Fuel Cells

Fuel Cells

Fuel cells are similar to batteries; they have a cathode, electrolyte and anode.

O$_2$ in

O$_2$

H$_2$O

Product gases and waste oxidant

Cathode

+ve ion

-ve ion

Anode

H$_2$

H$_2$O

Fuel in

Product gases and waste fuel
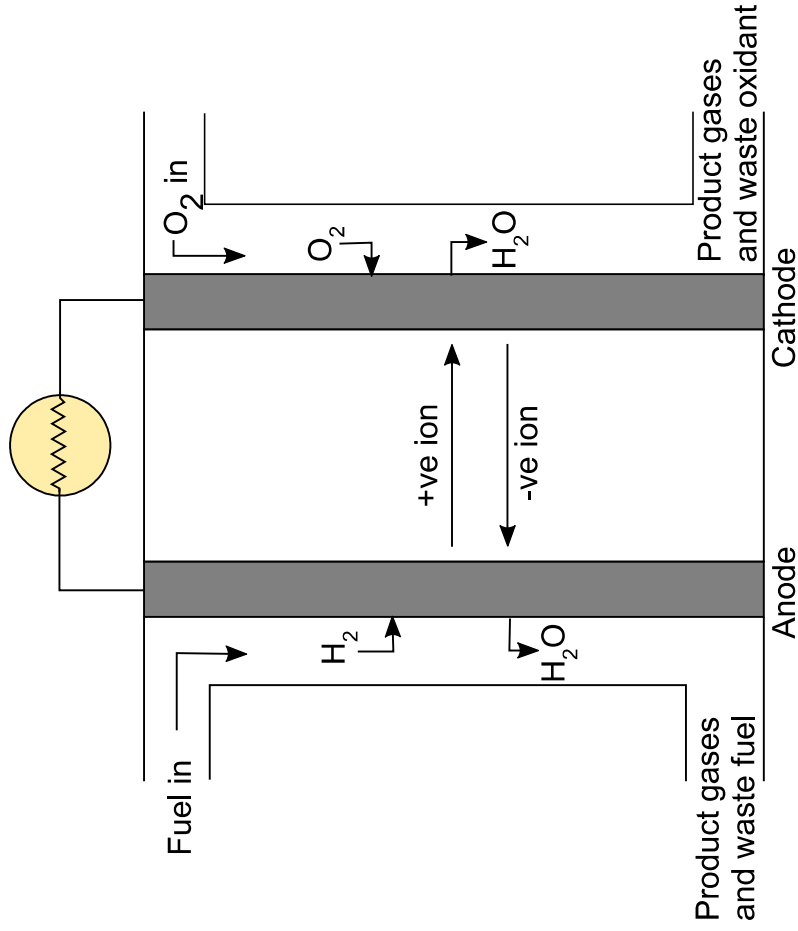
Fuel cell history

1801 — Humphry Davy demonstrates the principle of what became fuel cells.

1839 — William Grove invents the 'gas battery', the first fuel cell.

1889 — Charles Langer and Ludwig Mond develop Grove's invention and name the fuel cell.

1950s — General Electric invents the proton exchange membrane fuel cell.

1959 — Francis Bacon demonstrates a 5 kW alkaline fuel cell.

1960s — NASA first uses fuel cells in space missions.

1970s — The oil crisis prompts the development of alternative energy technologies including PAFC.

1980s — US Navy uses fuel cells in submarines.

1990s — Large stationary fuel cells are developed for commercial and industrial locations.

2007 — Fuel cells begin to be sold commercially as APU and for stationary backup power.

2008 — Honda begins leasing the FCX Clarity fuel cell electric vehicle.

2009 — Residential fuel cell micro-CHP units become commercially available in Japan. Also thousands of portable fuel cell battery chargers are sold.

Fuel cell fundamentals

$$\text{Fuel} + O_2 \longrightarrow H_2O + nCO_2$$

- Fuel cells a divided into *low-temperature (LT)* (< 200 °C) and *high-temperature (HT)* (> 450 °C).
- H_2 is the preferred fuel
  - Particularly for LT devices.
  - Doesn't produce CO_2

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- Other fuels (*e.g.* CH_3OH, CH_4, NH_3) can also be used, particularly for HT devices

  - *e.g.* for CH_4, steam reforming ($CH_4 + H_2O \xrightarrow{>700°C} CO + 3\,H_2$) can be achieved HT cells, but must be performed separately for LT cells.

Fuel cell efficiency

Fuel cells are *very* efficient

- Convert fuel $\rightarrow$ electricity directly, rather than fuel $\rightarrow$ heat $\rightarrow$ electricity (as in combustion)

$$\text{Thermodynamic efficiency} = \frac{\Delta G}{\Delta H}$$

e.g. for $2\,H_2 + O_2 \longrightarrow 2\,H_2O$ $(\Delta H = -571.6\text{kJ mol}^{-1})$:

Cathode:	$4\,H^+ + O_2 + 4\,e^- \longrightarrow 2\,H_2O$	$E = +1.229$ V
Anode:	$4\,H^+ + 4\,e^- \longrightarrow 2\,H_2$	$E = 0.00$ V

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$\Delta G = -nFE$

$\quad\ = -4 \times F \times 1.29$

$\quad\ = -474.3\,\text{kJ mol}^{-1} \qquad$ (per mole O_2)
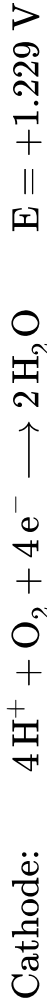
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$$= -474.3\ \mathrm{kJ\ mol^{-1}} \qquad \text{(per mole } \mathrm{O_2}\text{)}$$

Efficiency = η = -474.3 / 571.6 = **83%**

Efficiency with temperature

$$\Delta G = \Delta H - T\Delta S, \quad \therefore \quad \frac{\Delta G}{\Delta H} = \eta = 1 - \frac{T\Delta S}{\Delta H}$$

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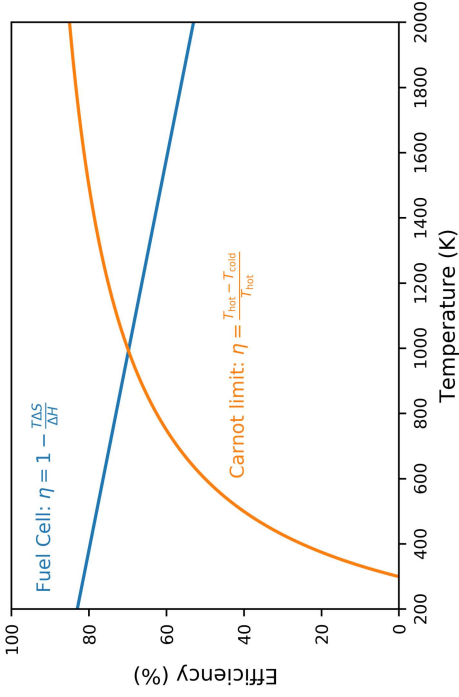
$$\eta = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}}$$

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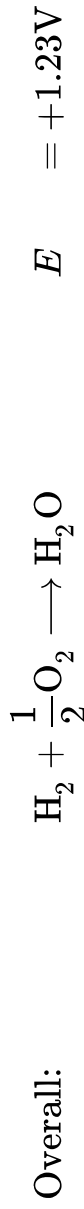

Fuel Cell: $\eta = 1 - \frac{T\Delta S}{\Delta H}$

Carnot limit: $\eta = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}}$

Types of fuel cell

Type	Mobile ion	Operating temperature (°C)	Applications
Alkaline	OH^-	50-100	Stationary power, space missions
Polymer	H^+/OH^-	50-100	Portable devices, transport
Phosphoric acid (PAFC)	H^+	220	Medium to large scale combined heat and power (CHP) systems
Molten Carbonate (MCFC)	CO_3^{2-}	650	
Solid Oxide (SOFC)	O^{2-}	500 - 1000	

L. Carrette, *Fuel Cells*, 2001, 5.

Alkaline Fuel cell (AFC)

Anode: $H_2 + 2\,OH^- \longrightarrow 2\,H_2O + 2\,e^-$ $E = 0V$

Cathode: $\dfrac{1}{2}O_2 + 2\,H_2O + 2\,e^- \longrightarrow 2\,OH^-$ $E = +1.23V$

Overall: $H_2 + \dfrac{1}{2}O_2 \longrightarrow H_2O$ $E = +1.23V$

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  - Updated version still used in current space shuttle
- Based around concentrated KOH electrolyte with Ni anode and catalytic cathode (such as Pt, Pd or Ag)
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- Susceptible to CO_2 poisoning:
  - $2\,KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$
  - K_2CO_3 goes on to block electrode

- Requires pure H_2 and O_2

Polymer [proton exchange membrane] fuel cell (PEMFC)

- First developed for the Gemini space vehicle
- Based around an acidic proton-conducting polymer
  - *e.g.* Nafion
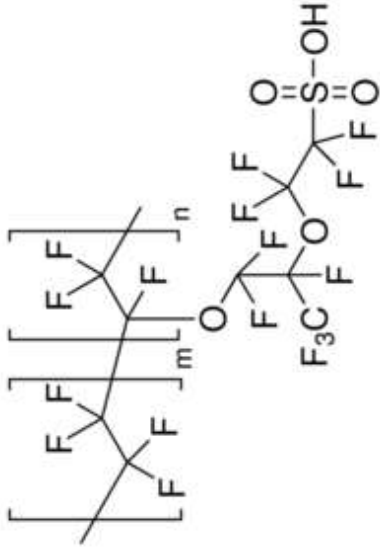
- Use H_2 as fuel, but can work with MeOH (less efficiently)

PEMFC

Anode	$2\,H^+ + 2\,e^- \longrightarrow H_2$	$E = 0V$
Cathode	$O_2 + 2\,H^+ + 2\,e^- \longrightarrow H_2O_2$	$E = 0.695V$
	$H_2O_2 + 2\,H^+ + 2\,e^- \longrightarrow 2\,H_2O$	$E = 1.776V$
Cathode (Overall)	$O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O$	$E = 1.229V$

PEMFC
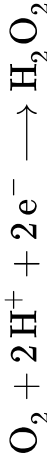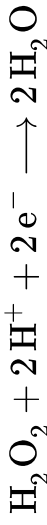
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- In acidic conditions, H_2O_2 forms
  - Corrodes carbon-containing electrodes
  - Lowers cell voltage
  - Requires Pt or Pd catalysts to promote H_2O_2 decomposition
    - ~0.5 mg cm^{-3}
    - Expensive
    - Poor tolerance to CO or NH_3
- PEMFCs give good Low-temperature (< 100 °C) operation
  - Quick to start/stop
  - Suitable for portable applications
- Require careful hydration to ensure H^+ conduction

Methanol fuel in PEMFC

Methanol is easier to store/transport than H_2 and almost as efficient

- Readily oxidised, does not require C-C bond breaking

Anode	$CO_2 + 6\,H^+ + 6\,e^- \longrightarrow CH_3OH + H_2O$	$E = 0.046\ \text{V}$
Cathode	$\dfrac{3}{2}O_2 + 6\,H^+ + 6\,e^- \longrightarrow 3\,H_2O$	$E = 1.229\ \text{V}$
Overall	$CH_3OH + \dfrac{3}{2}O_2 \longrightarrow CO_2 + 2\,H_2O$	$E = 1.183\ \text{V}$

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Overall	$CH_3OH + \dfrac{3}{2}\,O_2 \longrightarrow CO_2 + 2\,H_2O$	$E = 1.183$ V

Problems:

- MeOH is fairly soluble in membrane, crossing from anode to cathode
  - Reduces cell voltage to ~0.5 V
- CO is formed in a side-reaction, blocking reaction sites
  - Improved by adding more Pt catalyst (~3 mg cm^{-2})

Towards alkaline polymers?

- OH⁻ conduction removes the problems associated with H_2O_2 formation
- pH change also modifies redox energies, allowing Ni catalysts to replace Pt
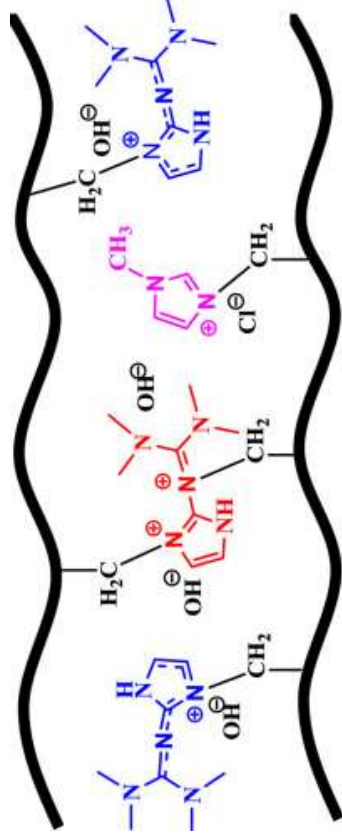
Unfortunately, OH⁻ conducting polymers currently have low ionic conductivity at practical temperatures!

Phosphoric Acid (PAFC)

Operates at 200 °C

- Below 150 °C conductivity is low
- Above 20 °C H_3PO_4 is volatile and decomposes
- High temperature acid prevents build up of H_2O_2
- Temperature makes cell more tolerant to CO_2 impurities
- Hot H_3PO_4 is highly corrosive!
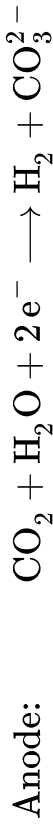 - ○ Materials stability challenge

Woking leisure centre

Molten Carbonate (MCFC)

- Optimum temperature 560 °C
- Range of fuel choices
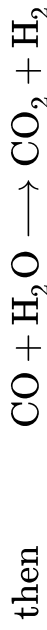 - ○ High temperature allows steam reforming to generate H_2:

$$CH_4 + 2\,H_2O \longrightarrow CO_2 + 4\,H_2$$

or

$$CH_4 + H_2O \longrightarrow CO + 3\,H_2$$

then

$$CO + H_2O \longrightarrow CO_2 + H_2$$

Anode:

$$CO_2 + H_2O + 2\,e^- \longrightarrow H_2 + CO_3^{2-}$$

Cathode:

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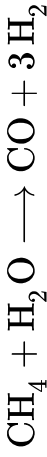
Cathode: $\qquad \dfrac{1}{2}O_2 + CO_2 + 2\,e^- \longrightarrow CO_3^{2-}$

- Cathode - porous NiO
- Anode - porous Ni
- No need for expensive catalyst materials
- Molten alkali-metal carbonates are highly corrosive
  - ○ Conductivity is also limited
- Ni electrodes are sensitive to sulfur contaminants

Solid Oxide (SOFC)

- All solid state system (*i.e.* solid electrolyte)
- Two sub-groups
  - ○ High-temperature (HT) SOFC: 800 - 1000 °C-C
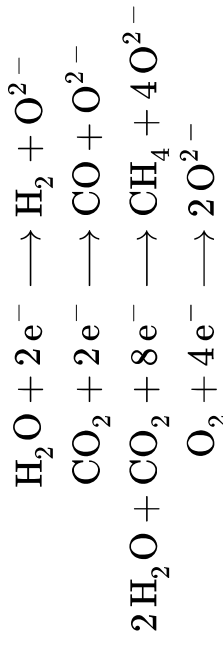 - ○ Intermediate temperature (IT) SOFC: 500 - 700 °C

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- Based around redox and conduction of O^{2-}:

Anode:
$$H_2O + 2\,e^- \longrightarrow H_2 + O^{2-}$$

or with hydrocarbon fuels
$$CO_2 + 2\,e^- \longrightarrow CO + O^{2-}$$

or
$$2\,H_2O + CO_2 + 8\,e^- \longrightarrow CH_4 + 4\,O^{2-}$$

Cathode:
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- The high temperature operation means that internal steam reforming occurs readily

  - a wide range of fuels can be used

- No precious metal catalysts are required
- Excess heat from exhaust gas can be used to increase efficiency (can reach ~90%)

  - *e.g.* drive a turbine to generate extra electricity

SOFC Limitations

High temperatures:

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- Cause problems in terms of reactivity between electrolyte and electrodes
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There is a delicate balance between optimum temperature for redox and/or ionic conductivity, and issues with thermal expansion, reactivity and device construction

- Intermediate-temperature (IT) SOFCs are the current optimum.

Requirements for SOFC materials

Anode

- High electronic conductivity
- High catalytic activity for fuel oxidation
- High ionic conductivity
- High stability under HT reducing conditions

Typically a cermet (*i.e.* mixture) of Ni and electrolyte

- Ni has high electronic conductivity and catalytic activity
- High ionic conductivity from electrolyte

Electrolyte

- High ionic conductivity
- Negligible electronic conductivity
- High stability in oxidising *and* reducing environments

e.g.

- $Gd_{0.1}Ce_{0.9}O_{1.95}$ (CGO)
- $Y_{0.15}Zr_{0.85}O_{1.925}$ (YSZ)

Cathode

- High electronic conductivity
- High catalytic activity for O_2 reduction
- High ionic conductivity
- Stable in HT oxidising conditions

- $La_{1-x}Sr_xCoO_{3-y}$ - a good mixed conductor, but with high thermal expansion
- La_2NiO_{4+x} - an interstitial oxide ion conductor

As well as: Chemical stability, Similar thermal expansion, Cost, …
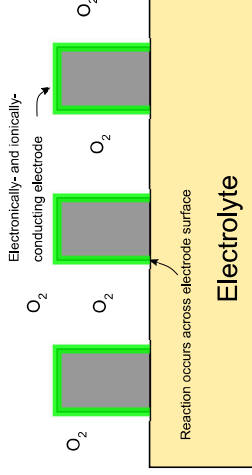
Improving electrodes

For cathode and anode, we ideally want a perfect mixed electronic/ionic conductor, with high chemical stability, high catalytic activity etc...

In reality, we can use a mixture of good (and chemically-stable) ionic and electronic conductors. Reactions will then occur at the **triple phase boundary**
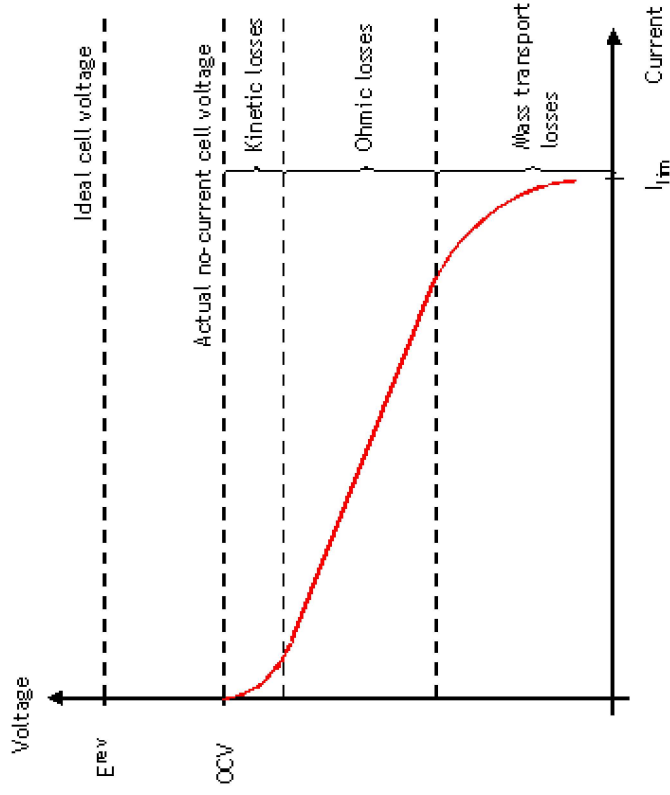
Electronic Conductor
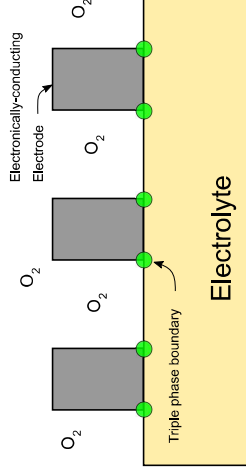
Mixed conductor

Practical efficiency

We can calculate maximum thermodynamic efficiencies, but how do realistic efficiencies compare?

Like batteries, the obtainable voltage (and efficiency) depends on the current rate:

Practical efficiency

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  ○ More pronounced for LT than HT cells

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  ○ Improved by higher temperatures or presence of catalysts
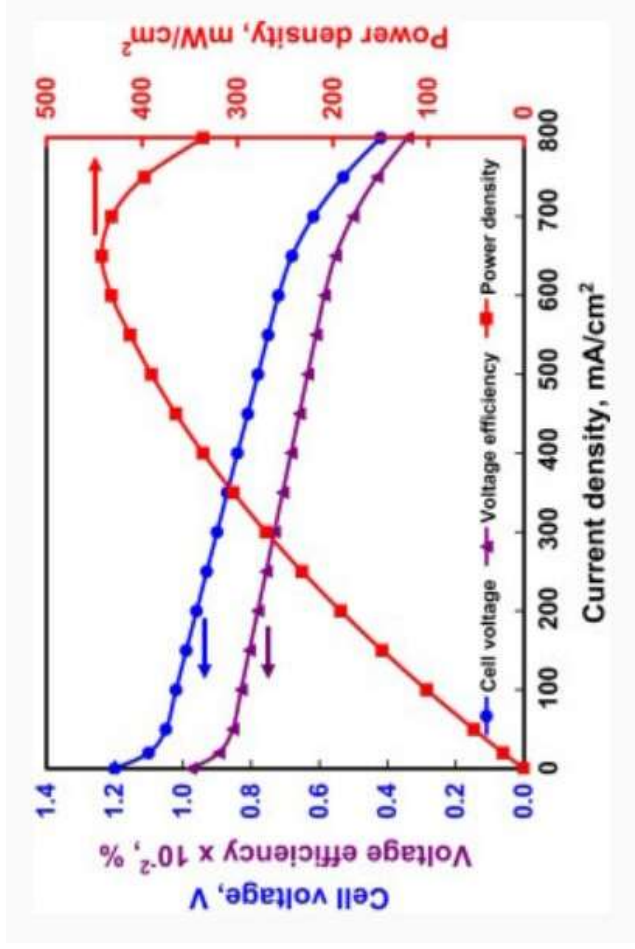
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- At high currents, **Mass transport** causes rapid voltage drop
  - At high rates, the concentration of fuel and/or O_2 at the electrode surface gets depleted
  - Occurs for both HT and LT cells
  - Higher rates can be achieved by better controlling gas flow

Power limits

Because voltage ↓ as current ↑, power (= IV) will show a peak:

Typically, these peak powers are lower than batteries

Figure: Ragone plot of Specific Energy [Whr/kg] versus Specific Power [W/kg] showing: Fuel Cells, Ni-Cd Batteries, Lead Acid Batteries, Li-ion Batteries, Combustion Engine/Gas Turbine, Flywheels, Ultra-Capacitors, and Capacitors. Diagonal time lines: 10 hr, 1 hr, 0.1 hr, 36 sec, 3.6 sec, 360 ms, 36 ms.