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High Temperature Electrolysis
Microreactor Integration Potential

Battelle Energy Alliance manages INL for the
U.S. Department of Energy's Office of Nuclear Energy

INL Idaho National Laboratory

Thermodynamic Considerations

- 1st Law of Thermodynamics
  - Energy is neither created nor destroyed
- 2nd Law of Thermodynamics
  - Entropy always increases over time

- Electrolysis is reversing a spontaneous reaction (oxidation of hydrogen)
  - Reduction will require ***at least as much energy*** as was released in the spontaneous reaction
  - Source(s) of energy can be **a bit squishy**…
  - Efficiency is a **tricky definition**

Temperature Impacts

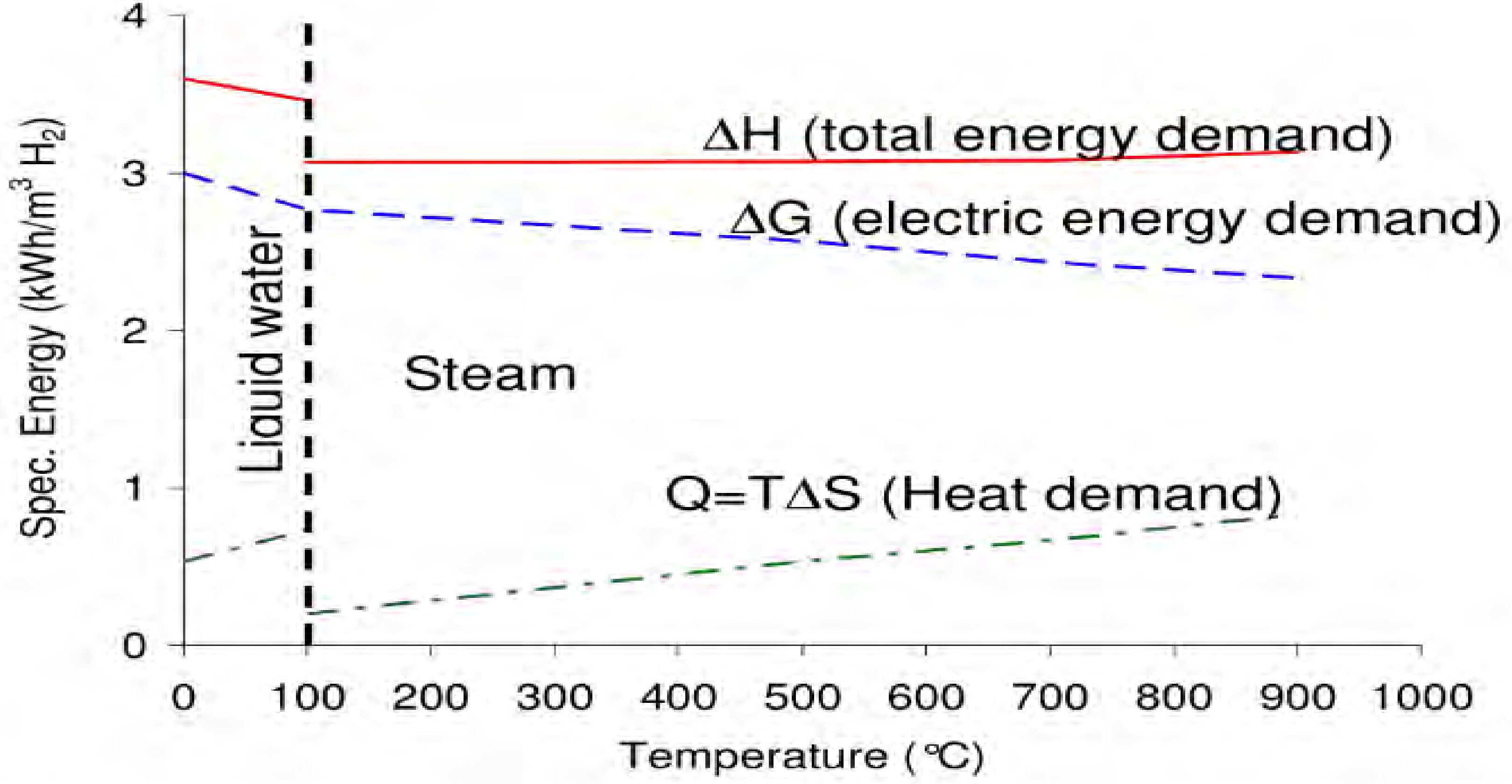


Figure 1: Energy demand of hydrogen operation versus operation temperature (Doenitz, W., et al., International Journal of Hydrogen Energy, 1980. 5: p. 55.).

Thermal energy can be substituted for electrical energy - Up to a point

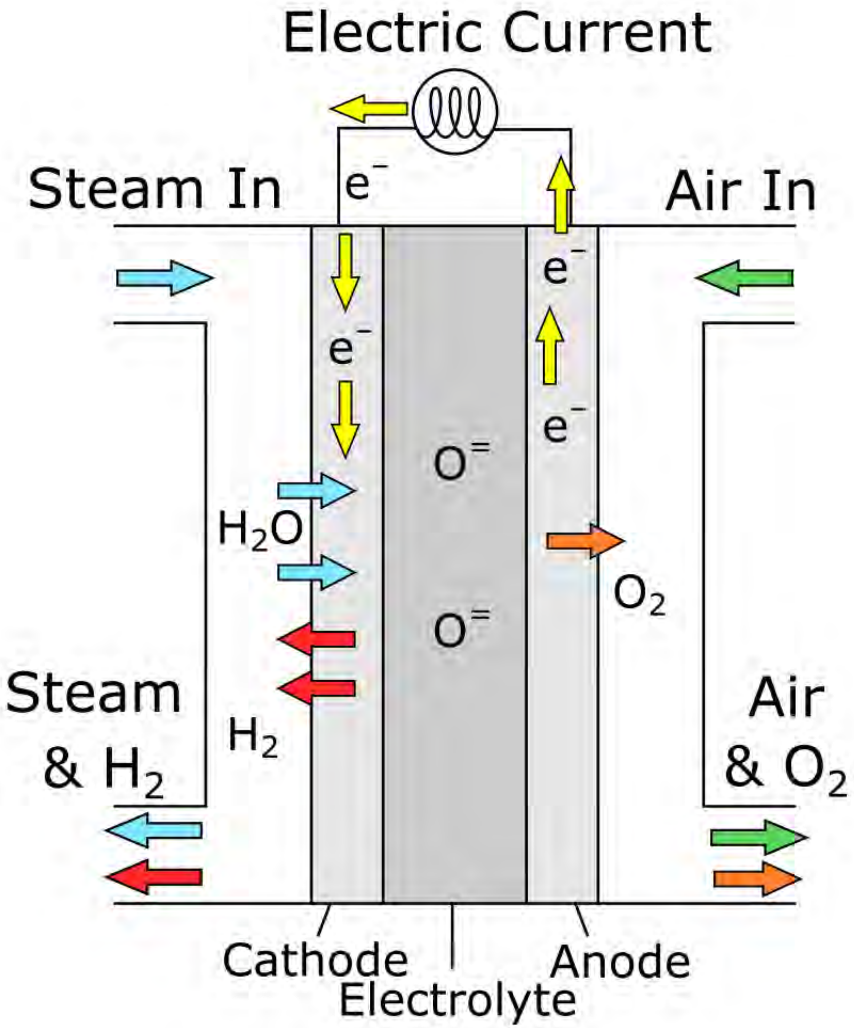
High temperature thermal energy is difficult to manage

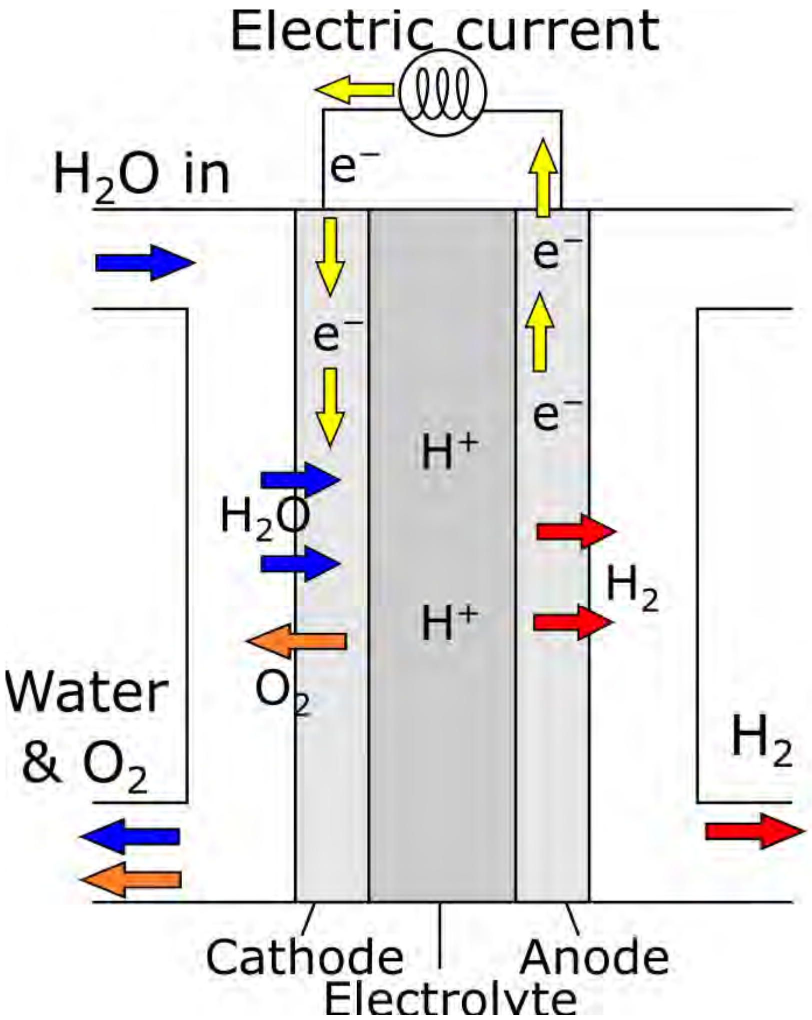
Electrochemistry: Alchemy in Action

- Electrochemical routes can provide **electrical energy** to reduce water
  - Total thermodynamic requirements must be observed
  - Temperature will determine how much electrical energy must be used
- The quantity ***nF*** is the bridge between energy and electricity
  - F = 96,485.33289 C/mol
  - n = # of electrons in reaction
  - Number of electrons in a kg is a **constant**
- **Current Drives Quantity – Voltage Drives Power/Energy/Efficiency**

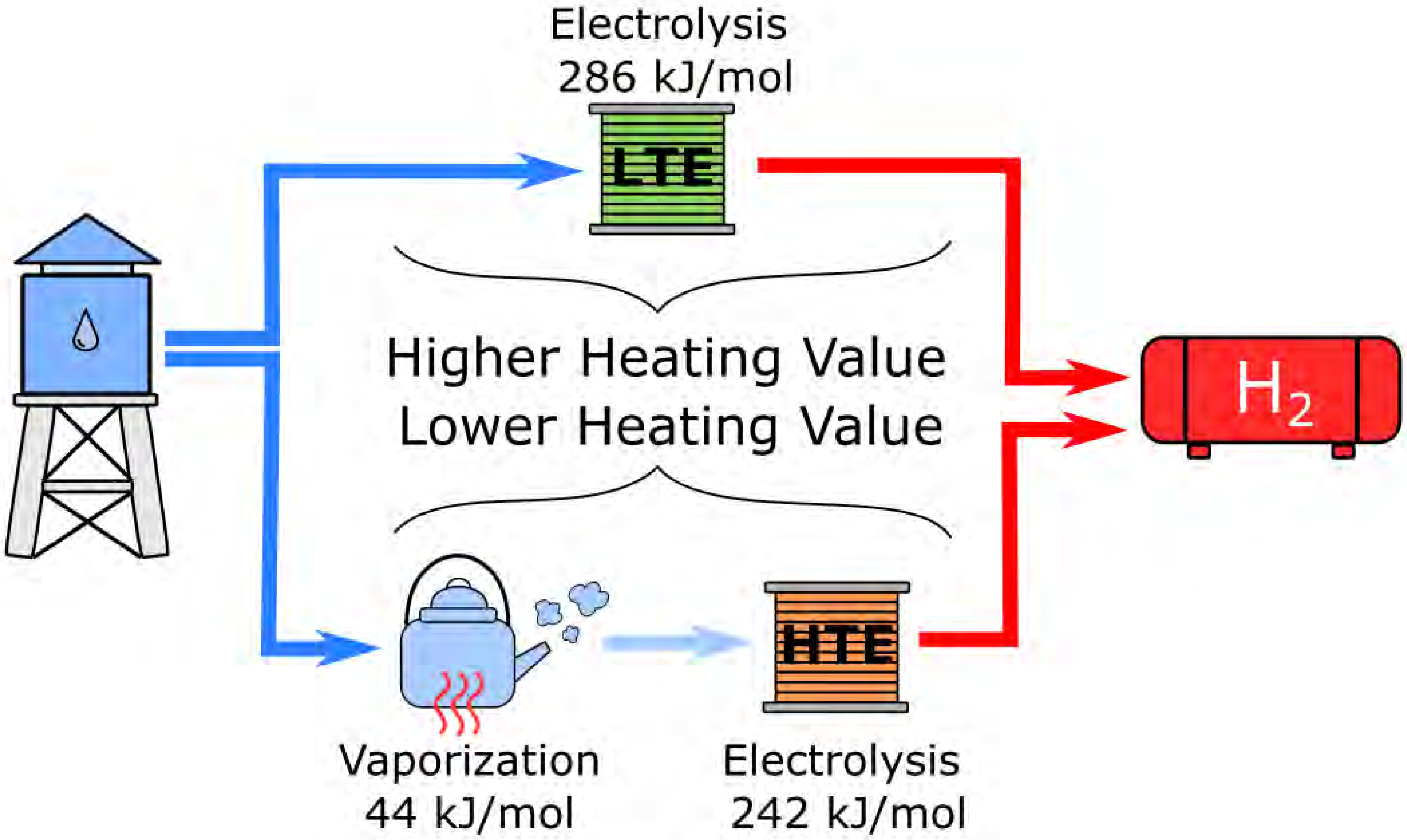
See appendix for calculation of Thermal Neutral Voltage(s)

Electrolysis Architectures – Charge Carrying Species



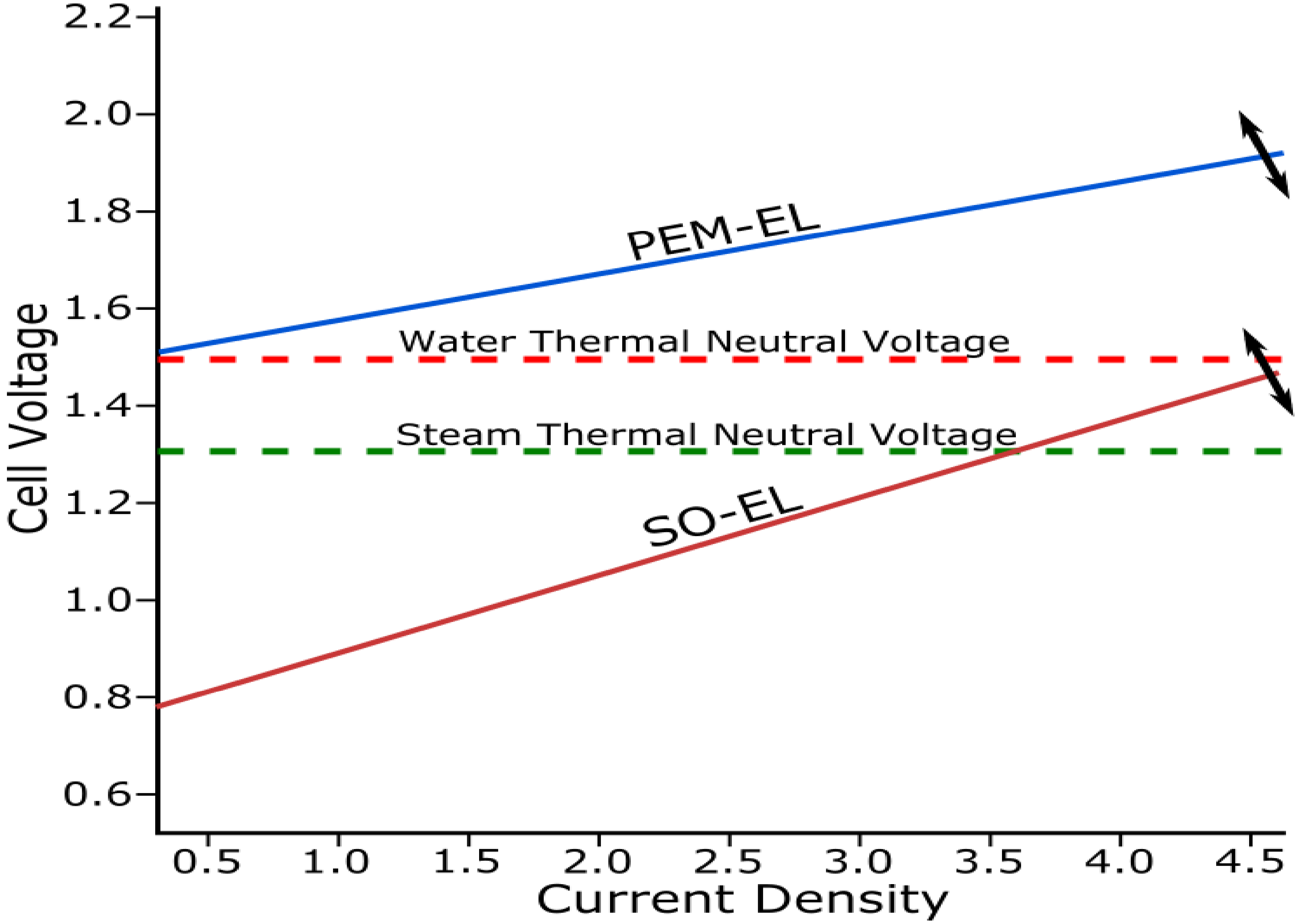


Reduction: Two Potential Routes



These are rough thermodynamic minimums – real reactions will exhibit losses

Voltage-Current (VI) Curves - Practical Cell Voltages



VI Curves are **Specific**

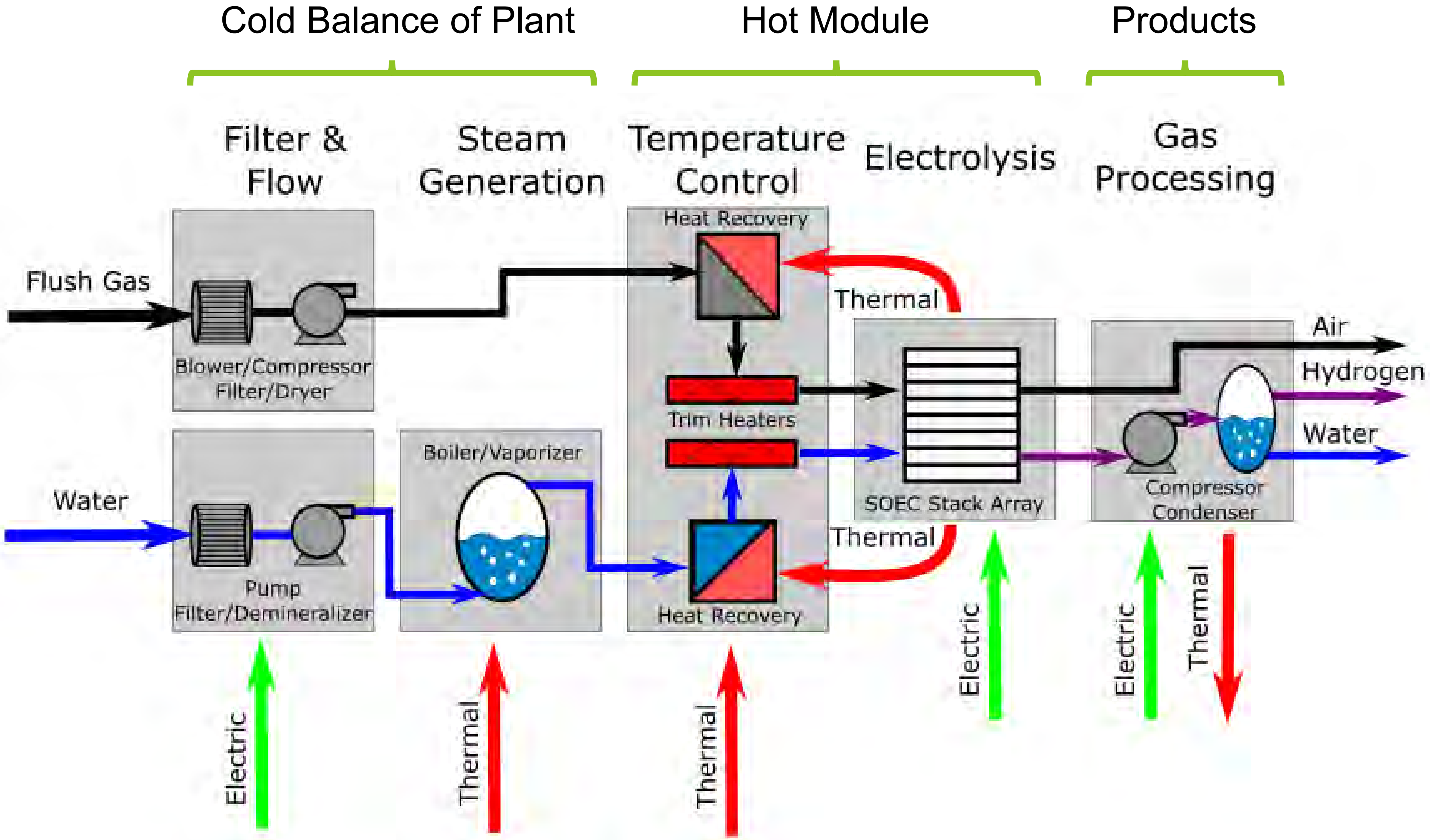
VI Curves are **Flexible**

VI Curves **Change**

Example System Power Inputs: 1 kg/hr

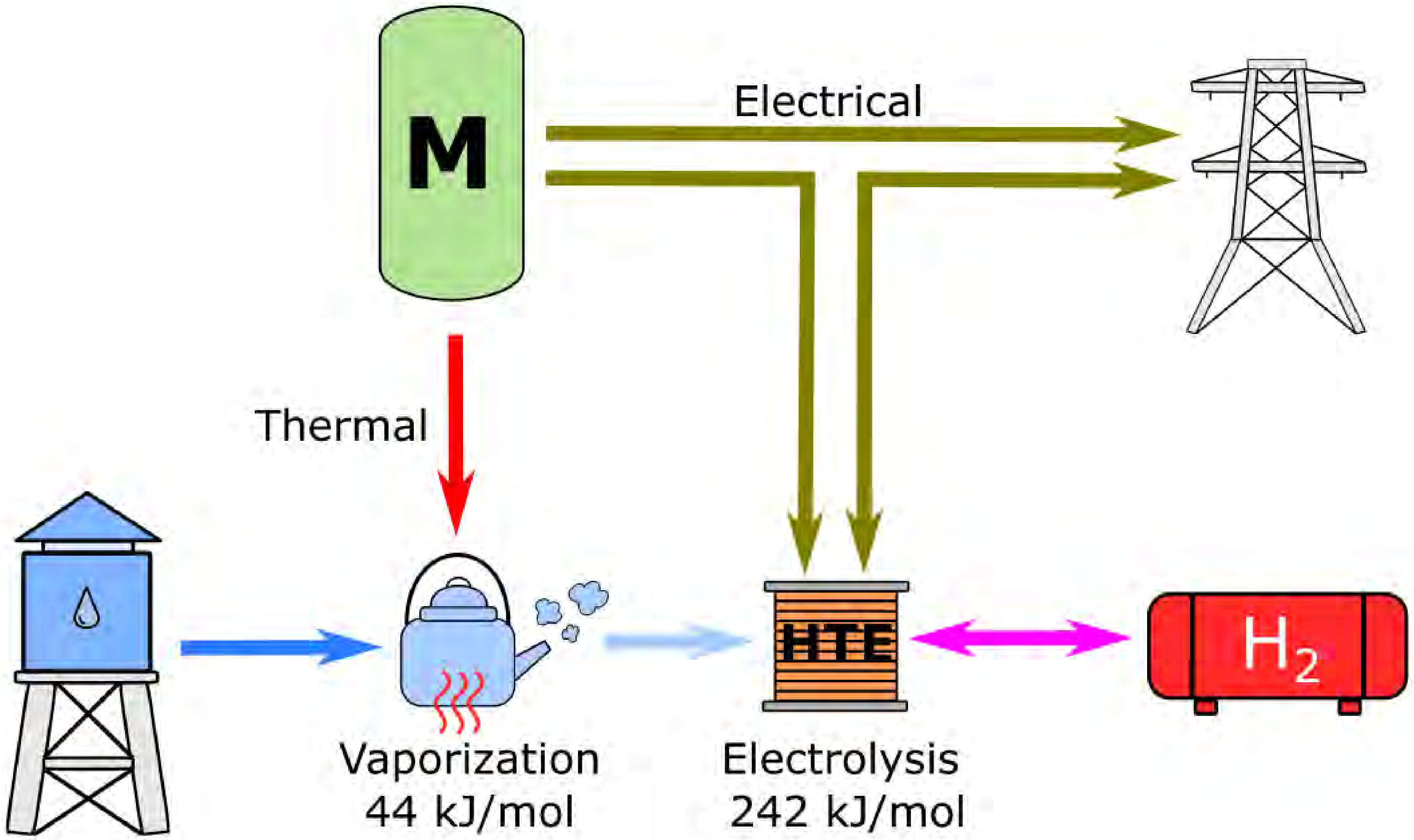
Power required to produce steam	**6.06 kW**
Electrical Power required electrolysis	**33.32 kW**
System Parasitics/losses (~10%)	**3.938 kW**
Total System Power	**43.5 kW**

System Block Diagram



Balance of plant components drive **system** efficiency

System Energy Flows



Example System Power Inputs: Simple Matched System

30 kW SOEC - Marvel Integration

Thermal Energy Available	**~25 kW**
Power required to produce steam	**6.06 kW**
Thermal Makeup Required	**0 kW**
Electrical Energy Available	**~30 kW**
Electrical Power required electrolysis	**33.32 kW**
Electrical Makeup Required	**~4-8 kW**
System Parasitic/losses (~10%)	**3.938 kW**
Total System Power	**43.5 kW**

Example System Power Inputs: Large Dynamic System

500 kW SOEC - Marvel Integration

Thermal Energy Available	**~100 kW**
Power required to produce steam	**~100 kW**
Thermal Makeup Required	**0 kW**
Electrical Energy Available	**0 kW**
Electrical Power required electrolysis	**500 kW**
Electrical Makeup Required	**500-550 kW**
System Parasitic/losses (~10%)	**~50 kW**
Total System Power	**~650 kW**

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Technical Backup

Developing Realistic HTE Systems:

Production Needs

- Inputs
  - Energy
    - Electrical
    - Thermal
  - Water
  - Flush Gas
  - Cover gases?
- Outputs
  - Further Gas processing required
  - Water Disposal
  - Gas Storage

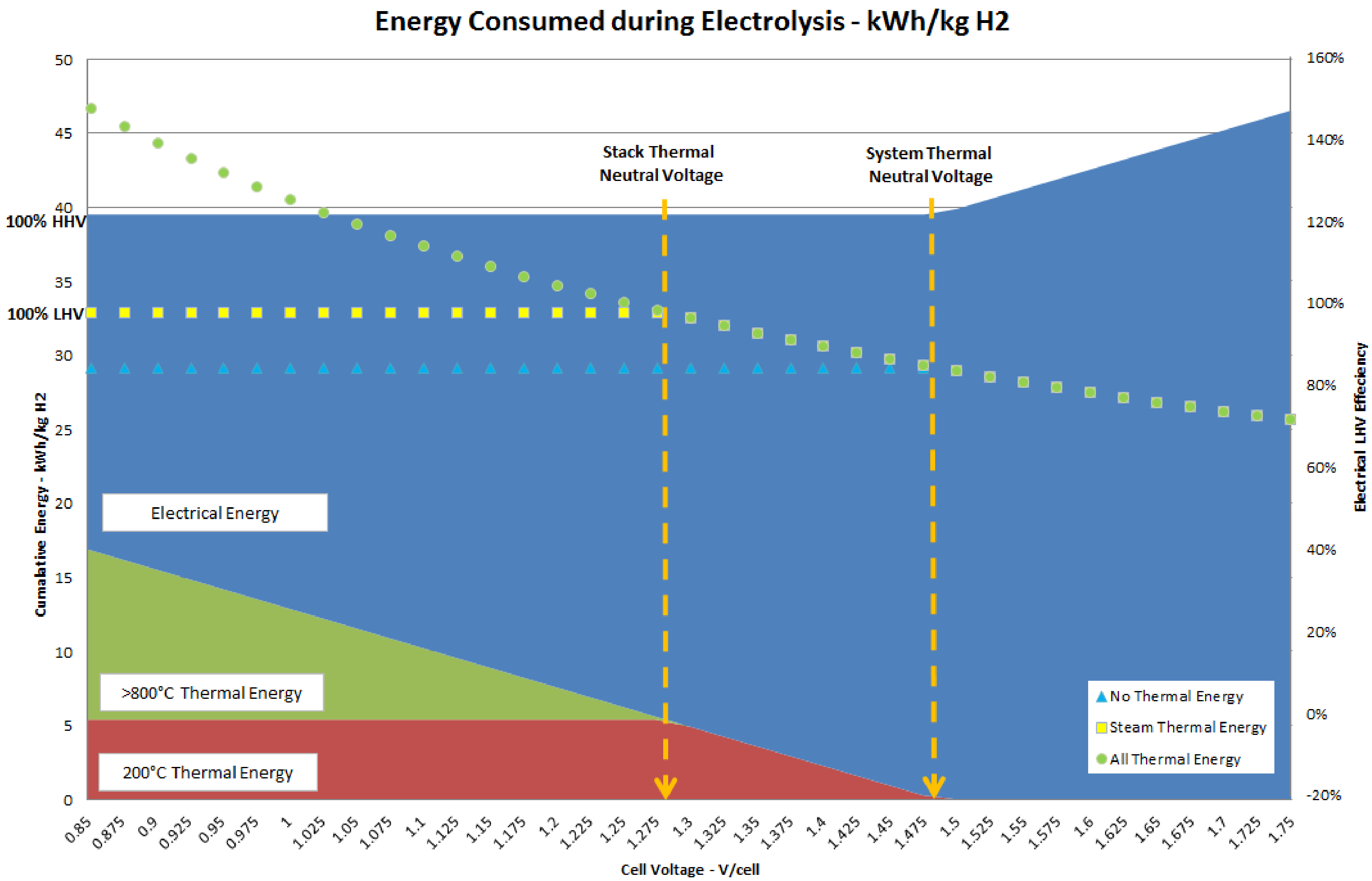
System Needs

- Controls
  - Local/remote
  - Allowable Ramp Rates
- Longevity
  - Degradation/Life
  - Environmental Tolerance
- Supplier
  - Production rate
  - Quality
- Safety
- Physical Size

Thermodynamic Implications

- Producing 1 kg hydrogen consumes ***at least***
  - 39.38 kWh/kg if liquid water to start
  - 33.32 kWh/kg if steam to start
- 1 mV delta results = 26Wh/kg delta
  - 37.7 mV delta= 1 kWh/kg delta!

Breakdown of Energy Type by Voltage for HTE



Voltage selection allows energy type substitution

These are thermodynamic minimums real reactions will exhibit losses

Appendix: Finding Thermal Neutral Voltage

$$\text{Total Charge: } Q = nF$$

$$1\ molecule\ of\ H_2 = 2\ electrons \rightarrow n = 2$$

$$2\frac{1}{mol\ H_2} * 1\ mol\ * 96{,}485.33\ \frac{C}{mol} = Q = 192{,}970\ \frac{C}{mol\ H_2}$$

$$\text{Charge: } C = A\ * S$$

$$\text{Electric Power: } W = V * A$$

$$\text{Power: } W = \frac{J}{s}$$

Unit Analysis:

$$\frac{kJ}{mol\ H_2} * \frac{1000\ J}{kJ} = \frac{1000\ J}{mol\ H_2} = 1000\frac{W * S}{mol\ H_2} = 1000\frac{V * A * S}{mol\ H_2} = 1000\frac{\frac{C}{S} * V * S}{mol\ H_2}$$

$$\frac{kJ}{mol\ H_2} = 1000\frac{C * V}{mol\ H_2}$$

Appendix: Finding Thermal Neutral Voltage

Recall that

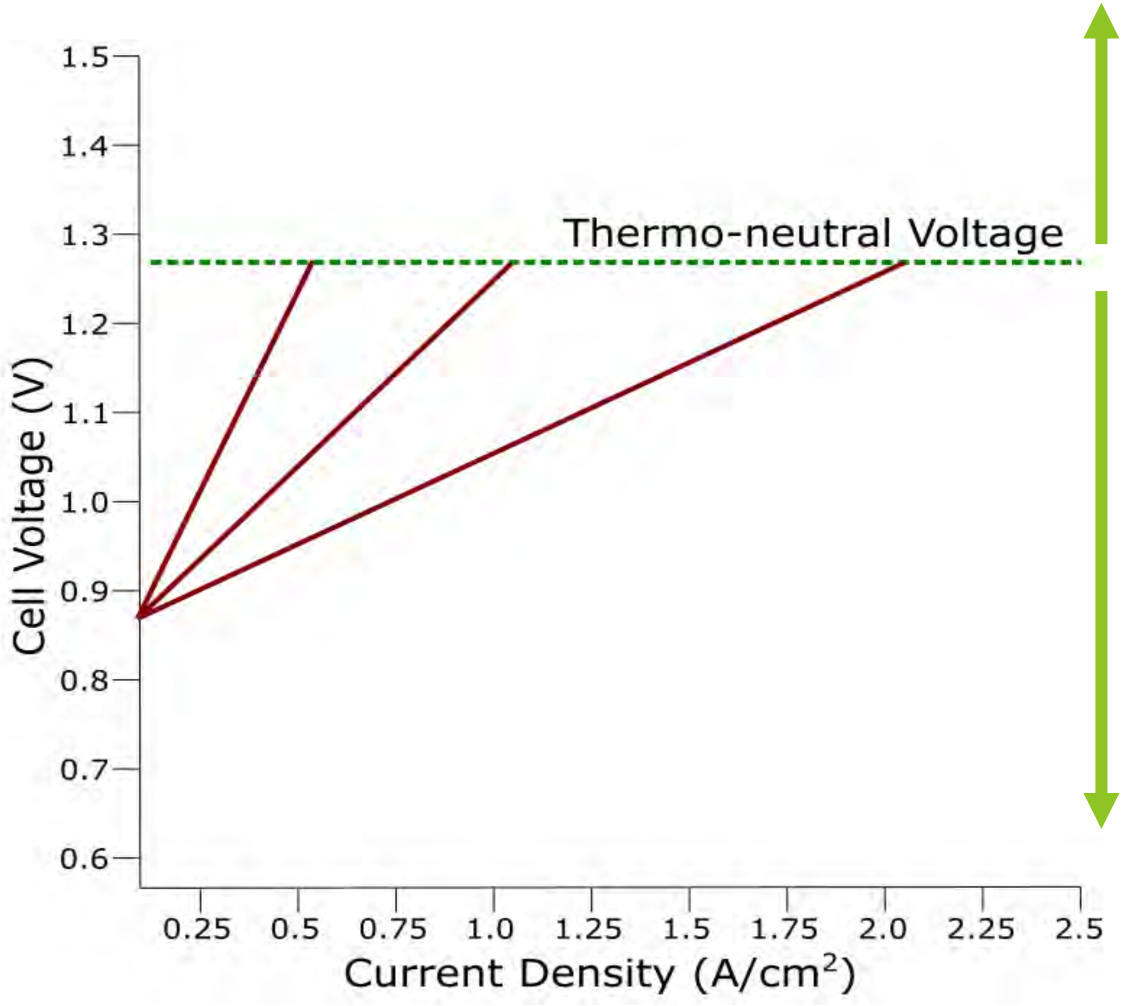
$$\frac{kJ}{mol\ H_2} = 1000\frac{C * V}{mol\ H_2}$$

Calculating Thermal Neutral Voltage (all electricity, no other energy input)

$$LHV\ = 242\ \frac{kJ}{mol\ H_2} = 242,000\frac{C * V}{mol\ H_2} \div 192,970\ \frac{C}{mol\ H_2} = 1.254\ V$$

$$HHV\ = 286\ \frac{kJ}{mol\ H_2} = 242,000\frac{C * V}{mol\ H_2} \div 192,970\ \frac{C}{mol\ H_2} = 1.482\ V$$

VI Curve – System Implications: Voltage



Decreasing Efficiency!
Unlikely Operation

Increasing Efficiency!
Unphysical Operation

Take Away: Operation is almost always performed at thermoneutral voltage.

Which means "Cell Efficiency" is the same

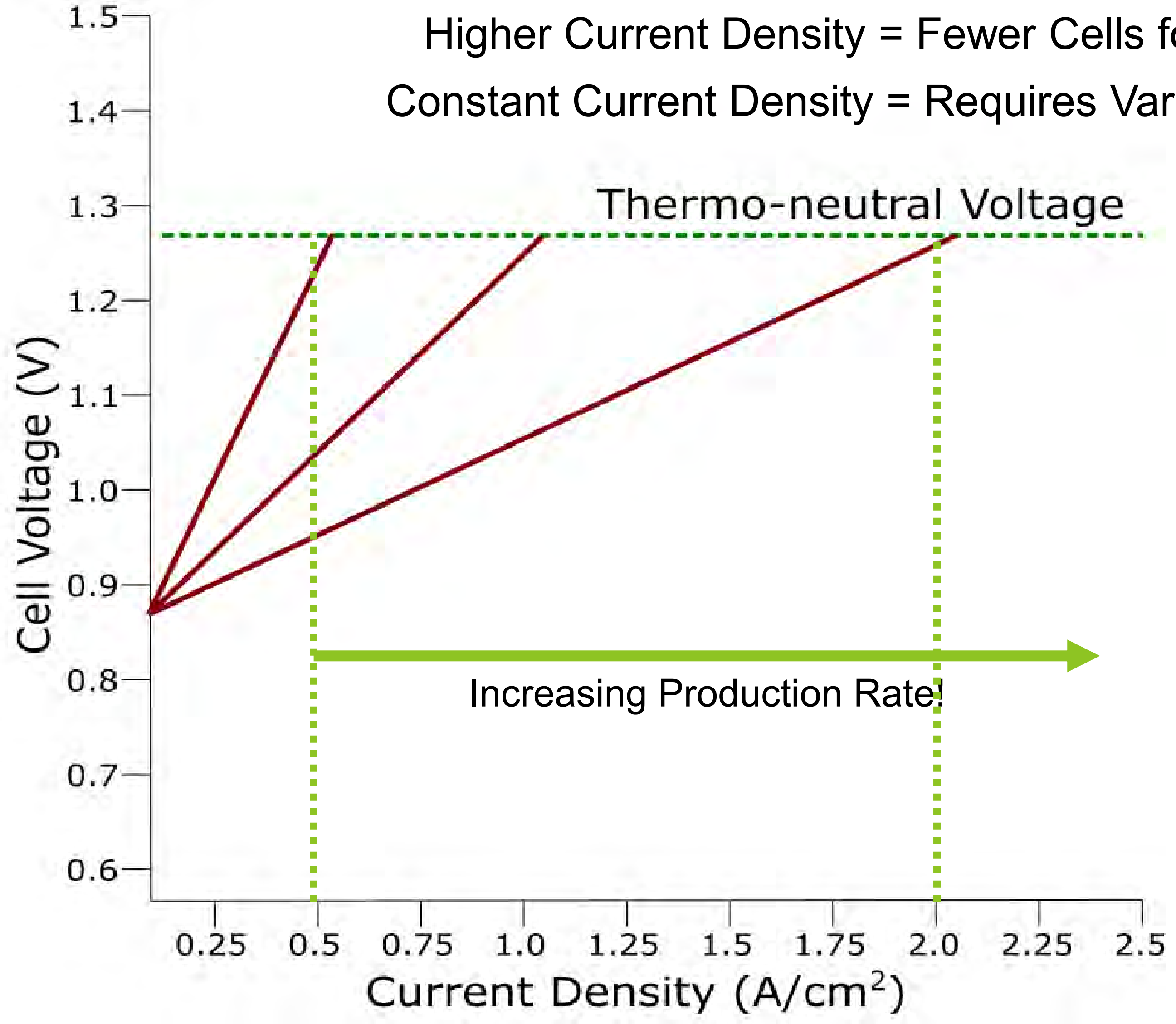
Operation below steam thermal neutral requires thermal energy
at/above electrolysis temperature to balance the total energy

VI Curve – System Implications: Current Density

Hydrogen Production = Total Current

Higher Current Density = Fewer Cells for Same Production

Constant Current Density = Requires Variable Energy Input



Higher current density may mean lower capital cost - but doesn’t affect efficiency

Degradation increases slope of VI curve over time