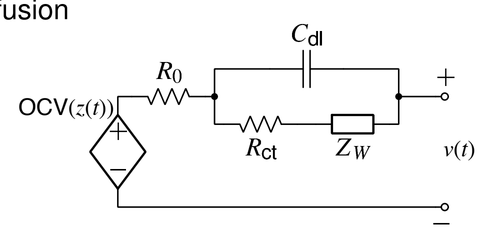
Randles circuit

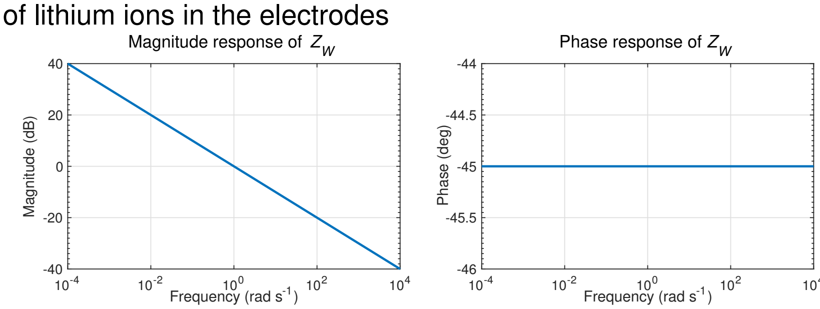
- Last lesson, you learned about the "Thévenin" cell model
  - OCV, R_0, plus R–C sub-circuit(s) to model diffusion
- In the literature, often see ECMs containing a "Warburg impedance" element, Z_W
- e.g., Randles circuit based on electrochemistry



  - R_0 models the electrolyte resistance,
  - R_{ct} is *charge-transfer resistance*, models voltage drop over the electrode–electrolyte interface due to a load,
  - C_{dl} is *double-layer capacitance*, models effect of charges building up in the electrolyte at electrode surface, and
  - Z_W is a Warburg impedance, models slow diffusion processes

Warburg impedance

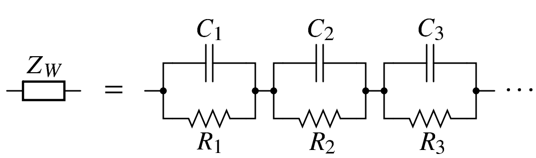
- Frequency-dependent Warburg impedance $Z_W = A_W/\sqrt{j\omega}$ models diffusion of lithium ions in the electrodes
- Magnitude decays at 10 dB per decade; phase is a constant $-45°$
- A "constant-phase" element



- No simple differential equation represents a Warburg impedance, which makes precise circuit simulation intractable

Approximating a Warburg impedance

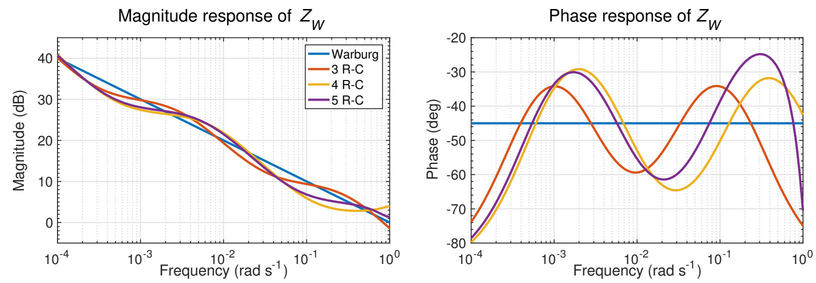
- But, it's possible to reproduce effect of a Warburg impedance using multiple resistor–capacitor networks in series



- For an exact equivalence, an infinite number of resistor–capacitor networks are needed; but, the circuit can often be modeled very well over some frequency range using a small number of R–C pairs

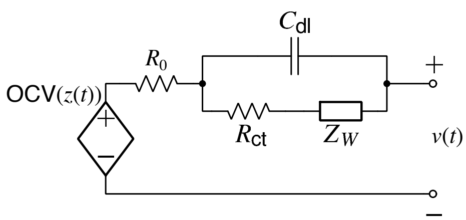
Approximating with R–C pairs

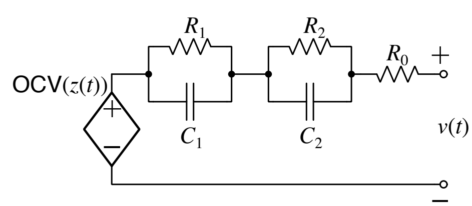
- R–C pairs can provide magnitude response segments with slope -20 dB decade and 0 db decade
- They can have phase response transitioning from $-90°$ to $0°$ and back
- By choosing different values for R_k and C_k, can approximate Warburg frequency response



Resulting model

- Double-layer capacitance often omitted: has little impact on Randles circuit performance except at very high frequencies





- With C_{dl} removed from the circuit, R_0 and R_{ct} combined, and Warburg impedance replaced by a small finite number of R–C circuits, model collapses to “Thévenin” model, with additional R–C pairs

Summary

- Randles circuit is an electrochemically inspired model
- Includes Warburg impedance, which cannot be modeled perfectly with a finite-order differential equation
- But, can be approximated well for frequencies of interest using a relatively small number of R–C pairs
- So, electrochemically inspired model reduces to Thévenin model, which gives us confidence that the Thévenin model is a reasonable description of cell dynamics