



Synthesis and characterization of lithium nickel-cobalt oxides for water oxidation catalysis

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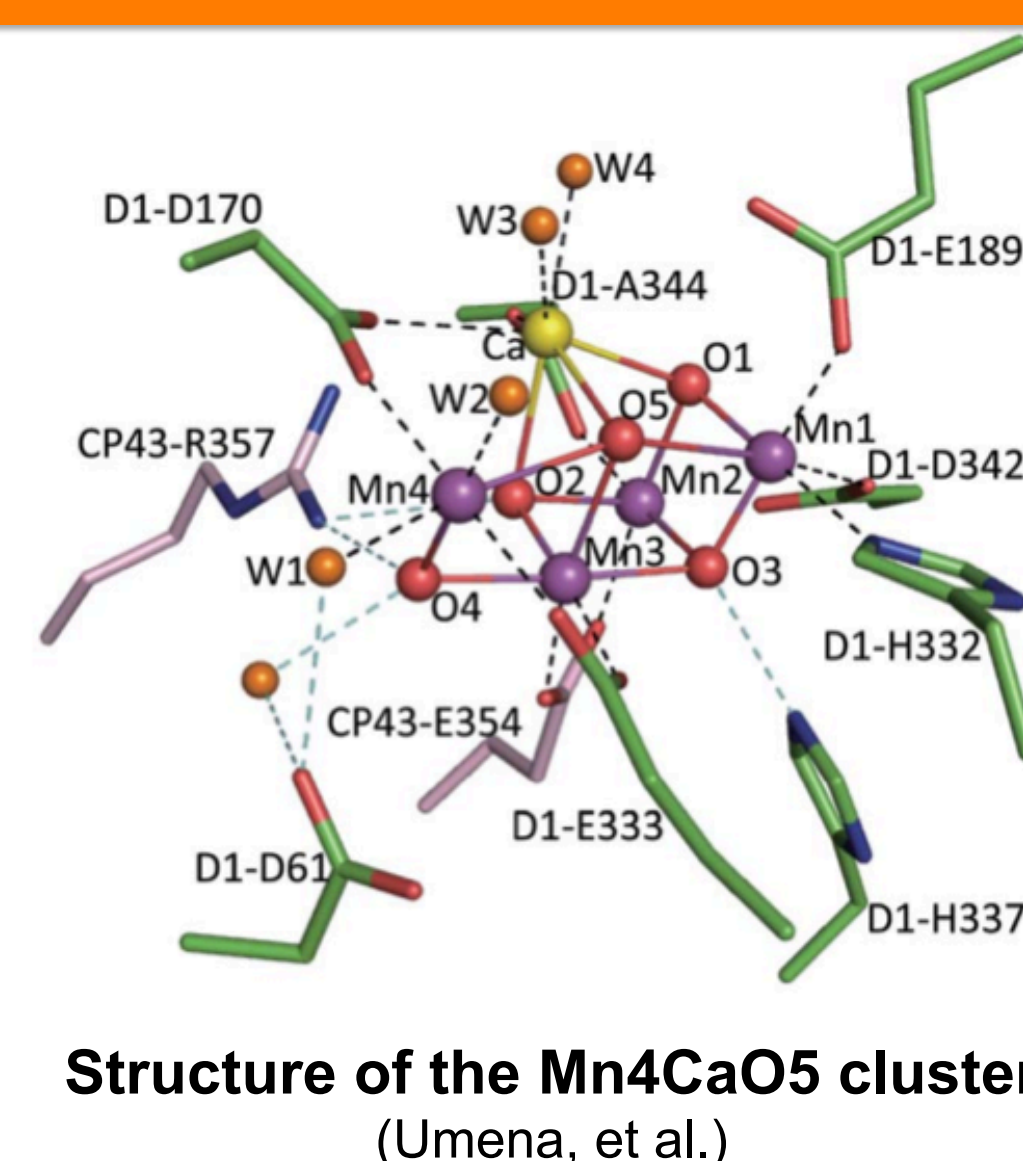
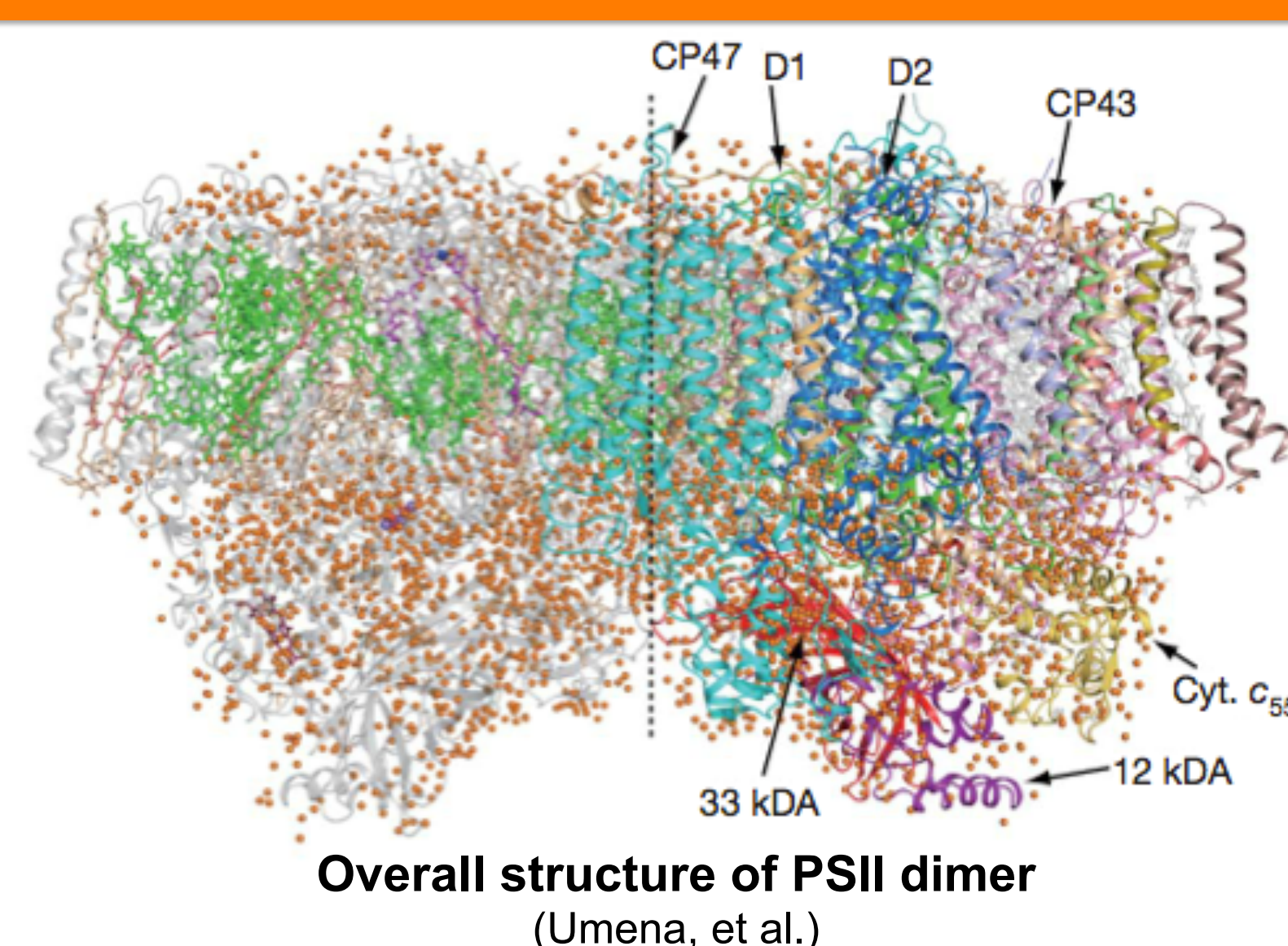
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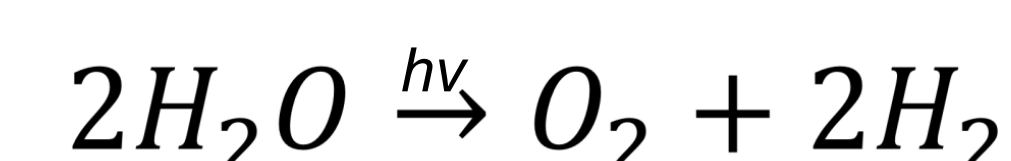
Abstract

Lithium cobalt oxide (LiCoO₂) has been shown to be an effective water oxidation catalyst when it is in the cubic phase/spinel-like (Fd3-m). Its molecular structure serves-as as an inorganic analogue of the manganese-calcium oxide (Mn₄CaO₅) cluster present in Photosystem II (PSII), which is responsible for catalyzing light-induced water oxidation present in oxygenic photosynthetic organisms. These materials can be incorporated into devices for producing hydrogen, lithium-based batteries, and treatment of contaminated water. We aim to possibly improve the catalytic activity by doping the cubic phase with nickel, because if nickel is in the proper oxidation state (Ni³⁺ or Ni⁴⁺) with octahedral coordination, the anti-bonding orbitals are populated and will cause distortion in the metal-oxygen bonds possibly weakening some of them enough to enhance water oxidation activity. We are therefore attempting to dope the cubic lithium cobalt oxide with different levels of nickel, such that it replaces cobalt atoms; and test them in our standard photochemically driven water oxidation assay - the ruthenium sensitized Clark electrode method. We synthesized a series of modified-spinel LiNi_xCo_{1-x}O₂ (x = 0.1, 0.3, 0.5) using different synthetic routes. Stoichiometry, calcination temperature and time have an effect on the purity of the final phase. Increasing temperature lowers the concentration of Co₃O₄ and increases the presence of the layered form. Turnover frequency (TOF) values imply that doping cubic phase LiCoO₂ with nickel decreases the catalyst's activity.

Introduction

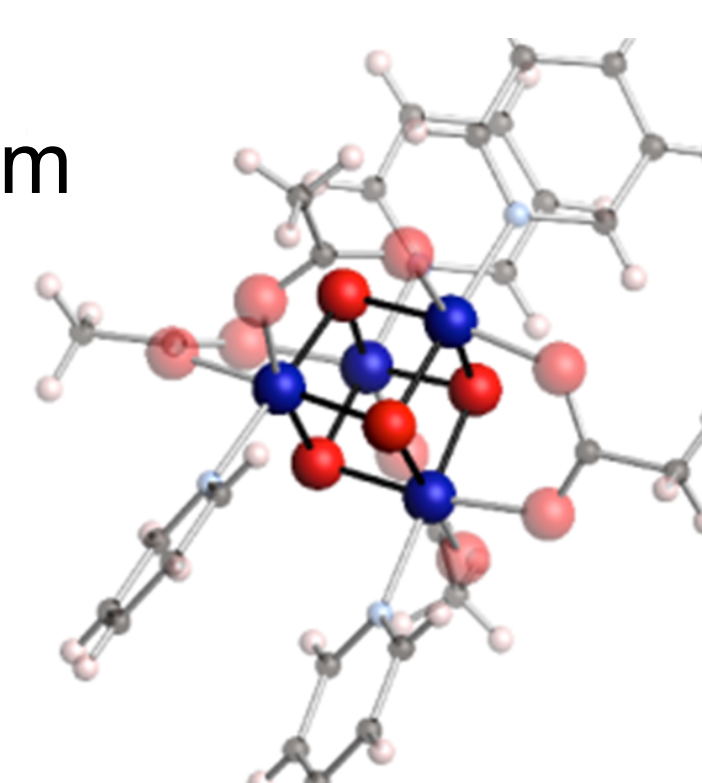


Photosystem II is a membrane protein complex present in oxygenic photosynthetic organisms, where natural photosynthetic water oxidation occurs. Mn₄CaO₅ cluster is the one responsible for oxidizing water to molecular O₂.

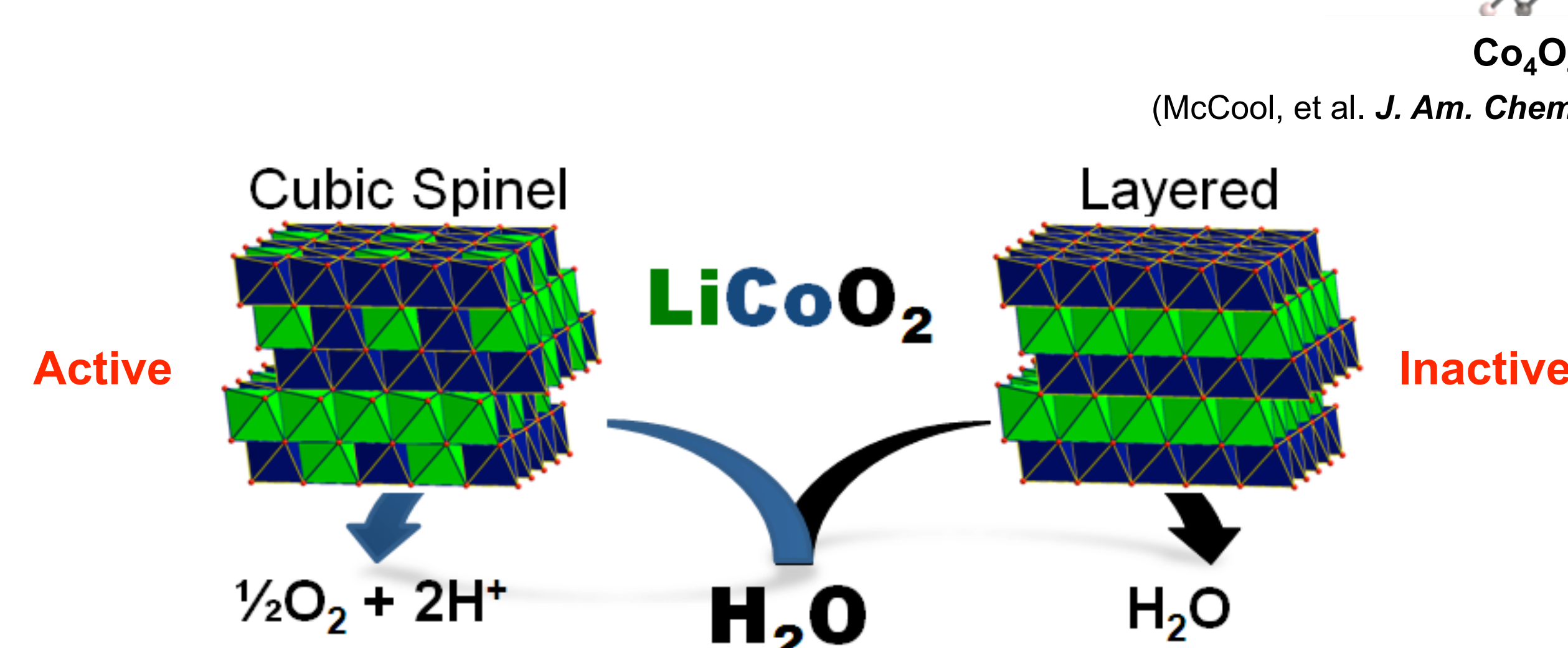


So far, the most active catalysts are made of Platinum and Iridium. But, the main problem is that these materials are very expensive. Alternate materials include first-row transition earth abundant metals like nickel and cobalt.

- Most expensive one is 10,000 times cheaper than Platinum
- Synthetically accessible
- Straight-forward characterization



Cubic-phase LiCoO₂ is a very active earth-abundant metal catalyst for the water oxidation reaction.



We aim to possibly improve the catalytic activity by doping the cubic-phase with nickel.

Hypothesis

Since nickel and cobalt are almost the same size, nickel will replace cobalt such that it goes into the octahedral 'B' sites. And if nickel is in the proper oxidation state (Ni³⁺ or Ni⁴⁺) with octahedral coordination, the populated anti-bonding orbitals will cause distortion in the metal-oxygen bonds, possibly weakening some of them just enough to enhance water oxidation activity.

Applications

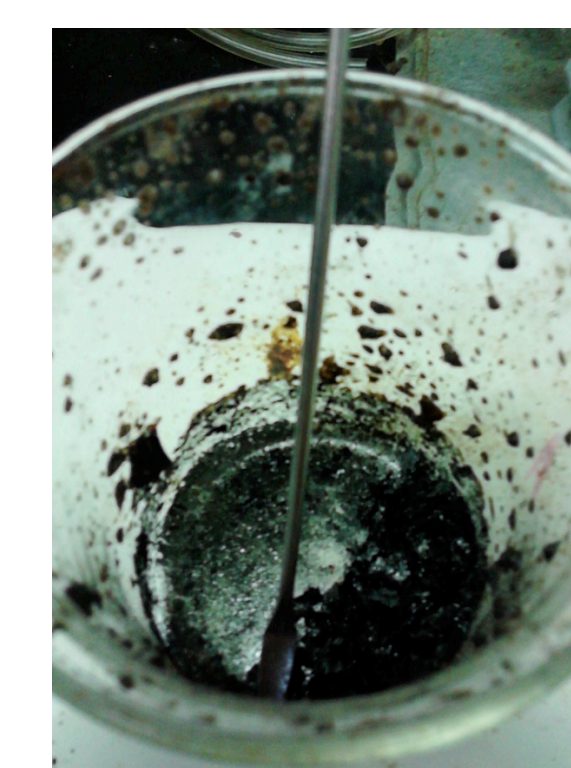
- Can be incorporated into electrolyzers for producing renewable hydrogen and lithium-based batteries.
- Can be introduced in contaminated water, air and soils treatment.
- Hydrogen generated from renewable energy is a non-CO₂ emitting energy source. (Current concentration of CO₂ is ~390 ppm)

Methods

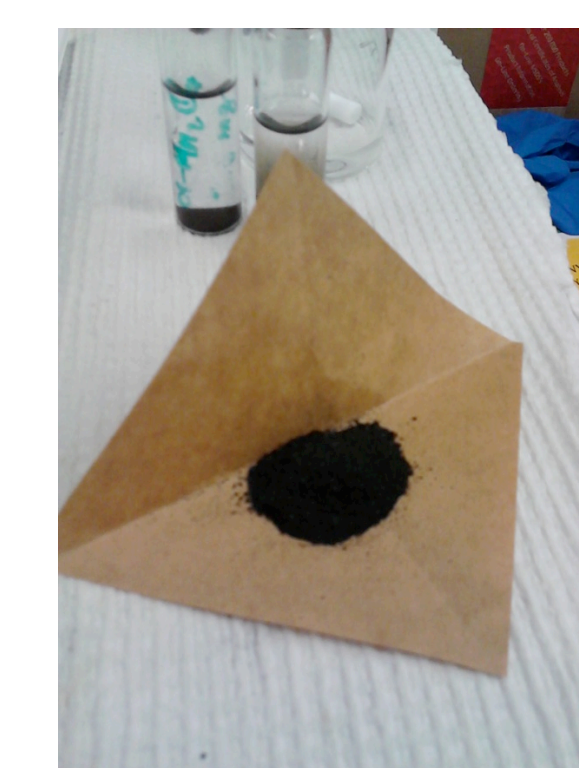
Synthesize a series of modified-spinel LiNi_xCo_{1-x}O₂ (x = 0.1, 0.3, or 0.5) using a sol-gel method at different calcination temperatures.



Evaporate solvent



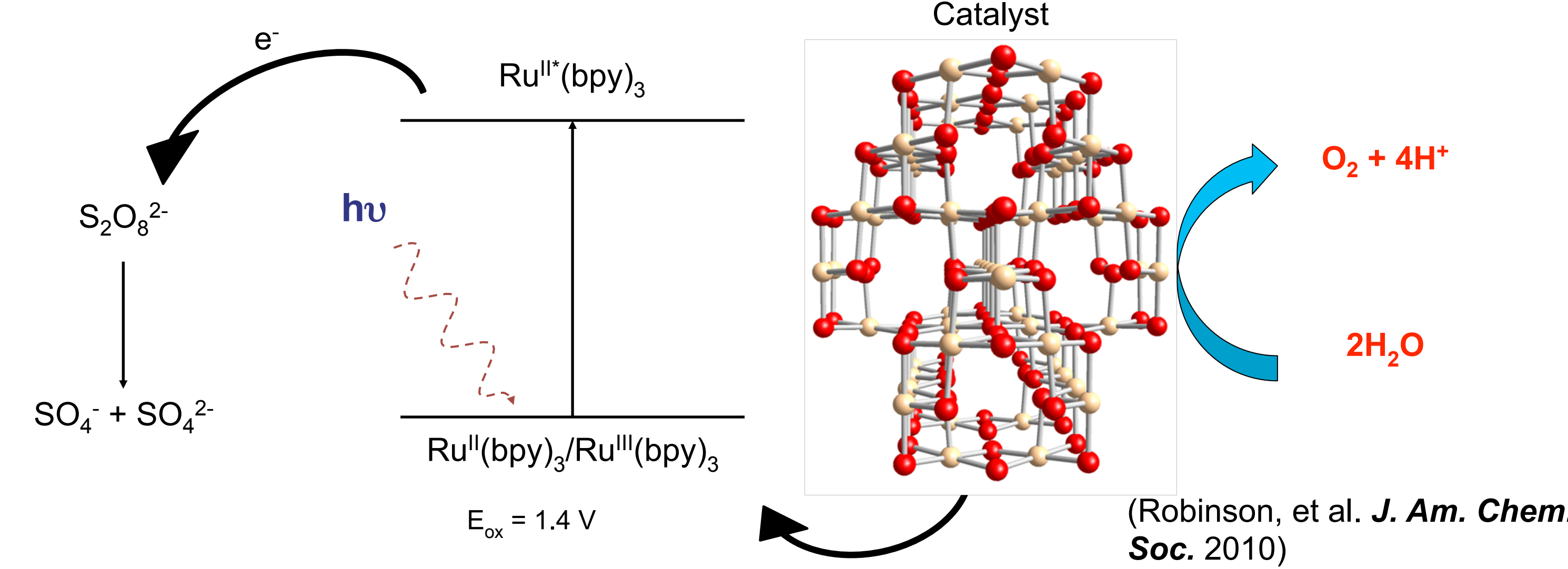
Heat overnight at 180°C



Calcination at 400°C/500°C for 6h/8h

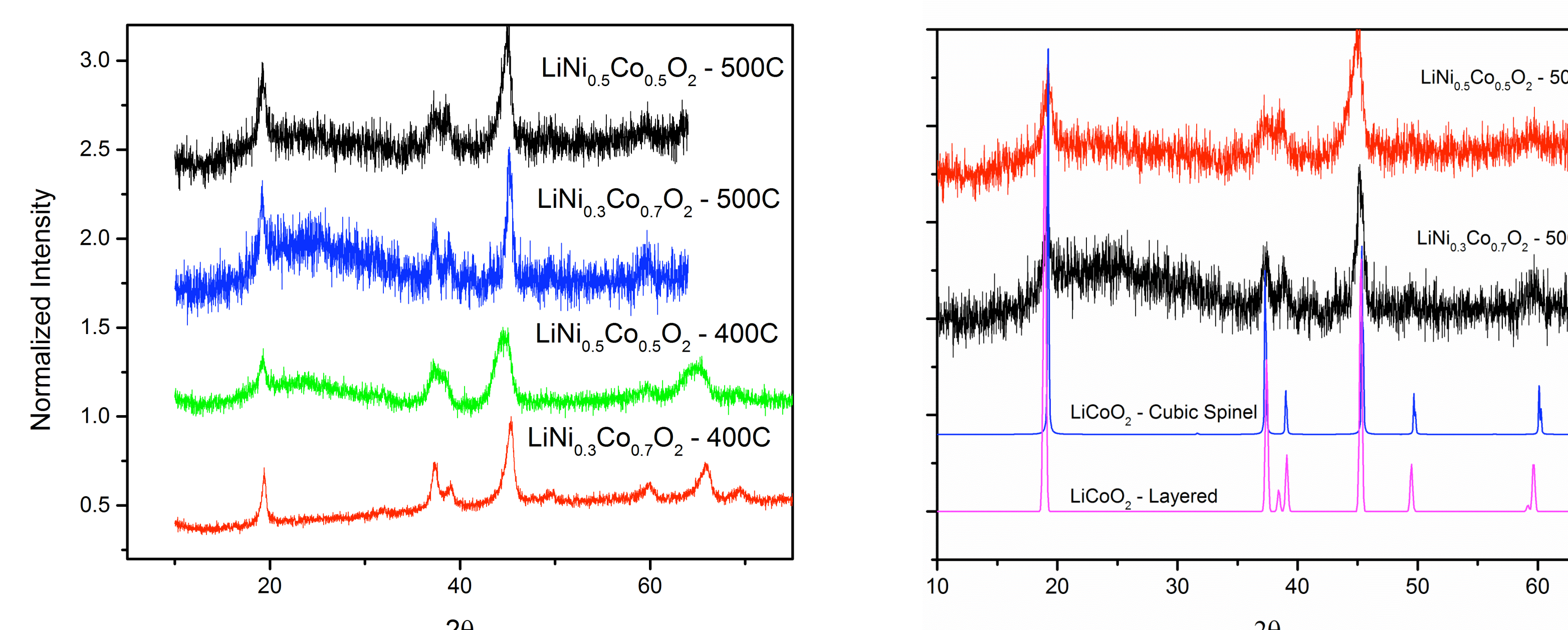
Later, we use PXRD to identify structure and a Clark electrode to measure the O₂ evolution rate.

Photochemical water oxidation assay



Results

Powder X-Ray Diffraction (PXRD) Data



Results

O₂ evolution rate measurements

Catalyst	TOF (s ⁻¹)
LT-LiCoO ₂ (control)	8.5E-04
LiNi _{0.3} Co _{0.7} O ₂	6.4E-04
LiNi _{0.5} Co _{0.5} O ₂	5.0E-04

PXRD patterns show that Co₃O₄ impurity is present in all samples. This impurity was lowered by increasing the calcination temperature, but the presence of layered material increased. This occurs because the layered phase starts forming at temperatures > 400 °C.

Sample peaks line up with the cubic-phase LiCoO₂ standard, which suggests that nickel atoms are replacing the cobalt atoms in the octahedral 'B' sites keeping the cubic (active) form.

Broad peaks between 20 and 30 (2θ) implies the presence of amorphous material.

O₂ evolution rates suggest that the turnover frequencies (TOF) are dependent from the Ni and Co concentrations, since TOF values decrease as the cobalt concentration also decreases.

Conclusions

- The hypothesis was rejected since doping cubic phase LiCoO₂ with nickel decreases the catalyst's activity.
- LiCoO₂ is the most active catalyst.
- Nickel replaces the cobalt atoms at the octahedral sites
- Purer LiNi_{0.3}Co_{0.7}O₂ and LiNi_{0.5}Co_{0.5}O₂ were obtained by increasing the calcination temperature and time.
- Increasing temperature lowers the concentration of Co₃O₄ and increases the presence of the layered form.

Future Work

- PXRD refinements
- Measurements of O₂ evolution rates of LiNi_{0.1}Co_{0.9}O₂
- Further electrochemical characterization, and SEM and TEM microscopy characterization to visualize its morphology

Acknowledgements



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References

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