode	Lower cathode over-potential	----	Increase in mass transport losses. Partial drop in pressure of gas. Cathode overvoltage.
GDL (Gas Diffusion Layer)	--	Oxygen gas access to cathode catalyst layer and better cell performance.	Reduced pore size, poor diffusivity of gases, thus increasing the concentration and surface over-potential of the fuel cell. Blockage of pores, degradation. Reactant starvation. Dissolution and diffusion of reactant gases into the liquid water flood.
MEA	Dry cell operations over-lengthy period of time can lead to irreversible damage to the membrane. Become brittle, developing cracks. Shrink in pores leading to low back diffusion rates. Drying of the proton conducting membrane. Decrease in conductivity. Increased ionic resistance and ohmic losses. Increase in voltage loss.	High proton conductivity Maintenance of mechanical stability of the PEMFC.	Oxygen concentration decreases. Non-uniform current density distribution. Corrosion and degradation of electrodes.

Table 1: Effects of water on the performance of PEFCs [30-34].

A Review of Computational Fluid Dynamics Simulations on PEFC Performance, Chen Y1*, Enearu OL1, Montalvao D2 and Sutharssan T1, Journal of Applied Mechanical Engineering

热管理

- **Schmittinger & Vahidi**研究发现，燃料电池温度超过**100℃**时，电池部件破坏/老化的风险会大幅增加
  - 降低长期性能和可靠性
  - 催化剂的化学稳定性会下降
- **Wang**的研究表明，温度的增加，
  - 可以降低**CO**中毒
  - 改善电化学效率
  - 由于燃料和冷却系统有明显的差异，可改善水管理和冷却效果

CFD的应用

- 气体分布
- 压降
- 水管理
- 热管理
- 电化学性能
- 参数敏感度分析
- 设计迭代
- ……

Fluent中质子交换膜燃料电池的几何模型

- **R17后， ANSYS-Fluent增加了微孔层**

物理模型

- **燃料电池涉及到的物理模型：**

ANSYS Fluent的标准功能

  - 多组分物质流动
  - 对流/导热（辐射）
  - 传质

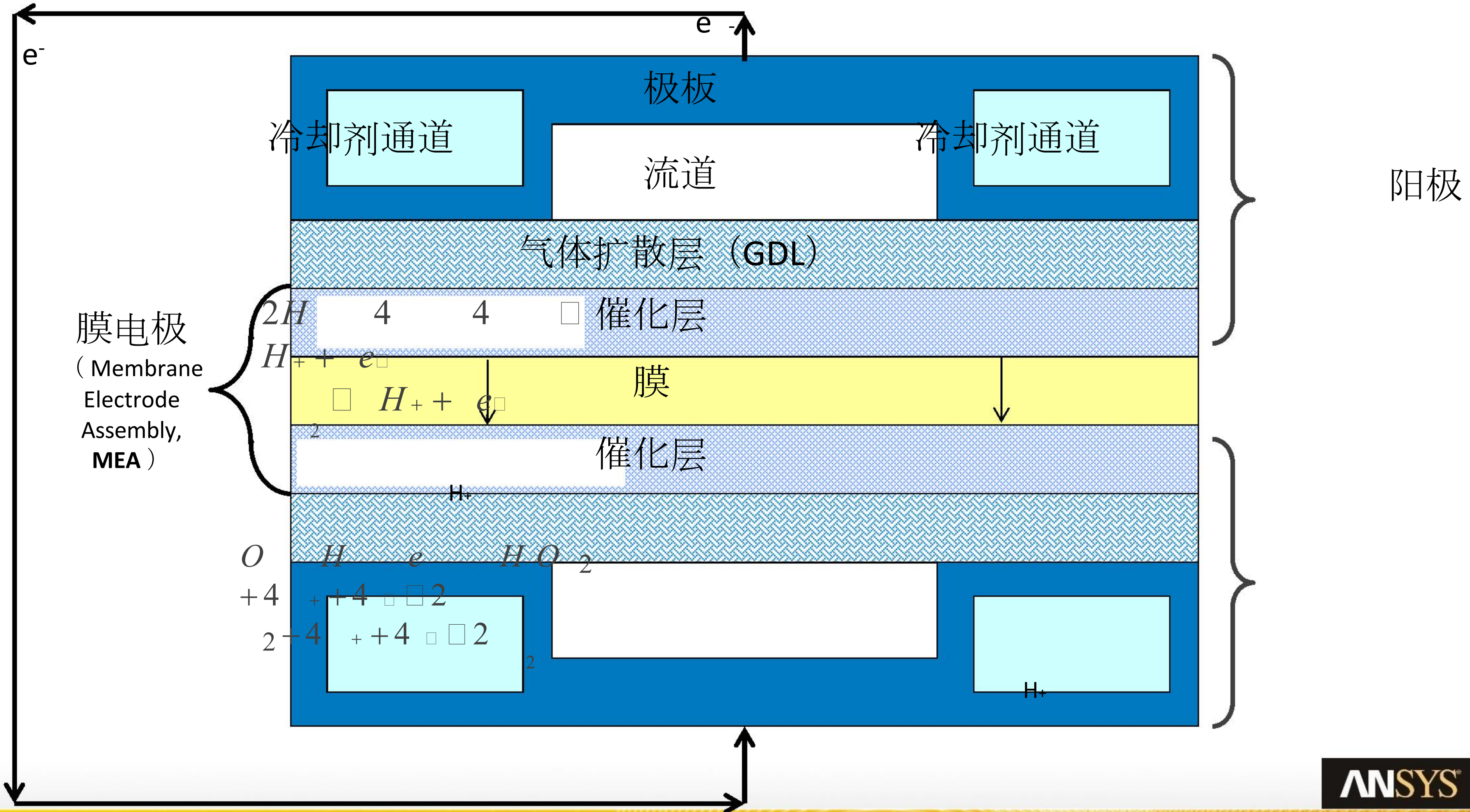
  - 各向异性电化学反应
  - 电势驱动的电流输运
  - 多相流动（PEMFC内存在的水的凝结）

ANSYS Fluent 燃料电池模块

物理模型

- 大量的物理模型被用来模拟 **PEMFC** 内部复杂的多物理现象：
  - 电化学子模型 – **model**模拟**MEA**表面的电流密度、电压、组份源/汇
  - 电模型 – 模拟多孔和固体区域的电流、电压分布
  - **MEA**子模型 – 模拟**MEA**中的电损失和水的流动
  - 多孔介质多相流模型 – 模拟多孔的气体扩散层中的液态水/气体的流动
  - 薄膜多相流模型（**Thin Film Multiphase submodel**） - 模拟阴极气体通道中液态水的流动

PEMFC模块 – 物理域的模拟



气体扩散层（GDL）

阴极

流道

冷却剂通道

冷却剂通道

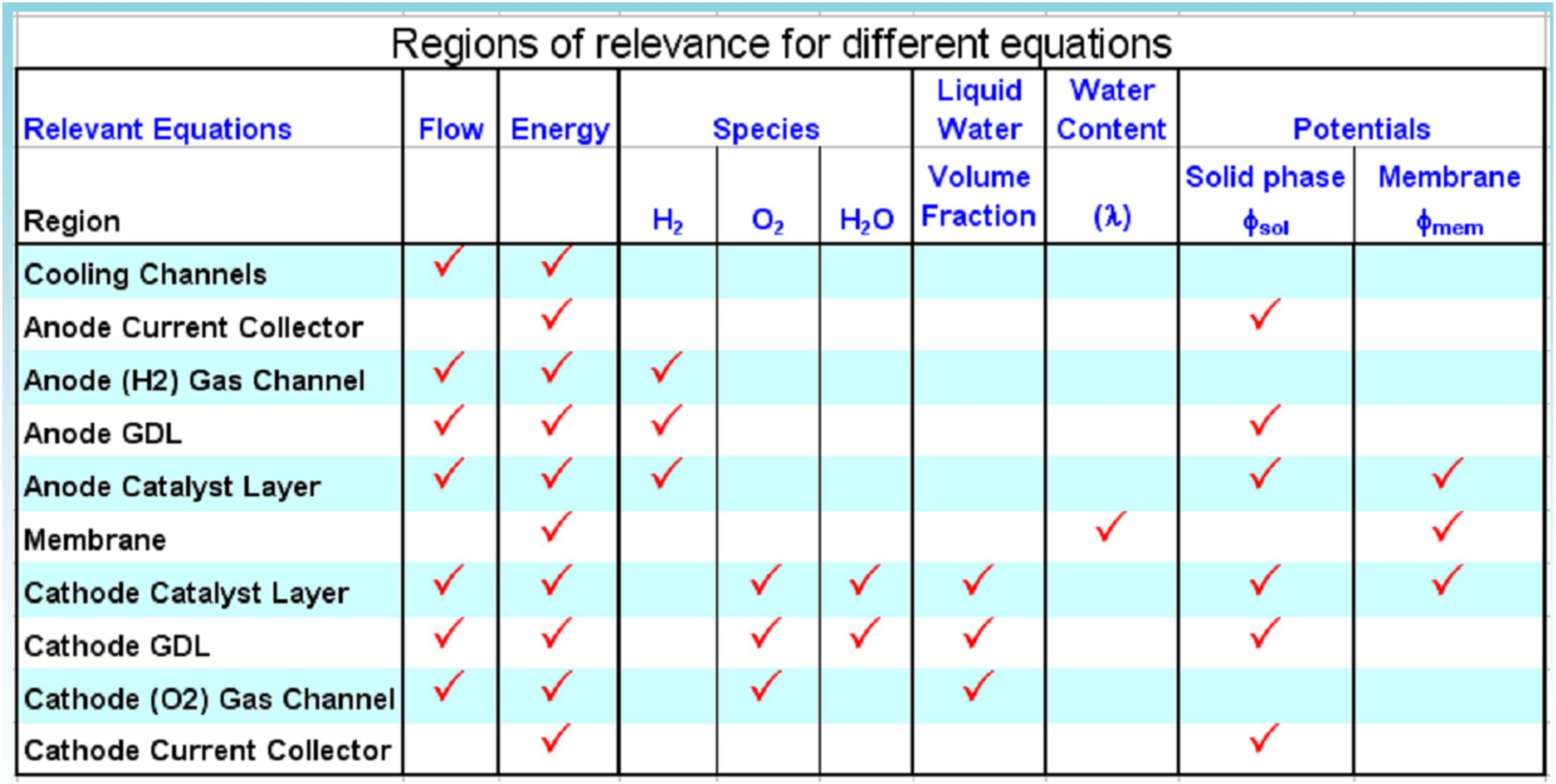
极板

e$^-$

e$^-$

ANSYS-Fluent PEMFC模块

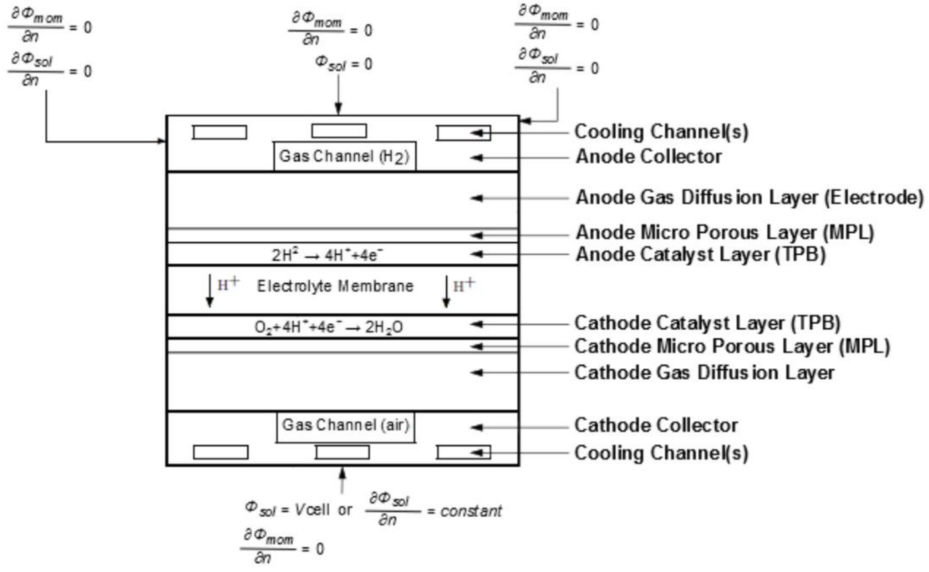
- 各区域所求解的方程



Regions of relevance for different equations

Relevant Equations	Flow	Energy	Species			Liquid Water	Water Content	Potentials	
Region			H_2	O_2	H_2O	Volume Fraction	(λ)	Solid phase ϕ_{sol}	Membrane ϕ_{mem}
Cooling Channels	✓	✓							
Anode Current Collector		✓						✓	
Anode (H2) Gas Channel	✓	✓	✓						
Anode GDL	✓	✓	✓					✓	
Anode Catalyst Layer	✓	✓	✓					✓	✓
Membrane		✓					✓		✓
Cathode Catalyst Layer	✓	✓		✓	✓	✓		✓	✓
Cathode GDL	✓	✓		✓	✓	✓		✓	
Cathode (O2) Gas Channel	✓	✓		✓		✓			
Cathode Current Collector		✓						✓	

子模型 – 电模型



- **Electric Sub-Model**
  - – 求解了两个电势
  - 固相电势（导电固体内**e-**的输运）
  - 膜相电势（**MEA**内**H+**的输运）

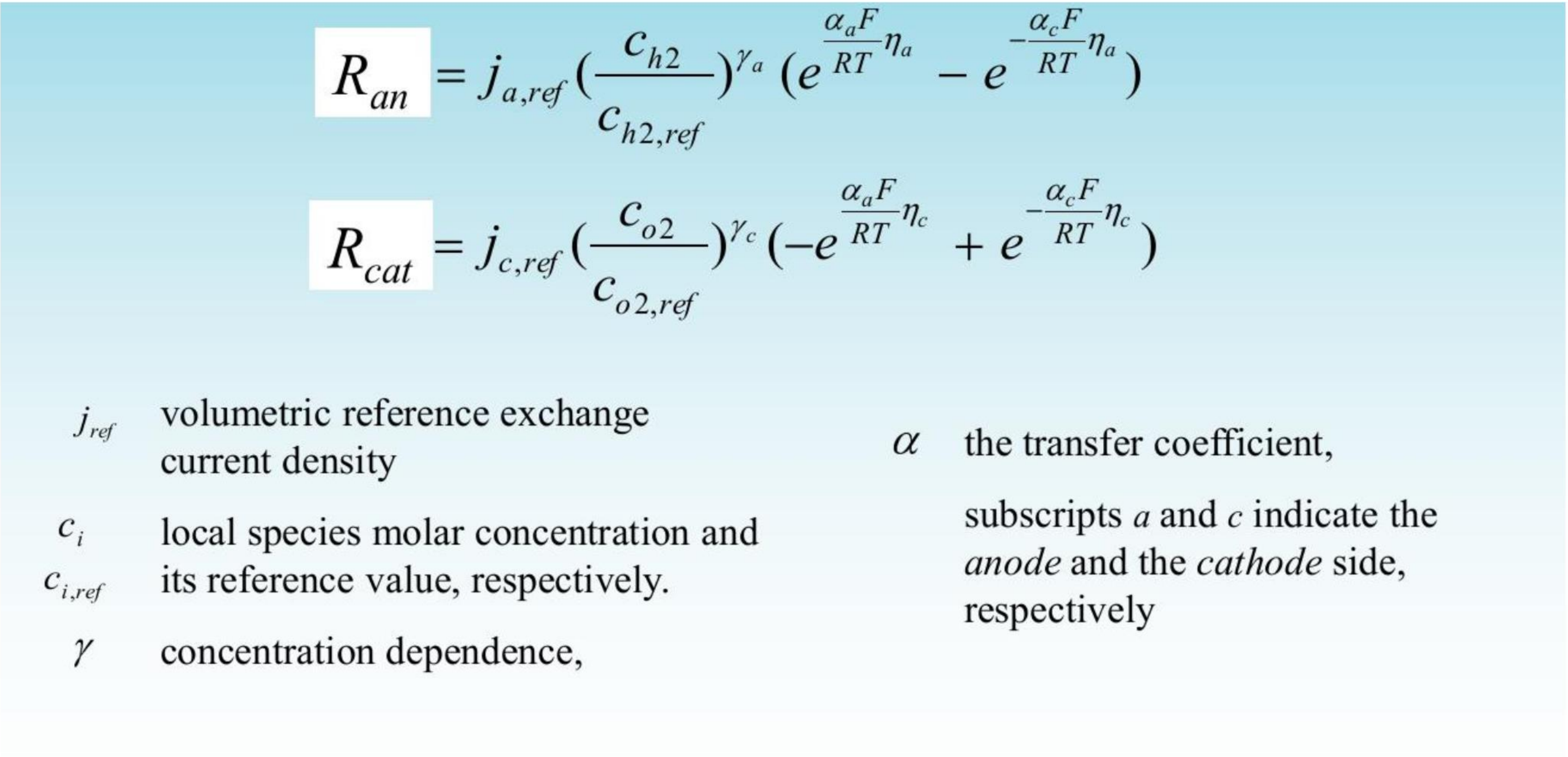
$$
\begin{aligned}
\nabla \cdot (\sigma_{\mathrm{sol}} \nabla \phi_{\mathrm{sol}}) + R_{\mathrm{sol}} &= 0 \\
\nabla \cdot (\sigma_{\mathrm{mem}} \nabla \phi_{\mathrm{mem}}) + R_{\mathrm{mem}} &= 0
\end{aligned}
$$

σ = electrical conductivity (1/ohm-m)
ϕ = electric potential (volts)
R = volumetric transfer current (A/m^3)

- 优点
  - 解释了所有区域的电流输运
  - 可以模拟材料界面间的接触电阻

子模型 – 电化学

- 电化学模型
  - 基于**Butler-Volmer**方程计算**R$_{an}$** 和 **R$_{cat}$**



$$R_{an} = j_{a,ref}\left(\frac{c_{h2}}{c_{h2,ref}}\right)^{\gamma_a}\left(e^{\frac{\alpha_a F}{RT}\eta_a} - e^{-\frac{\alpha_c F}{RT}\eta_a}\right)$$

$$R_{cat} = j_{c,ref}\left(\frac{c_{o2}}{c_{o2,ref}}\right)^{\gamma_c}\left(-e^{\frac{\alpha_a F}{RT}\eta_c} + e^{-\frac{\alpha_c F}{RT}\eta_c}\right)$$

j_{ref}	volumetric reference exchange current density
c_i $c_{i,ref}$	local species molar concentration and its reference value, respectively.
γ	concentration dependence,
α	the transfer coefficient,
	subscripts *a* and *c* indicate the *anode* and the *cathode* side, respectively