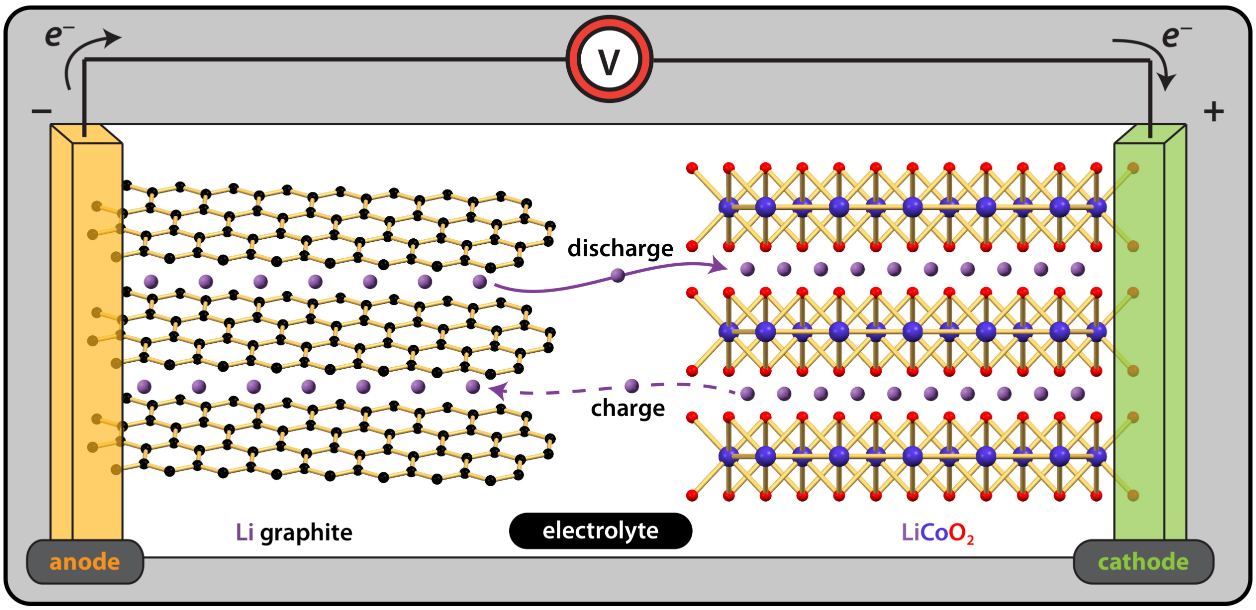
Redox Chemistry and Modern Battery Technology

1. Rechargeable lithium ion batteries have revolutionized many modern electronic devices. Shown below is a schematic of a typical Li-ion battery.



The specific energy density of Li-ion batteries can reach a maximum of about 250 Wh/kg. The net redox reaction responsible for energy storage in a standard battery can be simplified as follows:

$$LiC_6 + CoO_2 \rightarrow LiCoO_2 + C_6$$

a. How many electrons are involved in this redox reaction? Is the reaction above balanced as written? Assign the cobalt oxidation states.

b. Write the individual half-reactions for this redox reaction. Assign each half-reaction to the cathode or anode process.

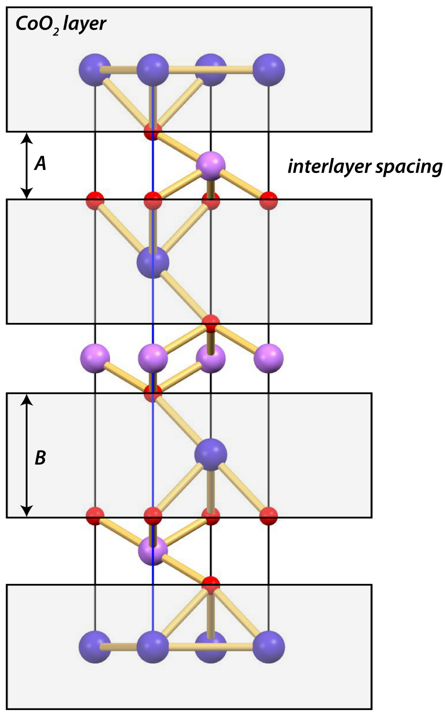
c. Aqueous reduction potentials under neutral conditions are given below for the redox couples in the Li-ion battery. Using these values, approximate $\mathcal{E}_{cell}$ for the battery.

Anode:	$Li^+ (aq) + e^- \rightarrow Li (s)$	$\mathcal{E}_{red} \approx -3.0$ V
Cathode:	$CoO_2 (s) + H^+ + e^- \rightarrow CoO(OH) (aq)$	$\mathcal{E}_{red} \approx +1.1$ V

d. Using your answer from part (b), estimate the specific energy density from the cell potential. Explain any discrepancies to the value of 250 Wh/kg quoted above. Comment on possible ways to improve specific energy density.

e. Which reaction, anode or cathode, is the more important factor in overall specific energy density for the Li-ion battery? Why is lithium so sought after as an anode material? What materials might outperform lithium, if any?

f. The cathode material, CoO_2, is an example of a layered metal oxide. The structure of the oxide is critical, as it allows for the reversible association and dissociation of Li cations. The unit cell of $LiCoO_2$ is shown below along with the metric parameters for a series of non-stoichiometric oxides (Li_xCoO_2). Describe how the metal oxide changes in response to varying amounts of Li.



x	*A*	*B*	*unit cell volume*
1.00	*1.690 Å*	*2.993 Å*	*96.34 Å³*
0.68	*2.733 Å*	*2.008 Å*	*97.31 Å³*
0.48	*2.823 Å*	*1.974 Å*	*98.33 Å³*
0.35	*2.858 Å*	*1.954 Å*	*98.51 Å³*

2. An alternative to the Li-ion battery in question 1 is the lithium-air battery. The key redox reaction that takes place in the Li-air battery is as follows:

$$2\ Li + O_2 \rightarrow Li_2O_2$$

a. How many electrons are involved in this redox reaction?

b. Given the following aqueous reduction potentials at pH 7 approximate $\mathcal{E}_{cell}$ for the Li-air battery.

Anode:	$Li^+(aq) + e^- \rightarrow Li(s)$	$\mathcal{E}_{red} \approx -3.0$ V
Cathode:	$O_2(g) + 2\ H^+ + 2\ e^- \rightarrow H_2O_2(aq)$	$\mathcal{E}_{red} \approx +0.3$ V

c. Estimate the specific energy density of the Li-air battery using the calculated cell potential. How does this compare with that calculated above for the Li-ion battery? What problems might you envision with the cathode reaction.