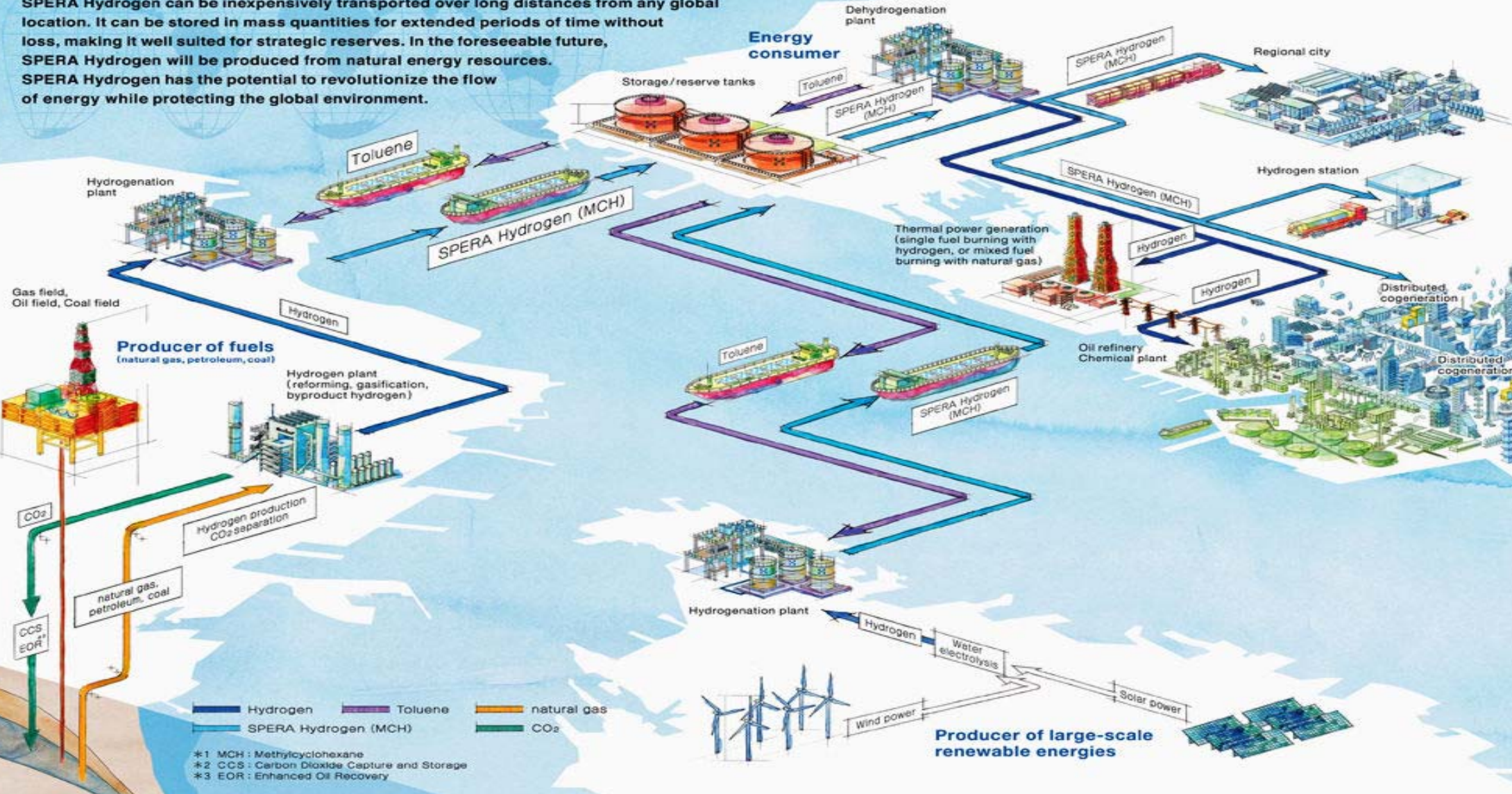


# Changing the world's energy landscape.

SPERA Hydrogen can be inexpensively transported over long distances from any global location. It can be stored in mass quantities for extended periods of time without loss, making it well suited for strategic reserves. In the foreseeable future, SPERA Hydrogen will be produced from natural energy resources. SPERA Hydrogen has the potential to revolutionize the flow of energy while protecting the global environment.



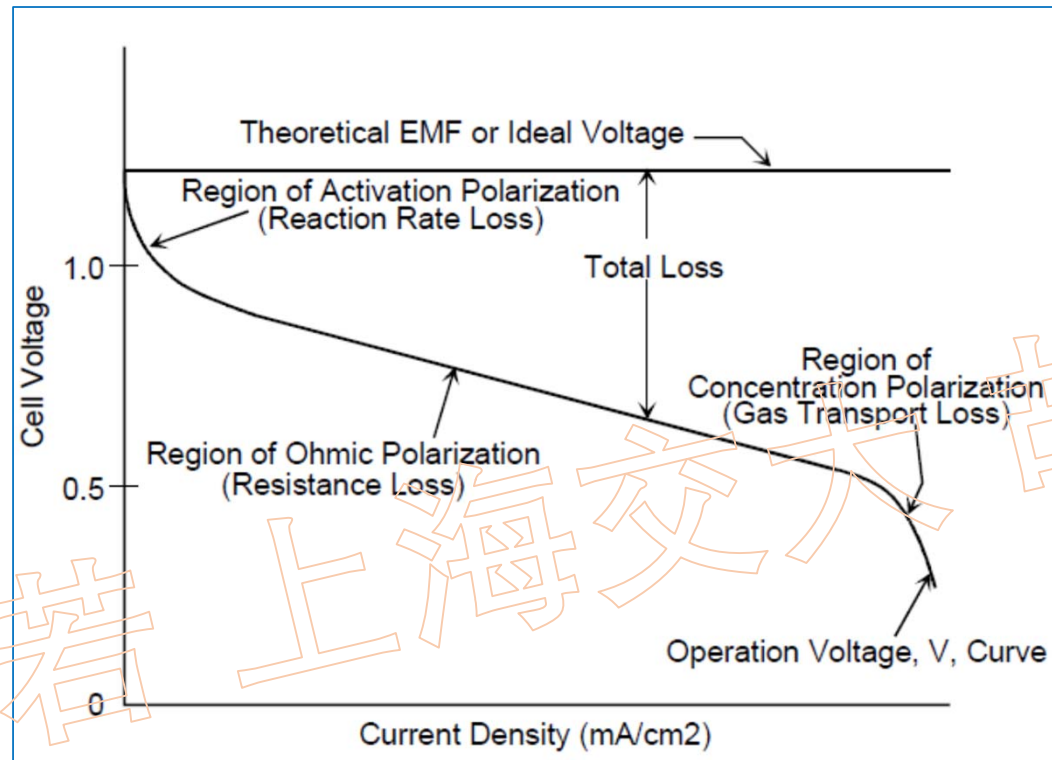
# 燃料电池电动车（FCEV）的水管理 及低温启动技术 ——还原丰田的技术思路

上海交通大学 燃料电池研究所  
胡鸣若

201809



## (1) 水管理的基本概念



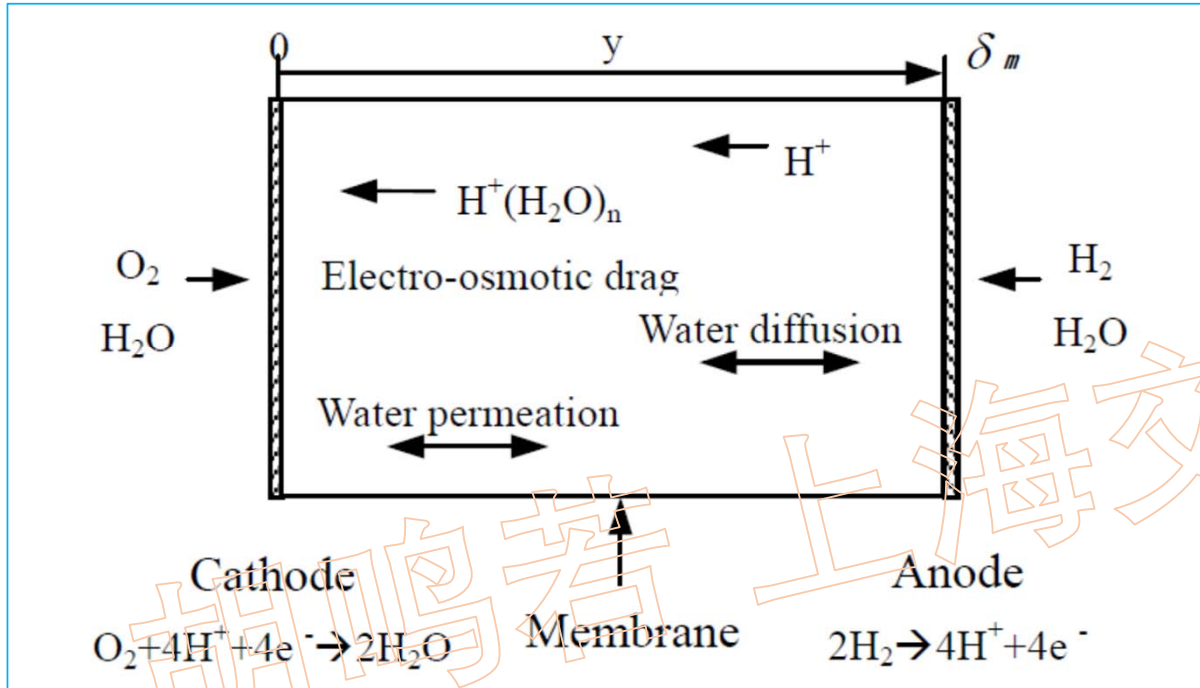
燃料电池的极化曲线

$$V_{cell} = E - \eta_{act} - \eta_{ohm} - \eta_{conc}$$

$$E = 1.23 - 0.9 \times 10^{-3}(T - 298) + 2.3 \frac{RT}{4F} \log(p_h^2 p_o)$$

图片和公式来源: Fuel cell Handbook (7<sup>th</sup> edition), US DOE, Nov., 2004

# 膜中水传递机理与欧姆极化 $\eta_{ohm}$



电渗力传递：电解质膜中的 $H^+$ 对 $H_2O$ 分子的吸引力。  
 扩散传递：由电池阴极和阳极侧电解质膜中水的浓度差异所引起。  
 渗透传递：由电池阴极和阳极侧的压力梯度引起的。

质子交换膜中水传递示意图

图片和公式来源：胡鸣若, 质子交换膜燃料电池数学模型及千瓦级电堆的实验研究, 博士学位论文, 2004. 1, 上海交通大学

$$N^w = n_d \frac{I}{F} - \frac{k_{p,m}}{\mu} C_m^w \frac{dp}{dy} - D_m^w \frac{dC_m^w}{dy}$$

$$N^w = 0.1136\lambda \frac{I}{F} - \frac{k_{p,m}}{\mu} \lambda c_f \frac{dp}{dy} - D_m^w c_f \frac{d\lambda}{dy}$$

$$\lambda = 0.043 + 17.81a - 39.85a^2 + 36.0a^3 \quad (0 < a \leq 1)$$

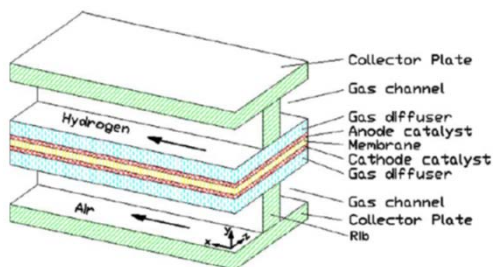
$$\lambda = 14.0 + 1.4(a - 1) \quad (1 < a \leq 3)$$

$$\lambda = 16.8 \quad (a \geq 3)$$

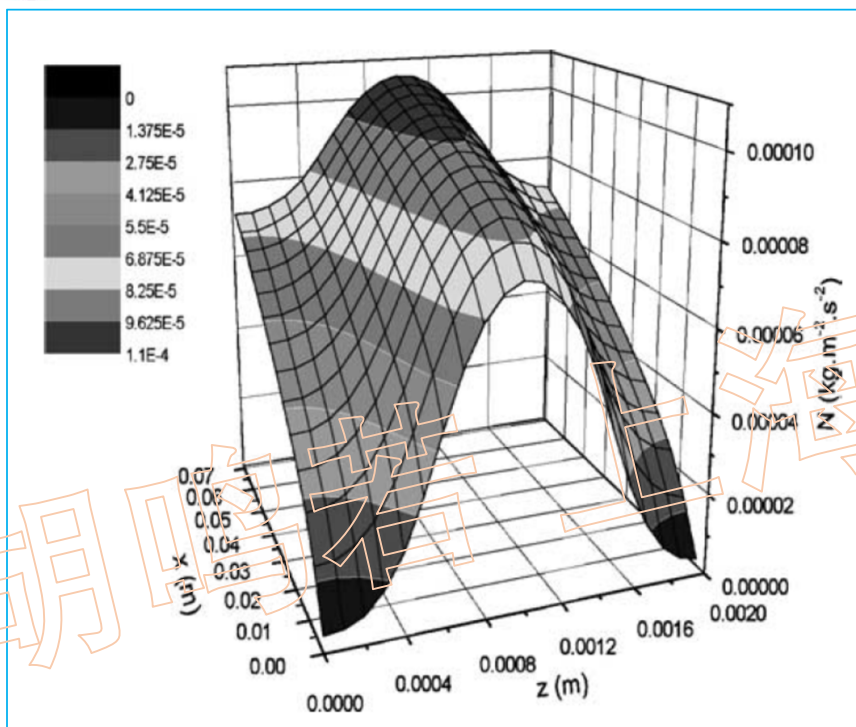
$$a = \frac{x_w P}{P_w^{Sat}}$$

$$\sigma(\lambda) = \exp\left[1268\left(\frac{1}{303} - \frac{1}{T}\right)\right](0.5139\lambda - 0.326)$$

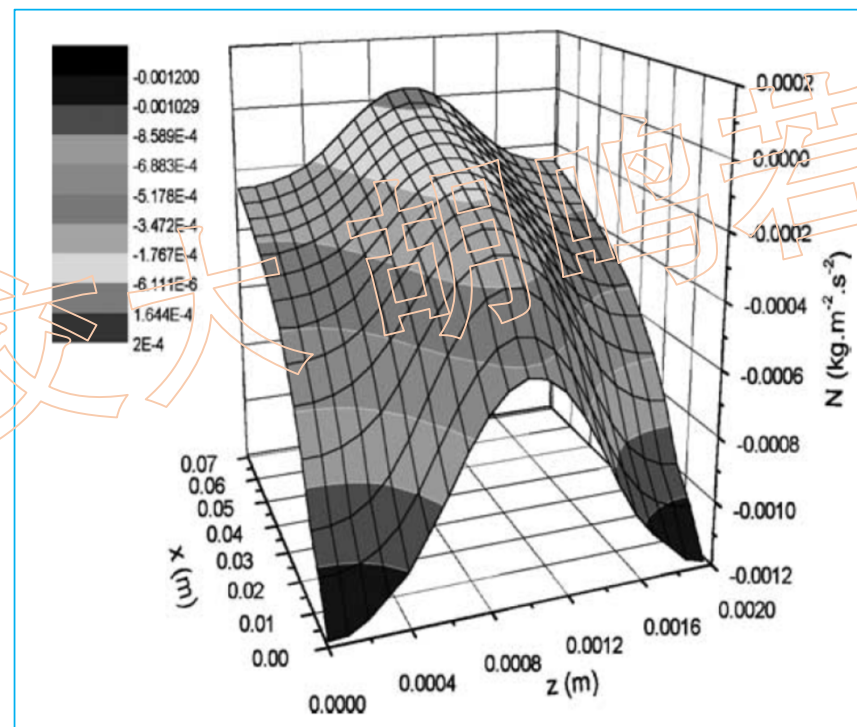
$$R_m = \int_0^{\delta_m} \frac{dy}{\sigma(\lambda)} \quad \eta_{ohm} = I \times R_m$$



质子交换膜中水的净通量模拟结果  
(负值：阳极向阴极传递，正值：阴极向阳极传递)



$I = 1665 \text{ Am}^{-2}$



$I = 7990 \text{ Am}^{-2}$

图片来源：

[1]Mingruo Hu, et al. Three-Dimensional, Two-Phase Flow Mathematical Model for PEM Fuel Cell: Part I. Model Development. Energy Conversion and Management, 2004, 45:1861-1882.

[2]Mingruo Hu, et al. Three-Dimensional, Two-Phase Flow Mathematical Model for PEM Fuel Cell: Part II. Analysis and discussion of the internal transport mechanisms. Energy Conversion and Management, 2004, 45: 1883-1916.

## 浓差极化

$$\eta_{\text{conc}} = -\frac{RT}{nF} \ln \left( 1 - \frac{I}{I_L} \right)$$

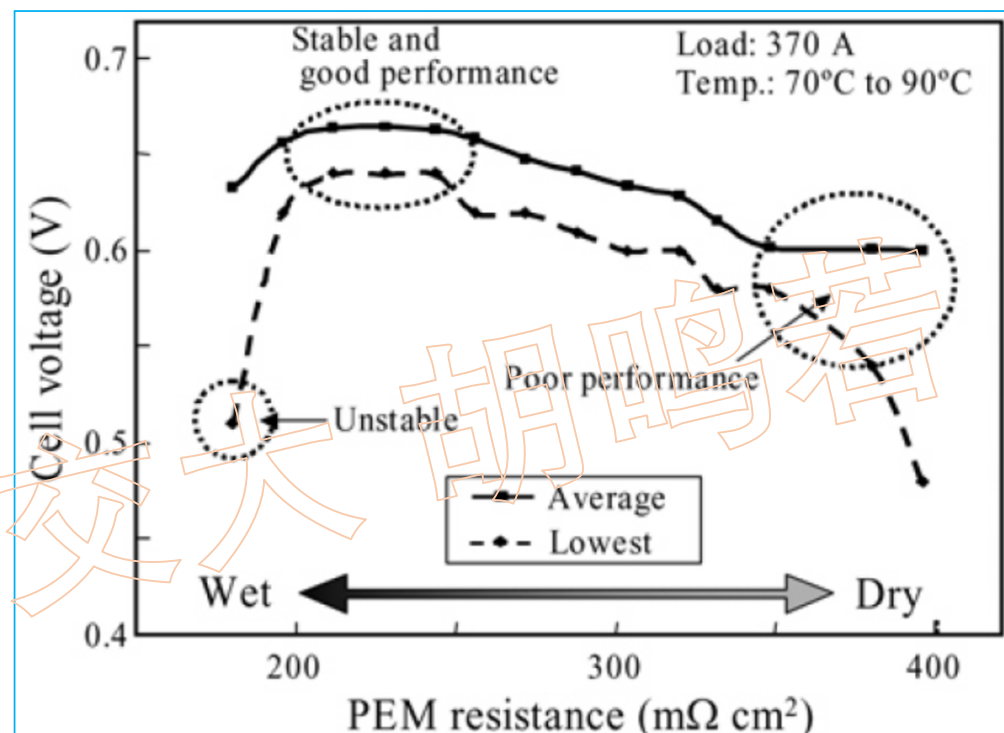
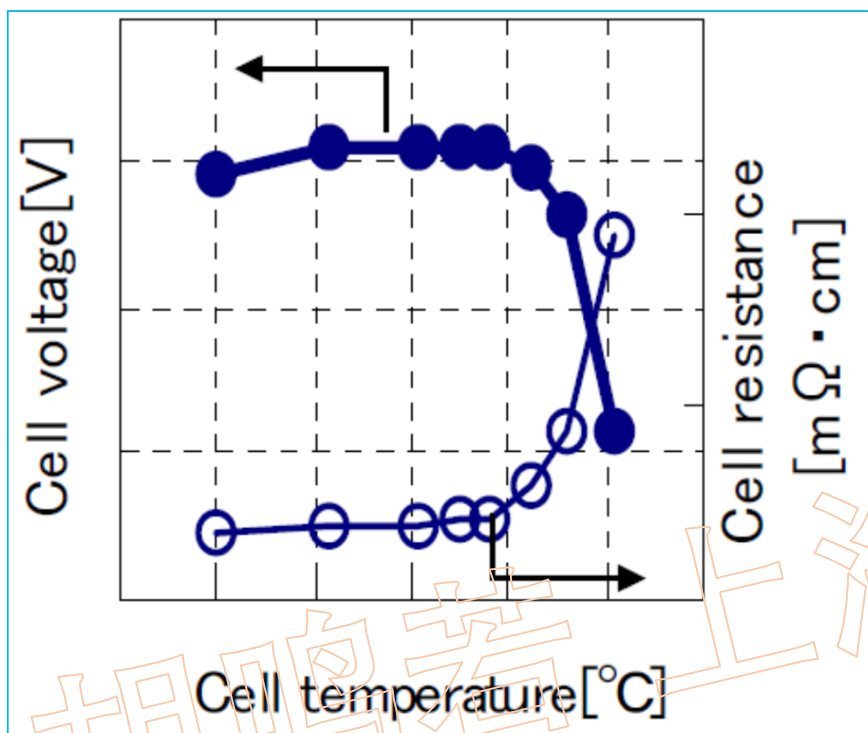
$$I_L = \frac{nFD_h C_{k,0}}{H_d}$$



质子交换膜燃料电池的流场可视化

公式来源: Mamdud Hossain, et al. Water dynamics inside a cathode channel of a polymer electrolyte membrane fuel cell. Renewable Energy, 2013(50):763-779.

图片来源: Mingruo Hu, Guangyi Cao. Research on the Performance Differences between a Standard PEMFC Single Cell and Transparent PEMFC Single Cells using optimized Transparent Flow Field Unit—Part I: Design Optimization of a Transparent Flow Field Unit, International Journal of Hydrogen Energy, 2016,41(4):2955-2966.

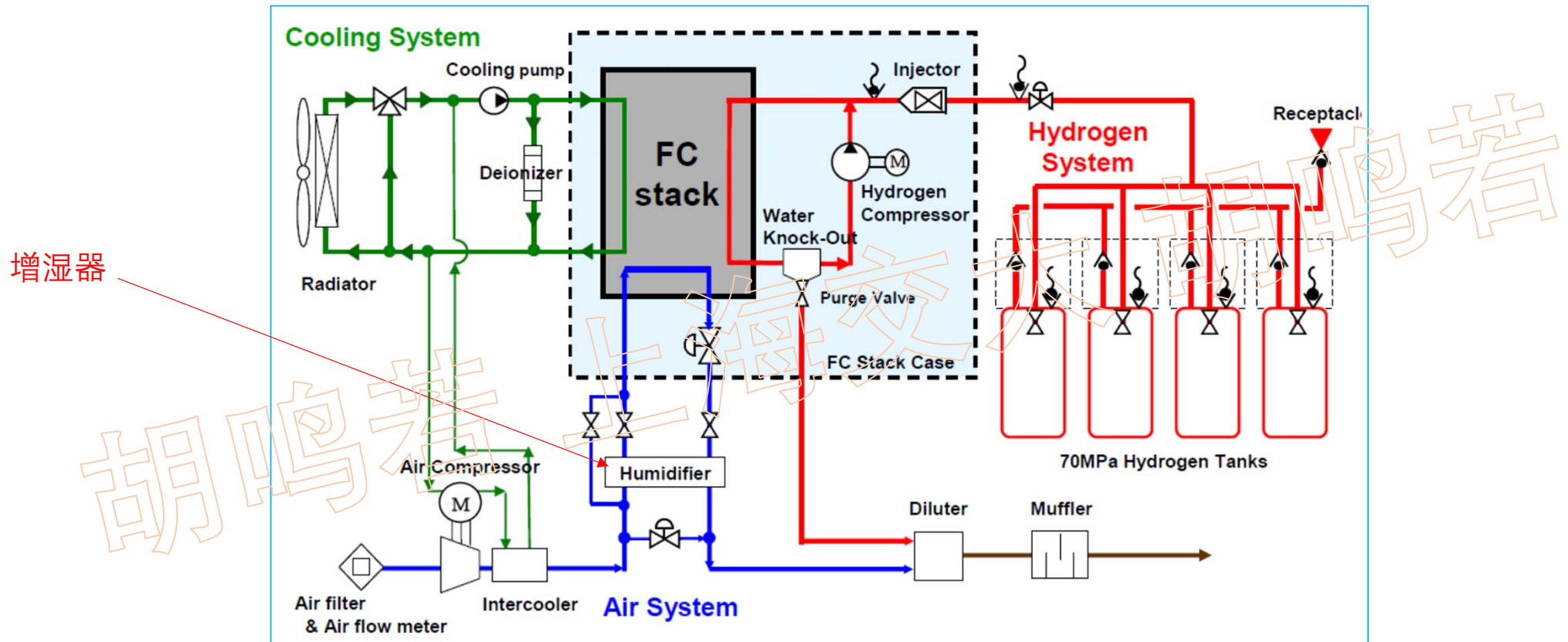


与水管理相关的质子交换膜燃料电池性能变化

图片来源：Joji Tomiyasu, et al. DEVELOPMENT OF ELECTRODE STRUCTURE FOR HIGH PERFORMANCE FUEL CELL USING CAE. Proceedings of the ASME 2010 Eighth International Fuel Cell Science, Engineering and Technology Conference, FuelCell2010, June 14-16, 2010, Brooklyn, New York, USA.

图片来源：Nobuyuki Kitamura, et al. Development of Water Content Control System for Fuel Cell Hybrid Vehicles Based on AC Impedance. SAE, 2010, doi:10.4271/2010-01-1088.

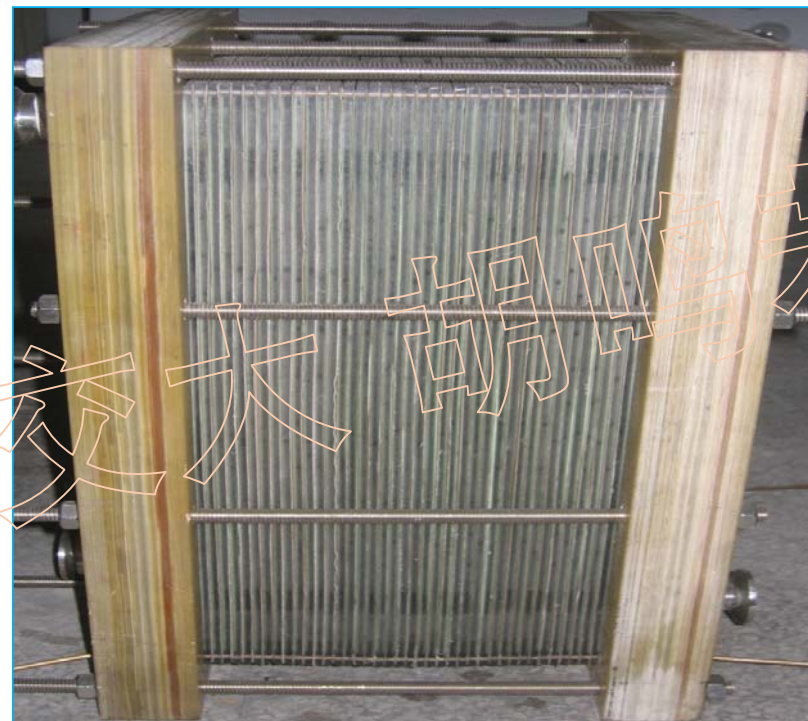
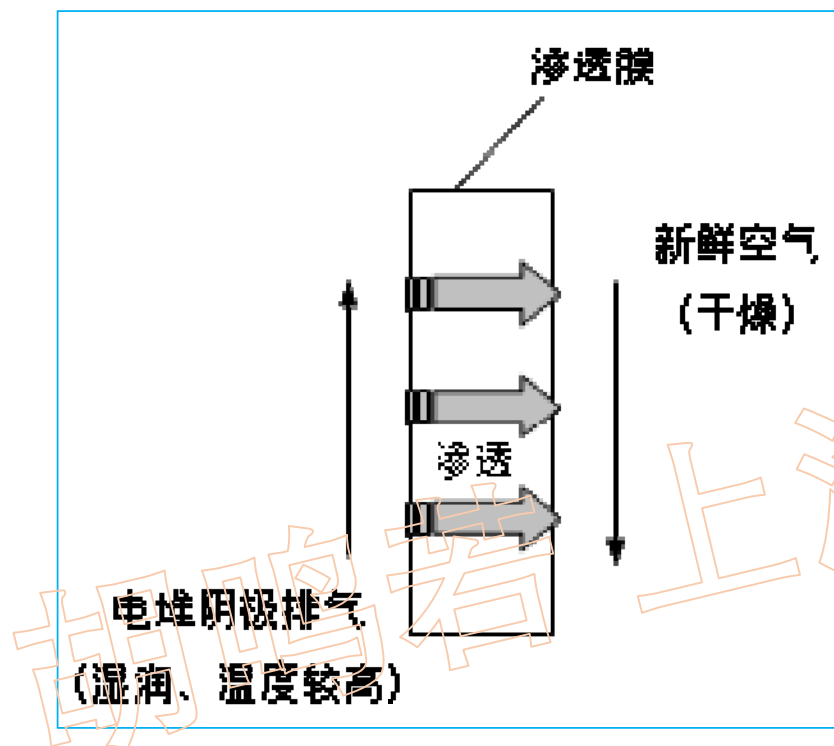
## (2) 水管理的基本方法



丰田FCHV-adv燃料电池系统流程图

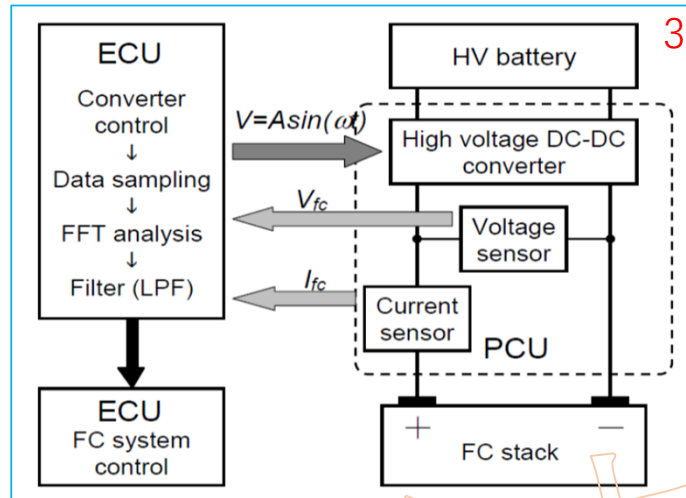
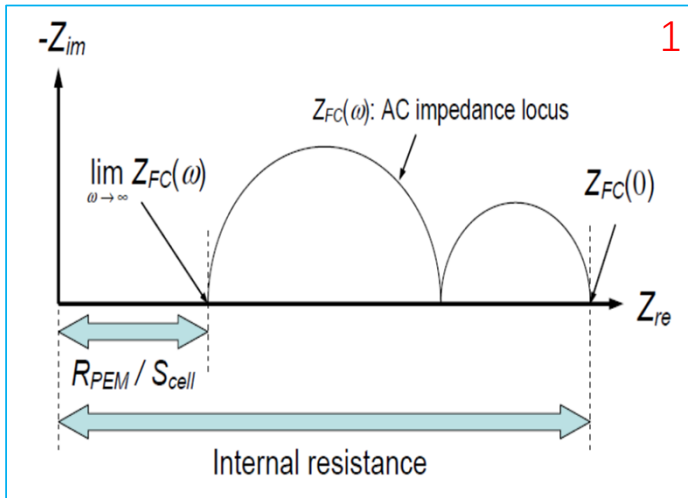
图片和公式来源: K. Sekizawaa, et al. Recent Advances in TOYOTA FCHV-adv Fuel Cell System. ECS Transactions, 2010, 33 (1): 1947-1957.



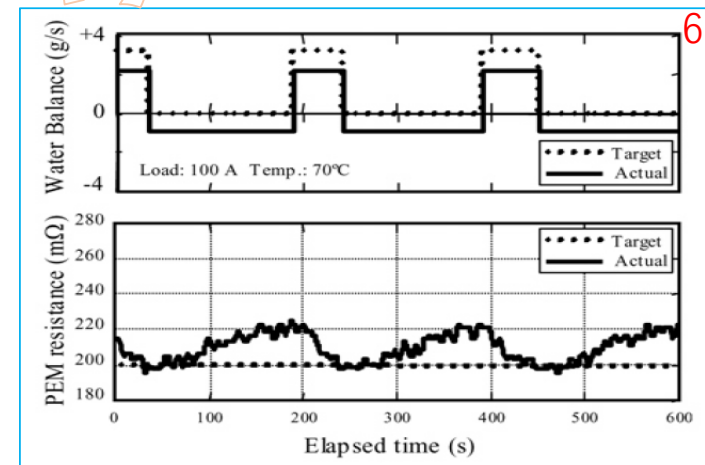
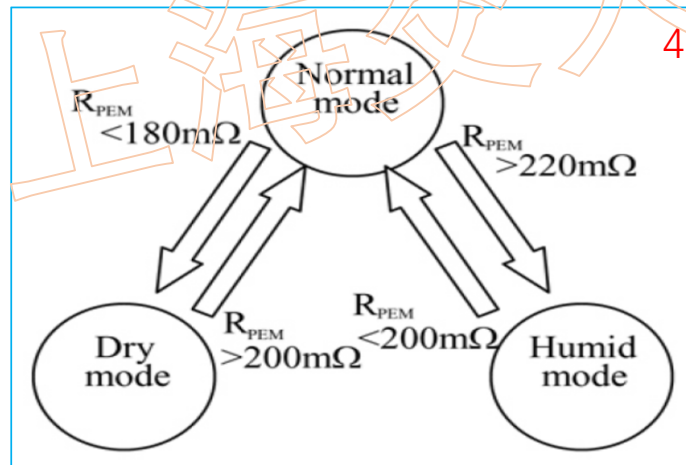
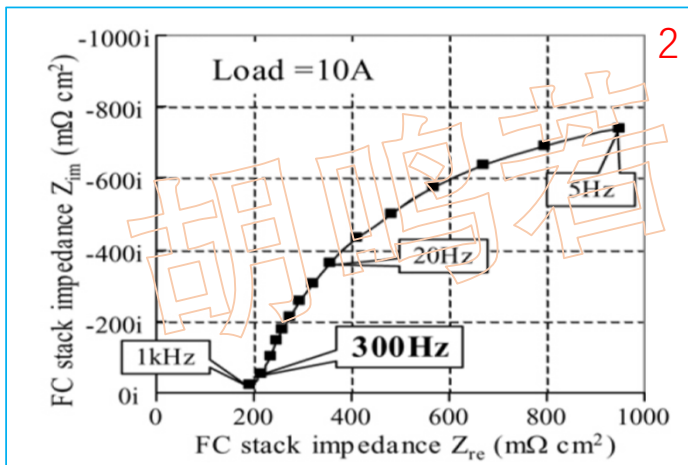


增湿器的原理和实验装置图

图片来源：Mingruo Hu, et al. Research and Development of a 10kW Class PEM Fuel Cell Stack Based on Catalyst Coated Membrane (CCM) Method. International Journal of Hydrogen Energy. 2006 (31), 8: 1010-1018.

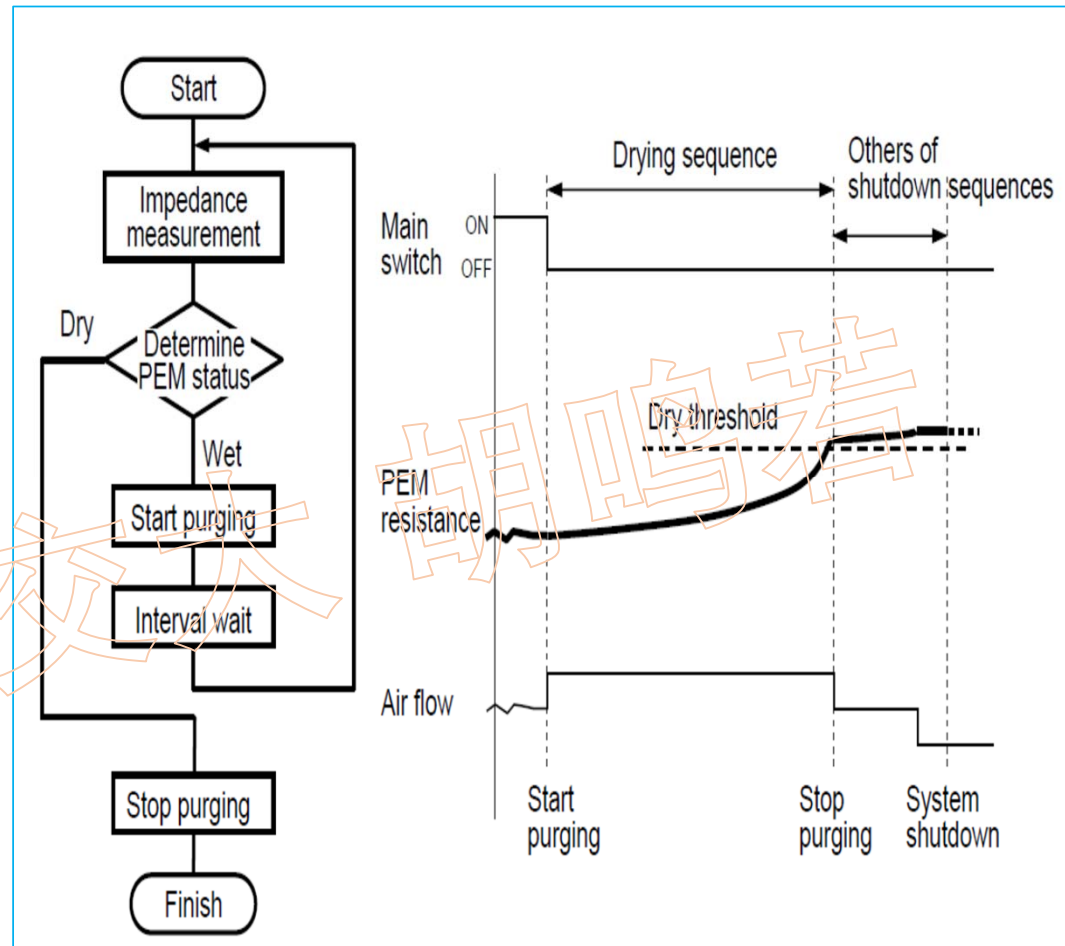
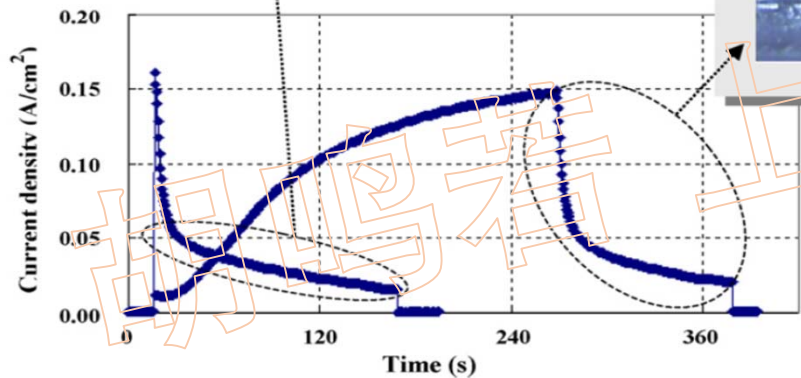
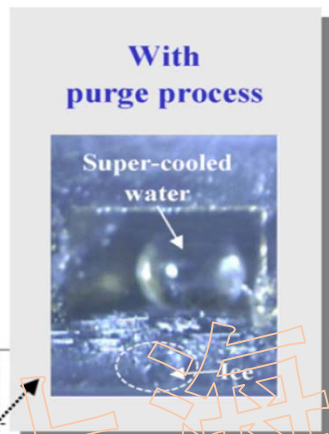
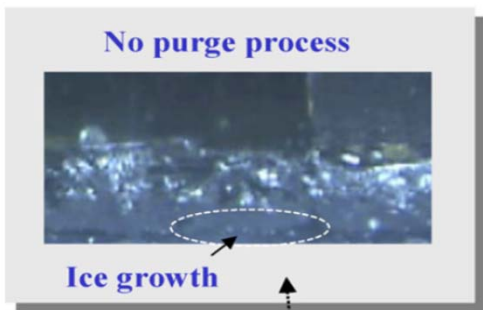


Modes	Dry	Normal	Humid
Cathode air pressure	Low	Adjust	High
Cathode air mass flow	Large	Adjust	Small
Coolant temperature	Keep constant	Keep constant	Keep constant



丰田FCHV-adv燃料电池系统的在线水管理方法——膜电阻监控：高频阻抗测量

图片来源: Nobuyuki Kitamura, et al. Development of Water Content Control System for Fuel Cell Hybrid Vehicles Based on AC Impedance. SAE, 2010, doi:10.4271/2010-01-1088.



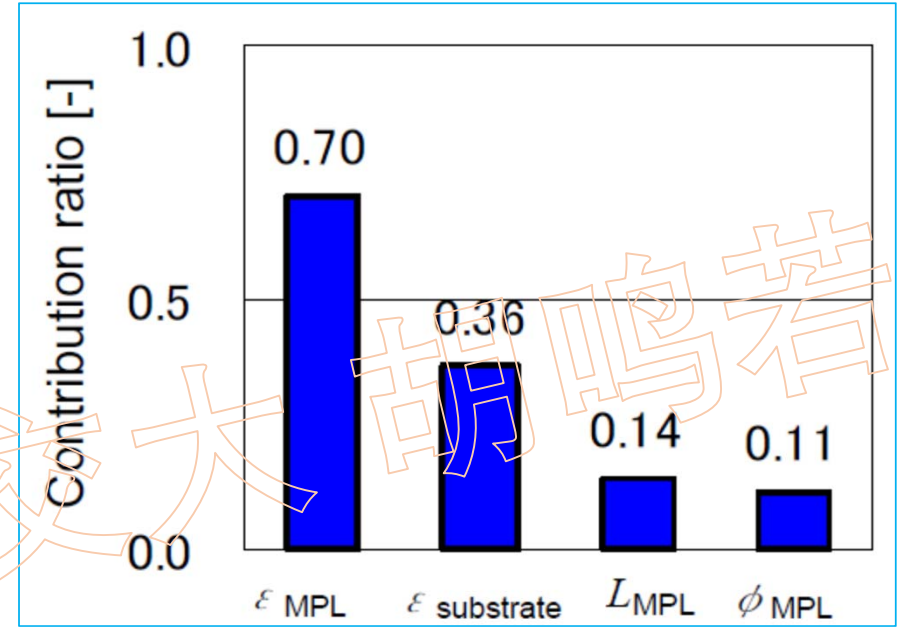
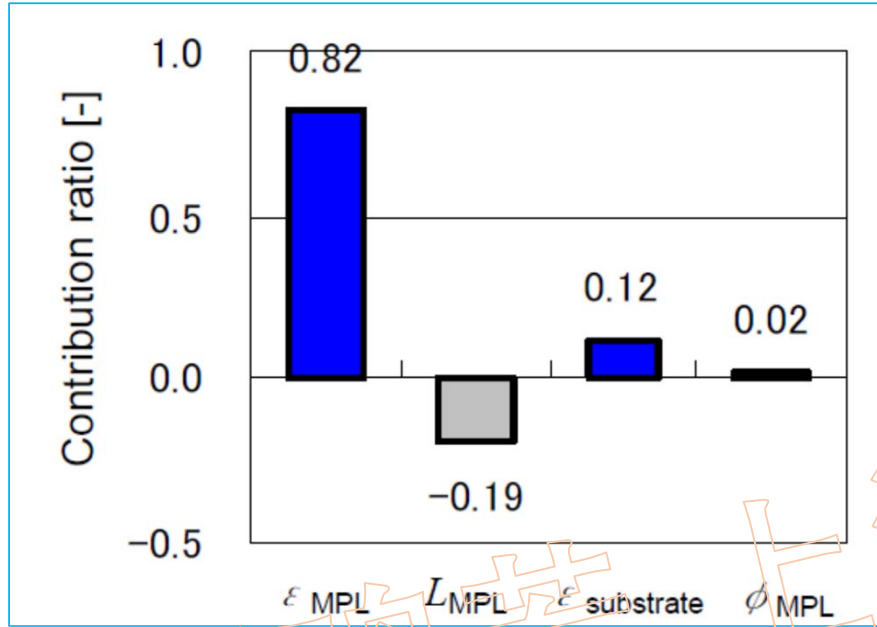
无吹扫过程的低温启动→已有冰核→生成水在GDL/CCM界面立刻结冰  
有吹扫过程的低温启动→生成水→过冷→再结冰

丰田FCHV-adv停车 (shutdown) 吹扫控制:膜电阻监控

图片来源: Y. Ishikawa, et al. Super-cooled water behavior inside polymer electrolyte fuel cell cross-section below freezing temperature. Journal of Power Sources, 2008 (179): 547 - 552.

图片来源: K. Sekizawaa, et al. Recent Advances in TOYOTA FCHV-adv Fuel Cell System. ECS Transactions, 2010, 33 (1): 1947-1957.

### (3) 水管理的优化



$$\frac{\partial \phi}{\partial t} = DV^2 \phi = D \left( \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} \right)$$

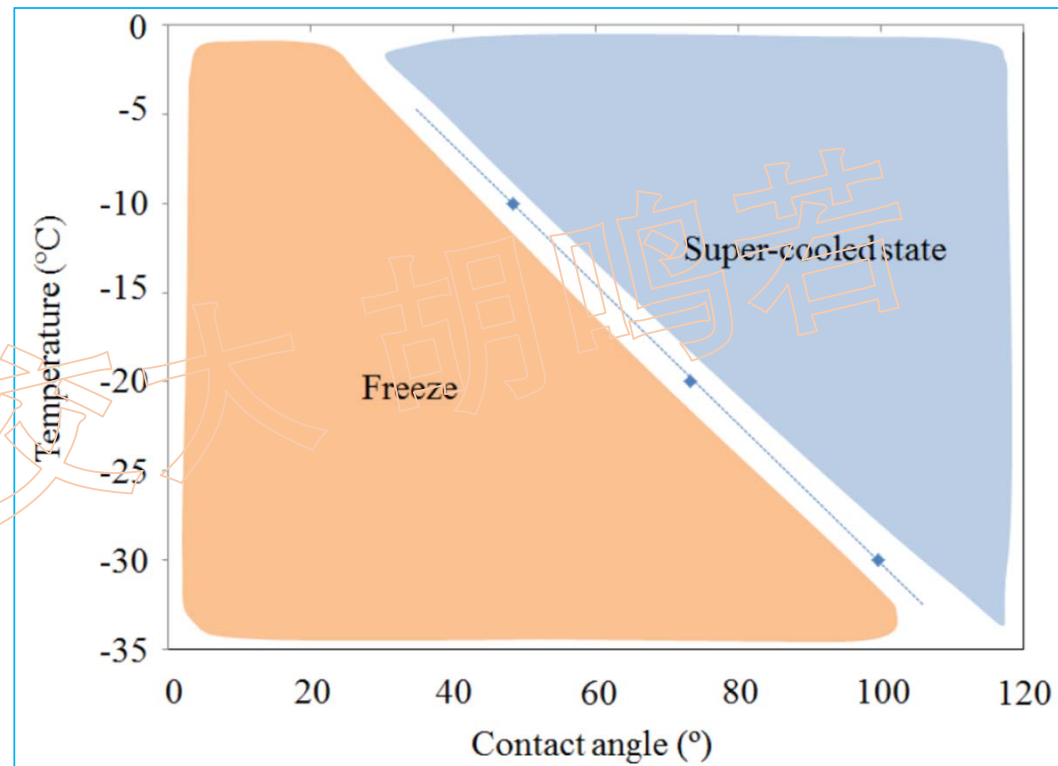
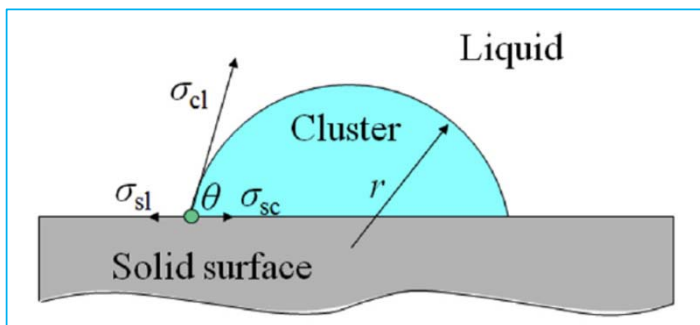
$$u = \frac{K \Delta P}{\mu L}$$

Temp ↑, E ↑, 需要 D ↓ → 保持较高的水蒸气  
 气 Pv →  $\eta_{ohm}$  ↓ →  $V_{cell}$  ↑

$K \Delta P$  ↑, u ↑ → 较快排出液态水 →  $\eta_{conc}$  →  $V_{cell}$  ↑

气体扩散层结构参数对于电池水管理敏感性影响

图片和公式来源: Joji Tomiyasu, et al. DEVELOPMENT OF ELECTRODE STRUCTURE FOR HIGH PERFORMANCE FUEL CELL USING CAE. Proceedings of the ASME 2010 Eighth International Fuel Cell Science, Engineering and Technology Conference, FuelCell2010, June 14-16, 2010, Brooklyn, New York, USA



$$J = \frac{n_L kT_{cell}}{h} \cdot \exp\left(\frac{-\Delta g}{kT_{cell}}\right) \cdot \exp\left(\frac{1}{kT_{cell}} \cdot \frac{-16\pi\sigma_{cl}^3}{3} \cdot \frac{T_e^2}{\rho_c^2 L^2 \Delta T^2} \cdot f(\theta)\right)$$

$$f(\theta) = \frac{1}{4}(2 - 3\cos\theta + \cos^3\theta)$$

$$I = \int_0^{t_0} J(T_{cell}, \theta) \cdot V_w(t) dt$$

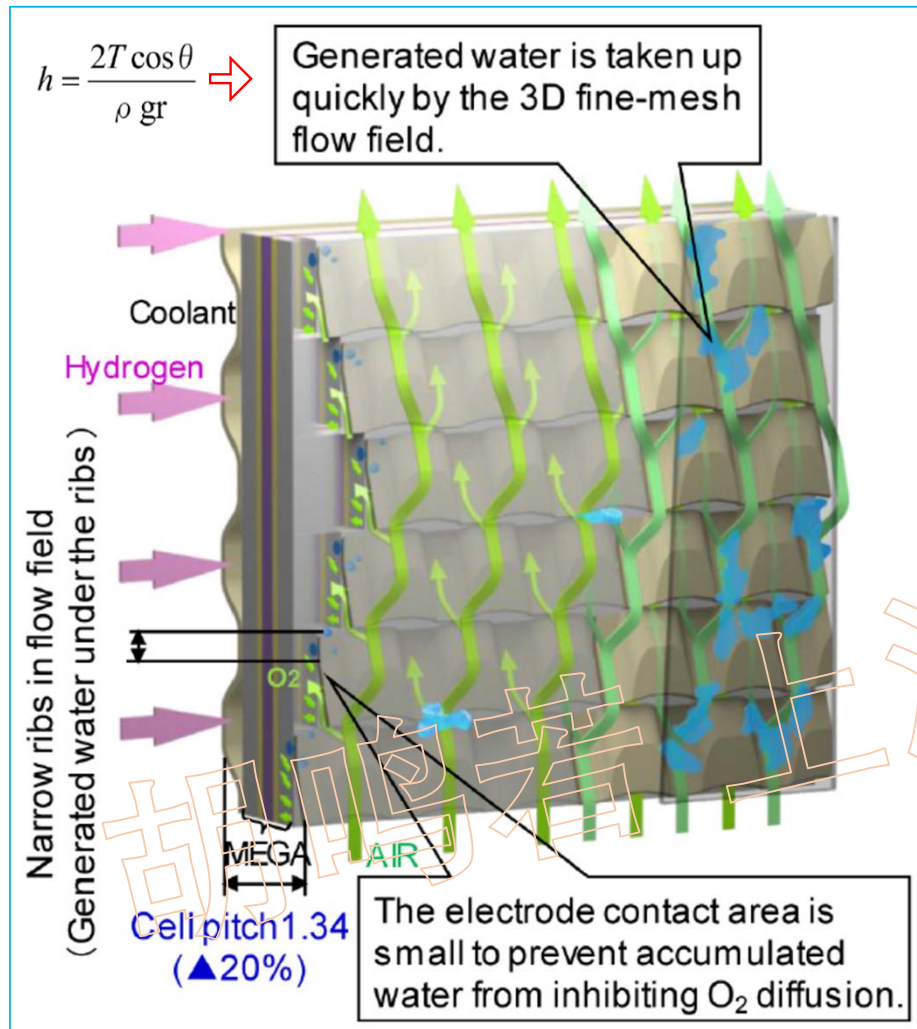
$$Q = (E_0 - E(t)) \cdot i(t)$$

$$C_{stack} \frac{dT_{cell}}{dt} = Q$$

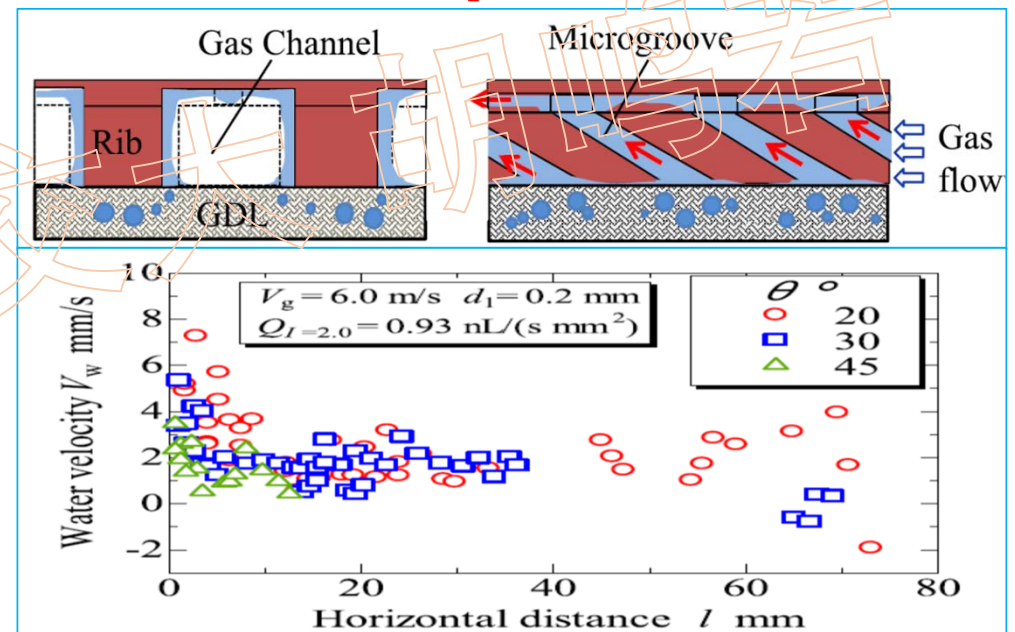
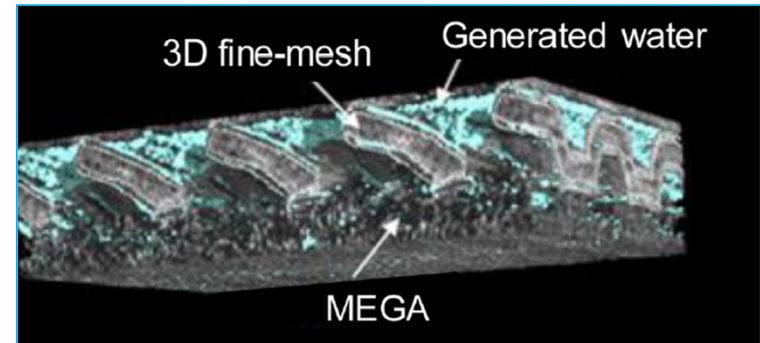
准则：冰核数  $I < 1$  时，  
 低位启动时产生的液  
 态水可以保持过冷态。

冰的异相成核理论分析 → 增加催化层表面接触角 → 过冷度 ↑ ， 过冷时间 ↑

图片和公式来源：Y. Ishikawa, et al. A Map to Start PEFC under Freezing Temperature: Theoretical Analysis of Super-cooled State in Cell. ECS Transactions, 2012, 50(2): 123-135.



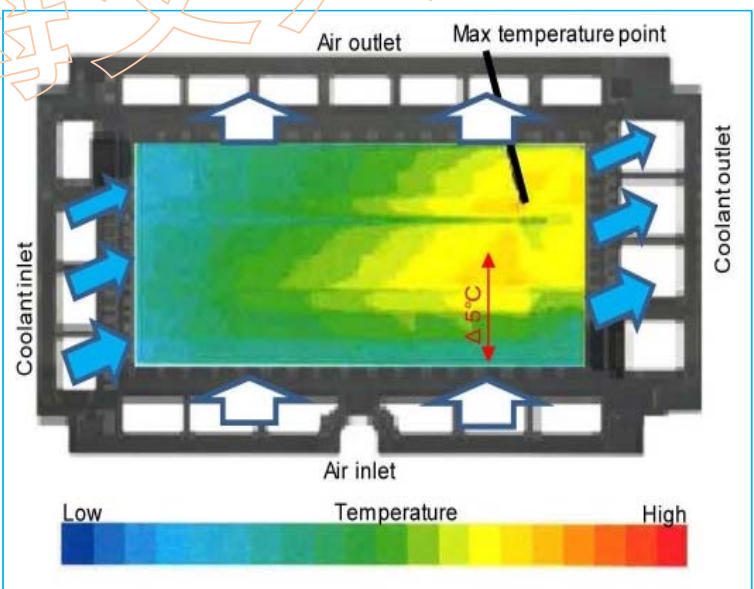
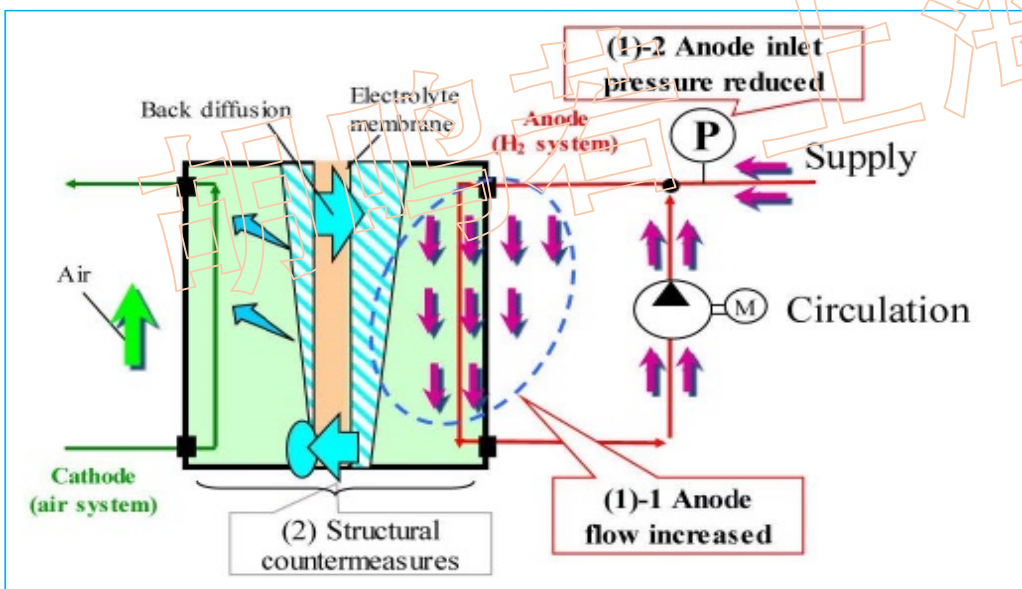
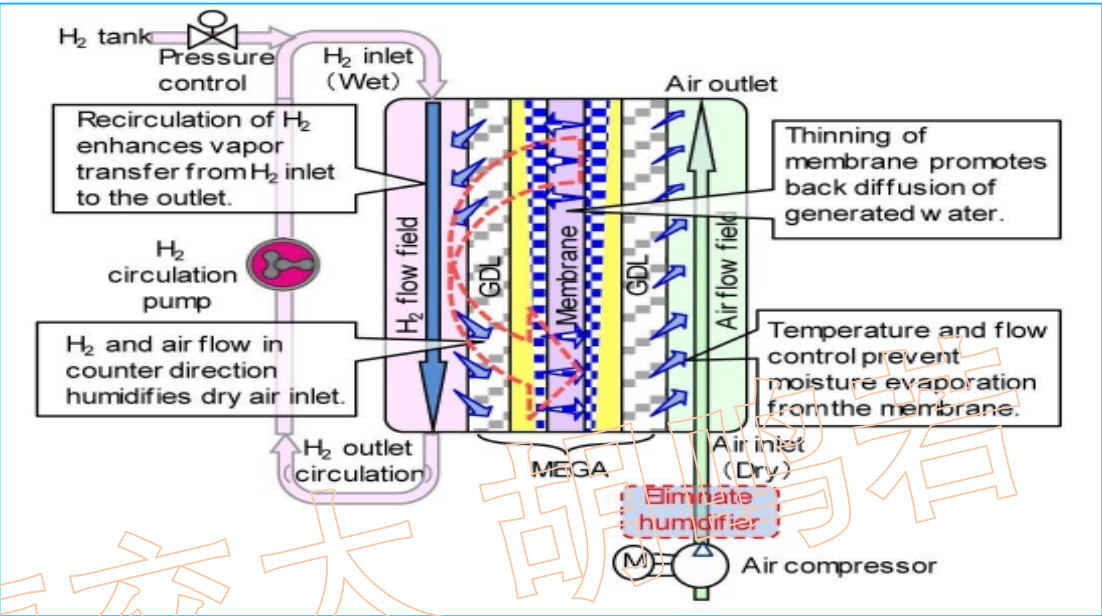
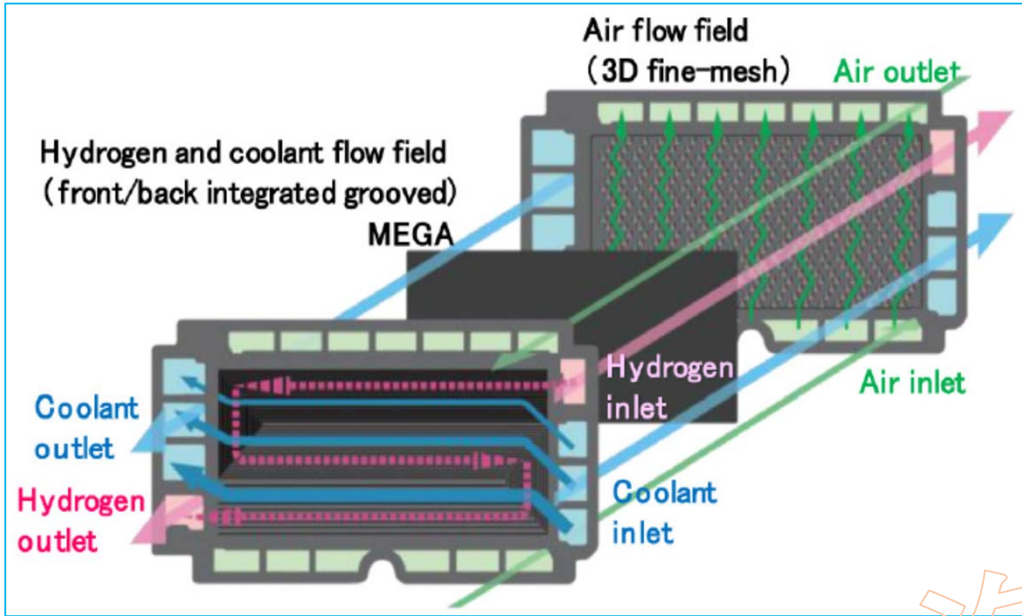
丰田Mirai PEMFC电堆的阴极3D流场设计



流道倾角对于排水速度的影响

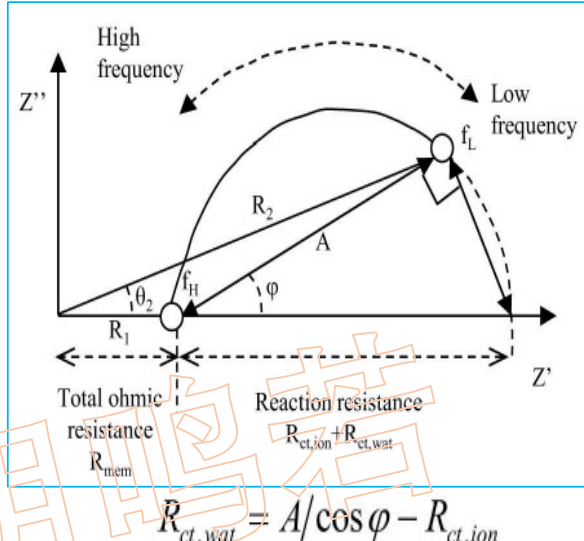
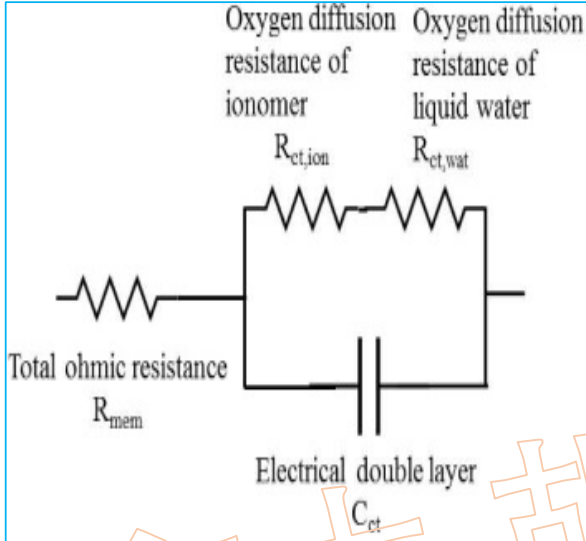
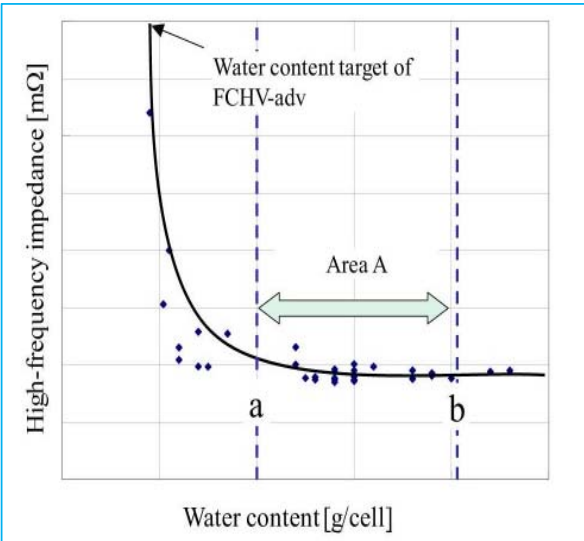
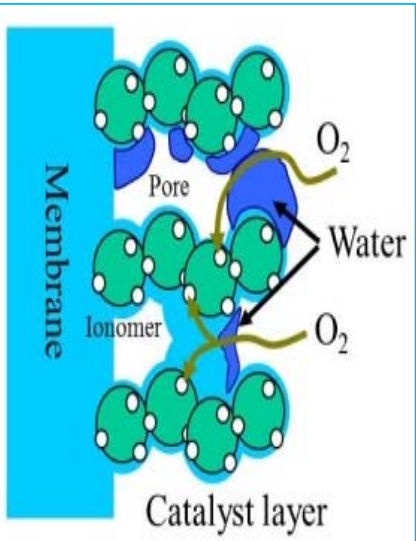
图片和公式来源: Norishige Konno, et al. Development of Compact and High-Performance Fuel Cell Stack. SAE: 2015-01-1175.

图片来源: Yoshio Utaka, et al. Proposal and examination of method of water removal from gas diffusion layer by applying slanted microgrooves inside gas channel in separator to improve polymer electrolyte fuel cell performance. Journal of Power Sources, 2015 (279): 533-539.

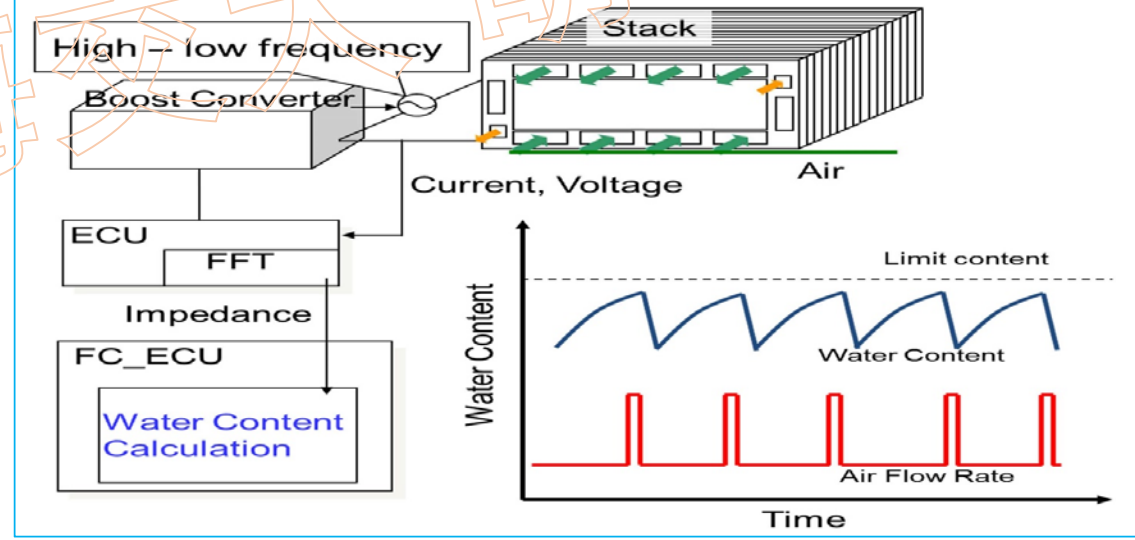
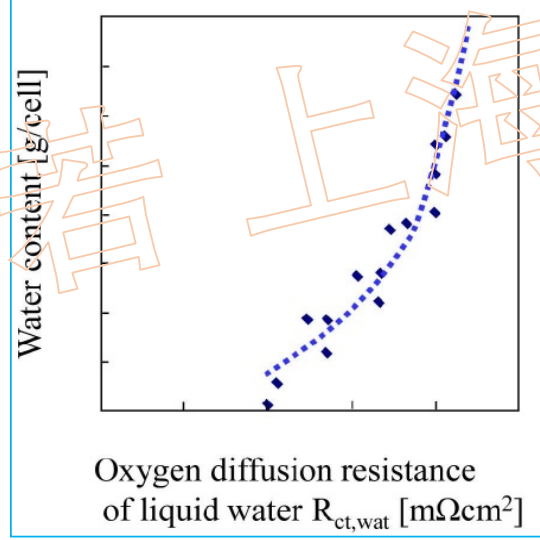


### 丰田Mirai PEMFC电堆的自增湿方法

图片来源：  
 Norishige Konno, et al. Development of Compact and High-Performance Fuel Cell Stack. SAE: 2015-01-1175.  
 Takahiko Hasegawa, et al. Development of the Fuel Cell System in the Mirai FCV. SAE: 2016-01-1185.



丰田Mirai PEMFC系统的在线水管理方法：通过催化层中孔隙/液态水氧气扩散阻抗测量

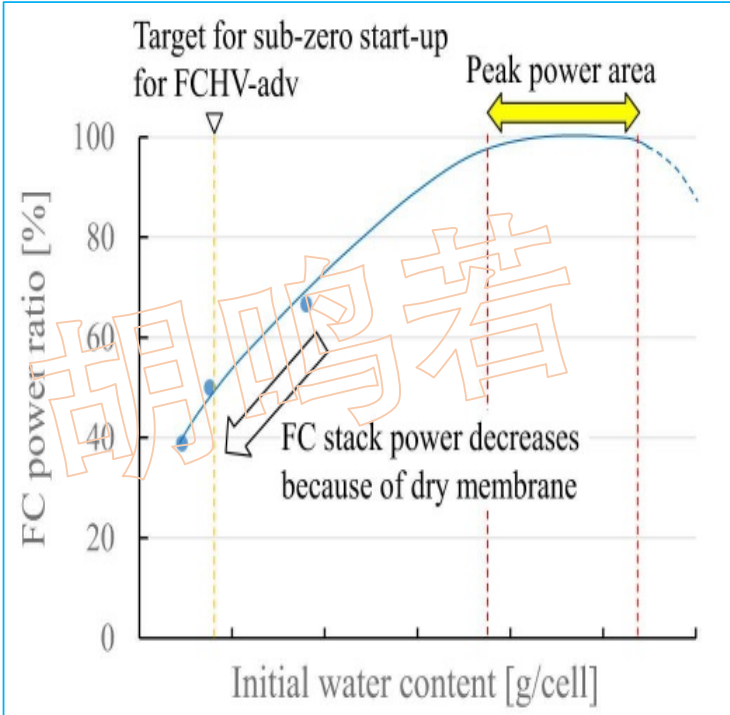
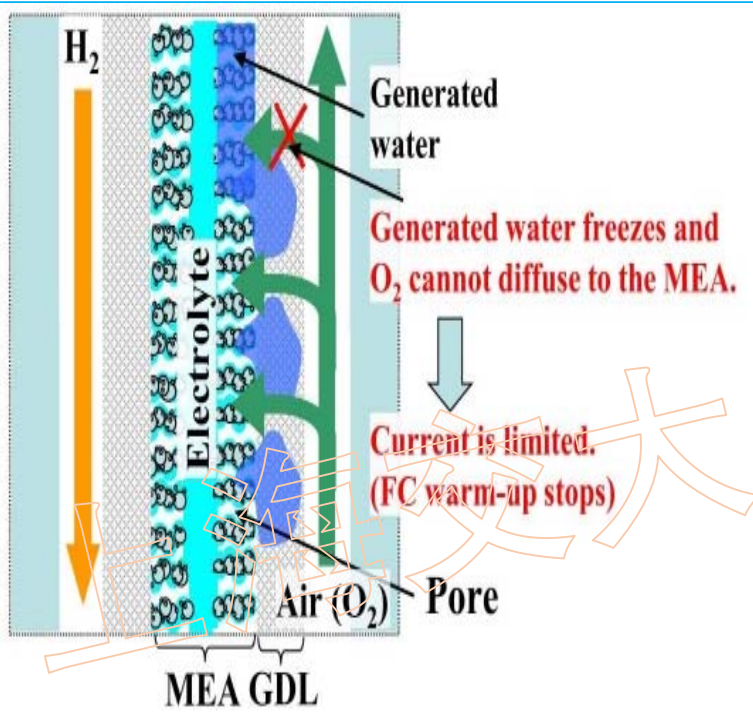
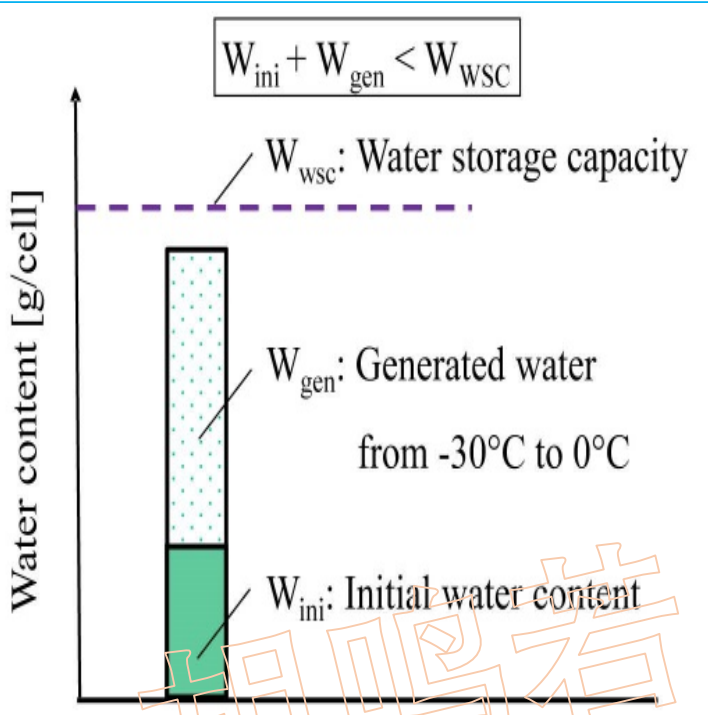


$$R_{ct,wat} = A / \cos \varphi - R_{ct,ion}$$

前5幅图片和公式来源：Yuji Ishikawa, et al. Development of Fuel Cell System Control for Sub-Zero Ambient Conditions. SAE: 2017-01-1189.

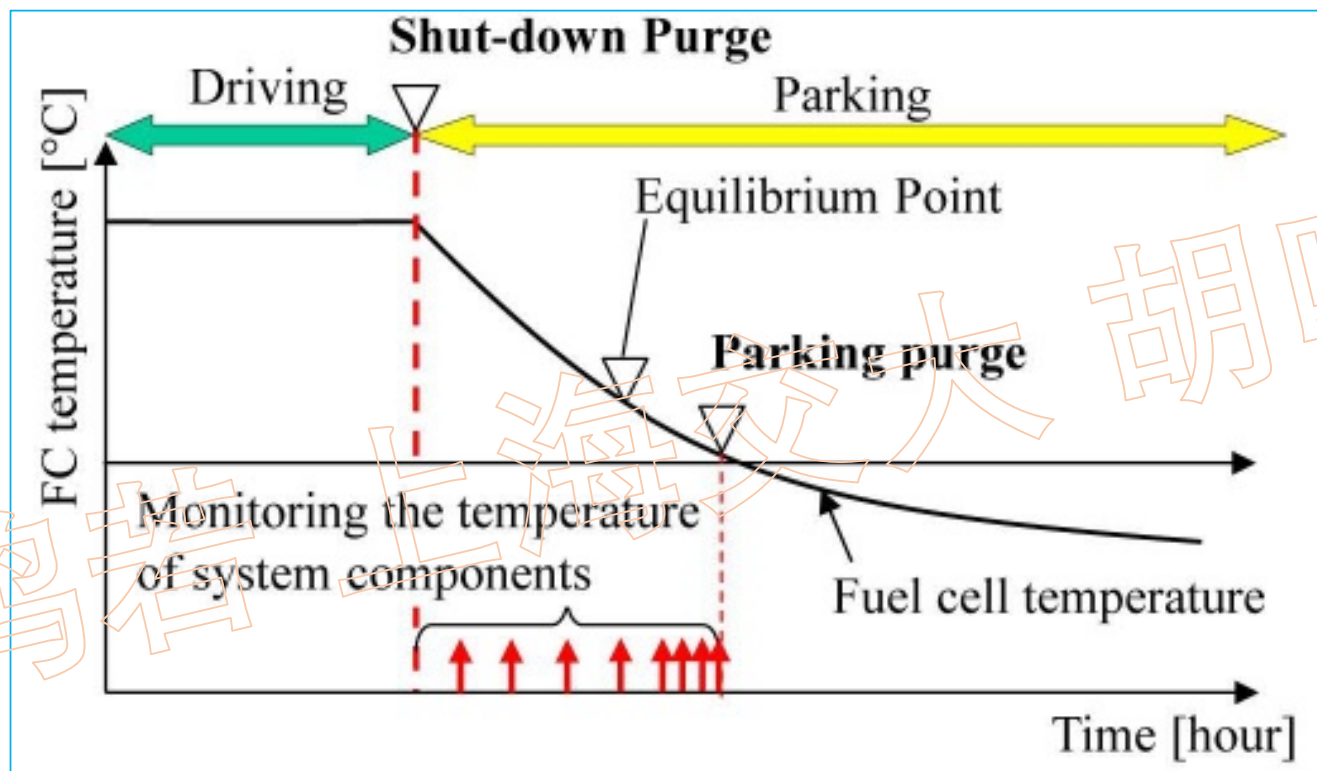
最后一幅图片来源：C. Mizutani, et al. On-board Control System of Water Content inside FCV Stack by Electrochemical Impedance Spectroscopy. ECS Transactions, 2017, 80(8): 357-365.





丰田Mirai PEMFC系统在线水管理对低温启动的作用

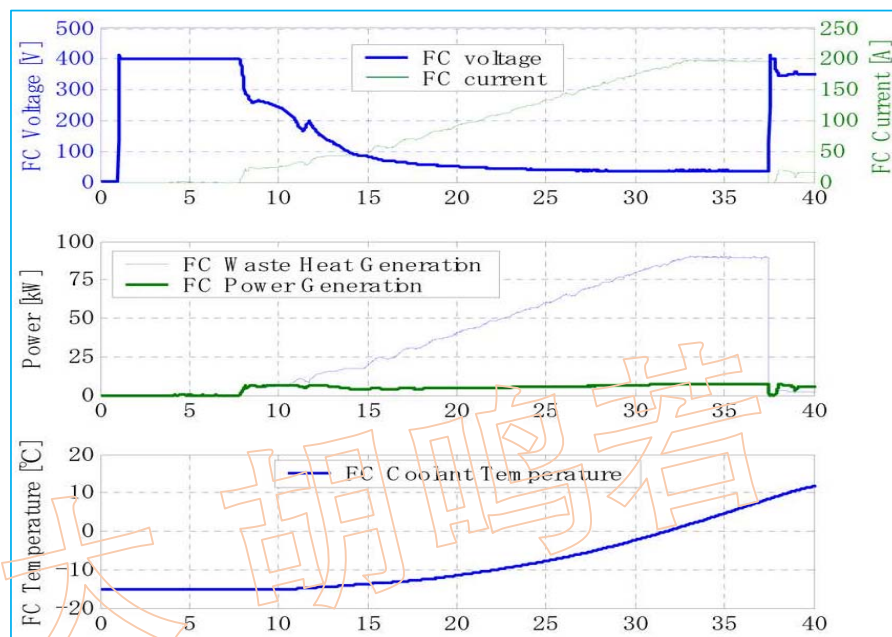
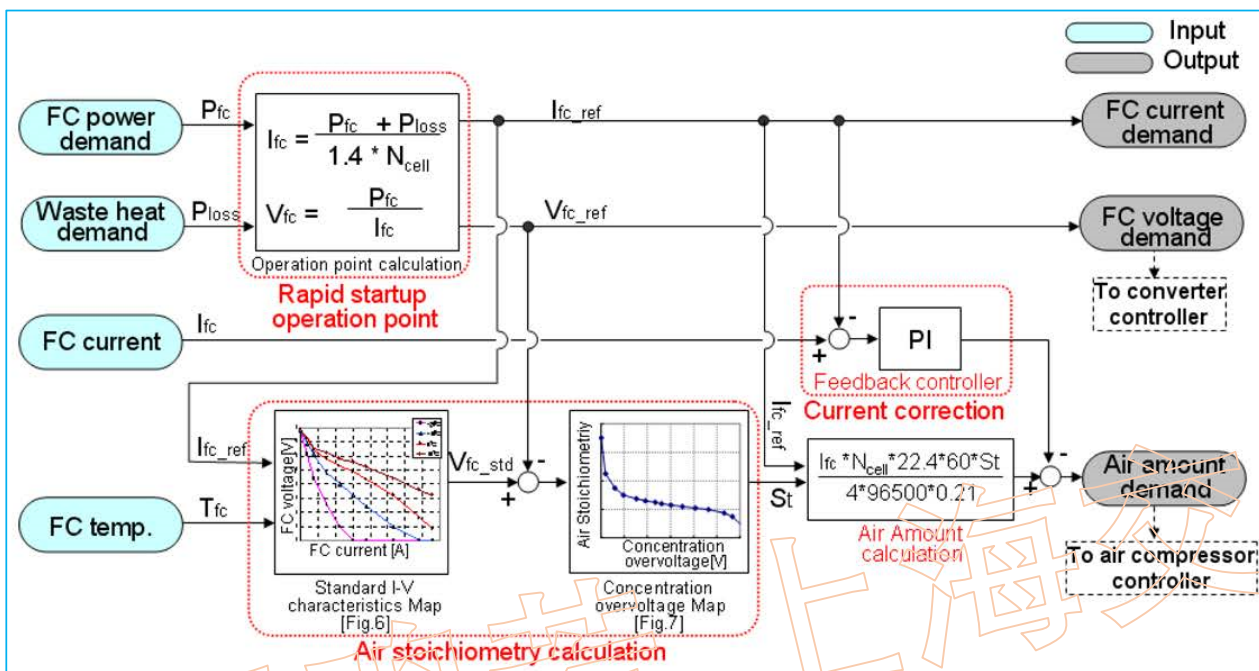
图片来源: Yuji Ishikawa, et al. Development of Fuel Cell System Control for Sub-Zero Ambient Conditions. SAE: 2017-01-1189.



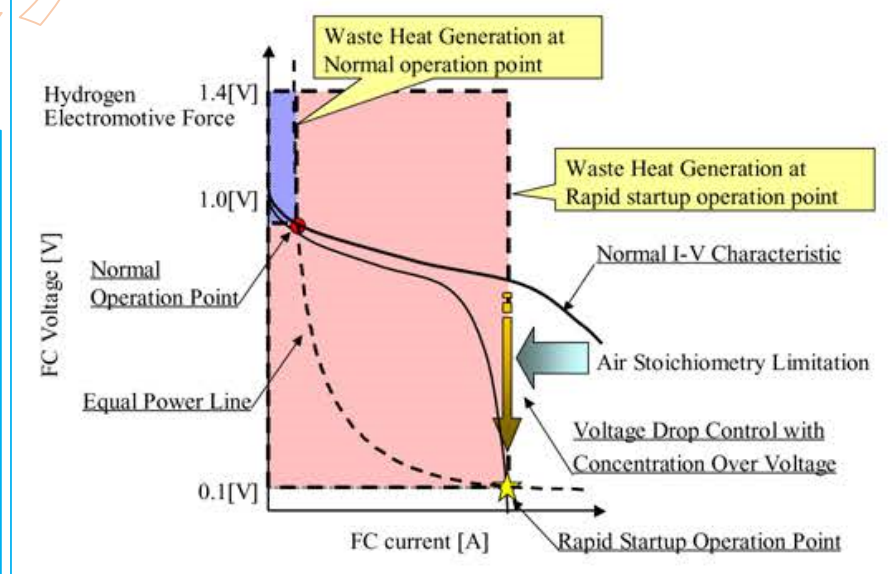
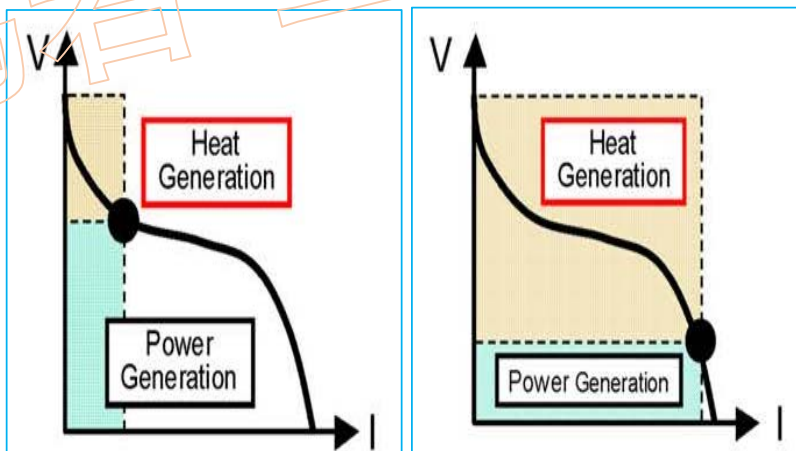
丰田Mirai PEMFC系统的泊车吹扫：防止氢气侧水结冰

图片来源：Yuji Ishikawa, et al. Development of Fuel Cell System Control for Sub-Zero Ambient Conditions. SAE: 2017-01-1189.

# (4) 低温启动技术



丰田FCEV低温启动的原理：  
 减少空气计量比 →  
 增加电池浓差过电位 →  
 产生的大量费热



图片来源: Kota Manabe, et al. Development of Fuel Cell Hybrid Vehicle Rapid Start-up from Sub-freezing Temperatures. SAE: 2010-01-1092.

# 谢谢！



胡鸣若个人主页: <http://fuelcell.sjtu.edu.cn/tpls/teacherInfo?id=2>

# 作者介绍



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副教授、绿色电化学系统和结构实验室主任

研究方向:

- (1) 质子交换膜燃料电池膜电极和电堆的制备技术。
- (2) 燃料电池系统和相关部件的优化设计。
- (3) 燃料电池内部传递机理和寿命衰减机理的研究。
- (4) 紧凑式燃料处理系统的设计。

研发经历:

- (1) 18年燃料电池及氢能技术领域研发经验。
- (2) 自2004年工作开始主持质子交换膜燃料电池项目20多项，包括企业委托研发项目、国家自然科学基金项目和上海市科委项目。
- (3) 拥有三十余项燃料电池技术领域的授权发明专利，包括美国专利和日本专利。
- (4) 撰写国内外学术论文30余篇。
- (5) 具有产学研项目创业及融资经历: 实验室样品原理级迭代→产品设计迭代→生产线设计和建设迭代→企业标准制定→特殊产品认证→产品上市→问题处理

# Changing the world's energy landscape.

SPERA Hydrogen can be inexpensively transported over long distances from any global location. It can be stored in mass quantities for extended periods of time without loss, making it well suited for strategic reserves. In the foreseeable future, SPERA Hydrogen will be produced from natural energy resources. SPERA Hydrogen has the potential to revolutionize the flow of energy while protecting the global environment.

