

Introduction/Aims

There is a high demand for sustainable, renewable energy generation and storage. One pathway, which is thought to be ideal for the storage of solar energy, is hydrogen production from the water splitting process. This experiment is aimed to provide an alternative catalyst for the energy storage of hydrogen from this process. Platinum is currently the most efficient catalyst but more abundant materials are preferred. Cobalt salen complexes are common catalysts for organic synthesis and are easy to prepare and modify, however they have been overlooked for water splitting. This project was synthesising various cobalt salen complexes and testing them using cyclic voltammetry in hope that they successfully oxidise and reduce the water.

Methods

Synthesis: 7 cobalt salen complexes were synthesised using similar techniques to one another. Each ligand was prepared firstly and then added to the Cobalt where it could then be oxidised if needed. Each structure varying slightly by either their side chains or the charge on the cobalt. Their structures were confirmed using analytical techniques such as NMR and IR.

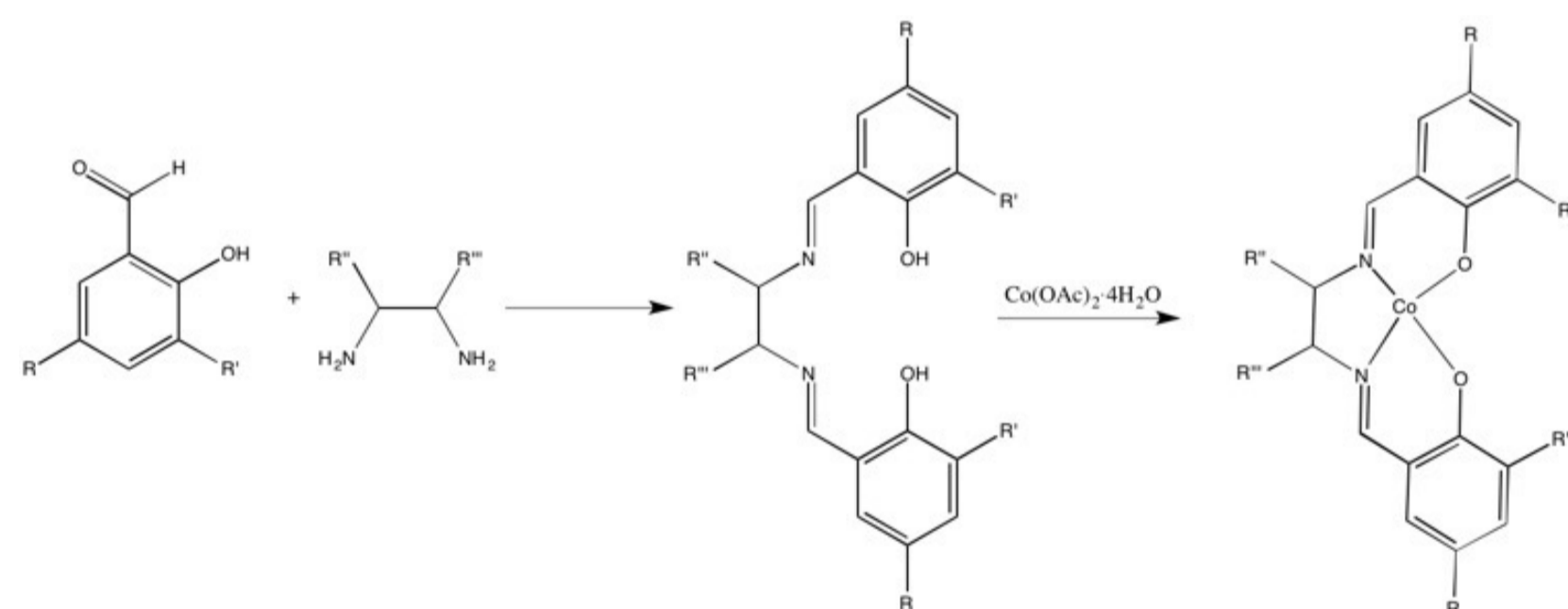


Figure 1: General reaction scheme for preparation of Cobalt salen complexes

Testing: Cyclic voltammetry

Each complex's ability to be oxidised and reduced was tested individually using cyclic voltammetry. The set up was a glassy carbon working electrode (area of 0.28cm²), Ag/AgCl reference electrode, platinum wire as a counter electrode. The supporting electrode solution was TBAP (0.1M) in DMSO with 3mM Cobalt salen complex. Solution being de-gassed with Nitrogen fully before each reading

Electrochemical water oxidation/reduction

The complexes were then tested electrochemically for their ability to oxidise and reduce water therefore mimicking the water splitting process. The set up was 1cm³ of 1.5mM cobalt salen complex in THF coated on a TEC8 FTO plate. Ag/AgCl was again used as the reference electrode with Platinum wire as the counter electrode, this was all in a phosphate buffer at pH 7. The solution was de-gassed with Argon before each reading.



Figure 2: CV set

Cobalt salen complexes

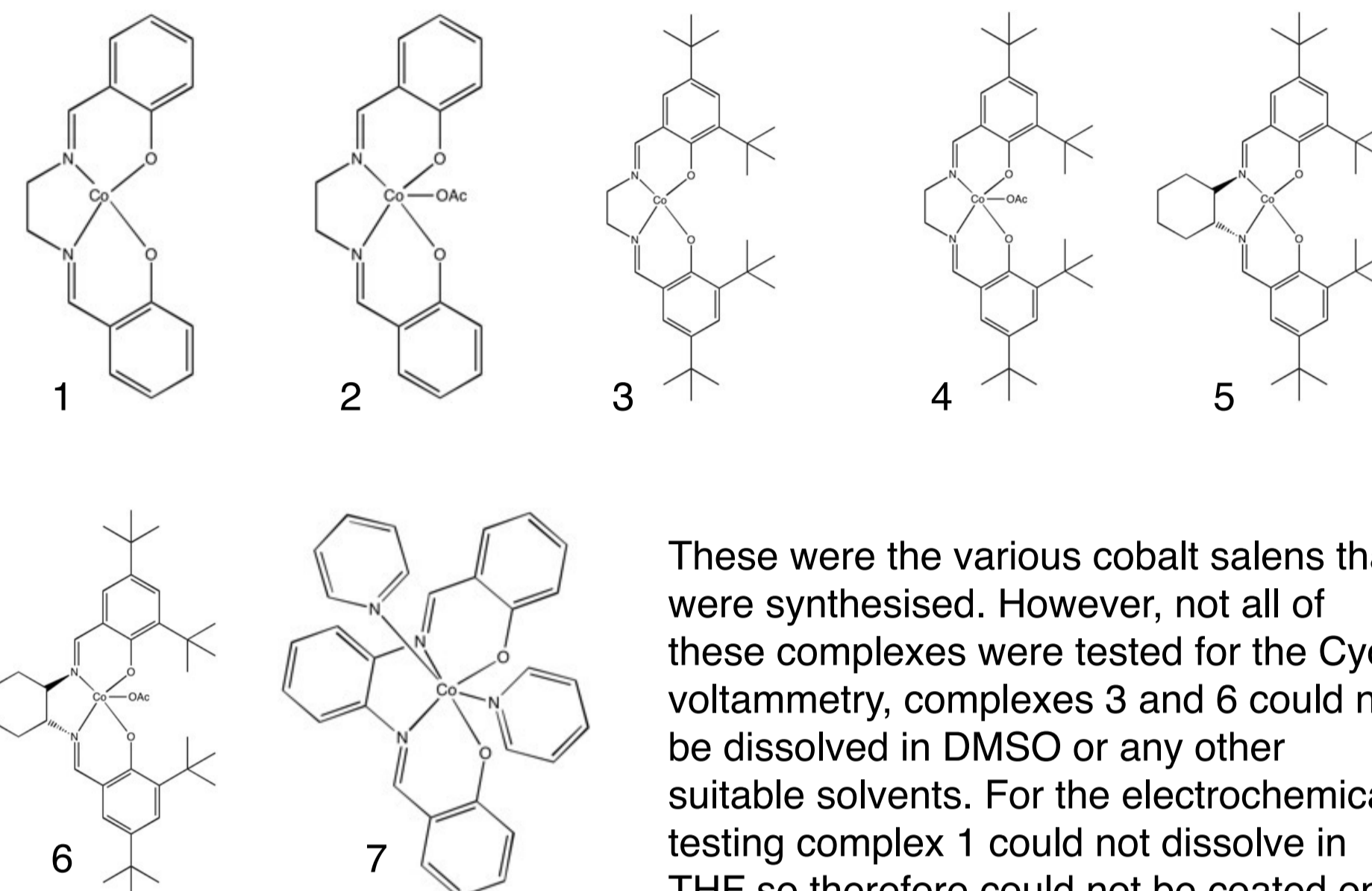


Figure 3: Complexes 1-7

These were the various cobalt salen that were synthesised. However, not all of these complexes were tested for the Cyclic voltammetry, complexes 3 and 6 could not be dissolved in DMSO or any other suitable solvents. For the electrochemical testing complex 1 could not dissolve in THF so therefore could not be coated onto the FTO plate.

Results

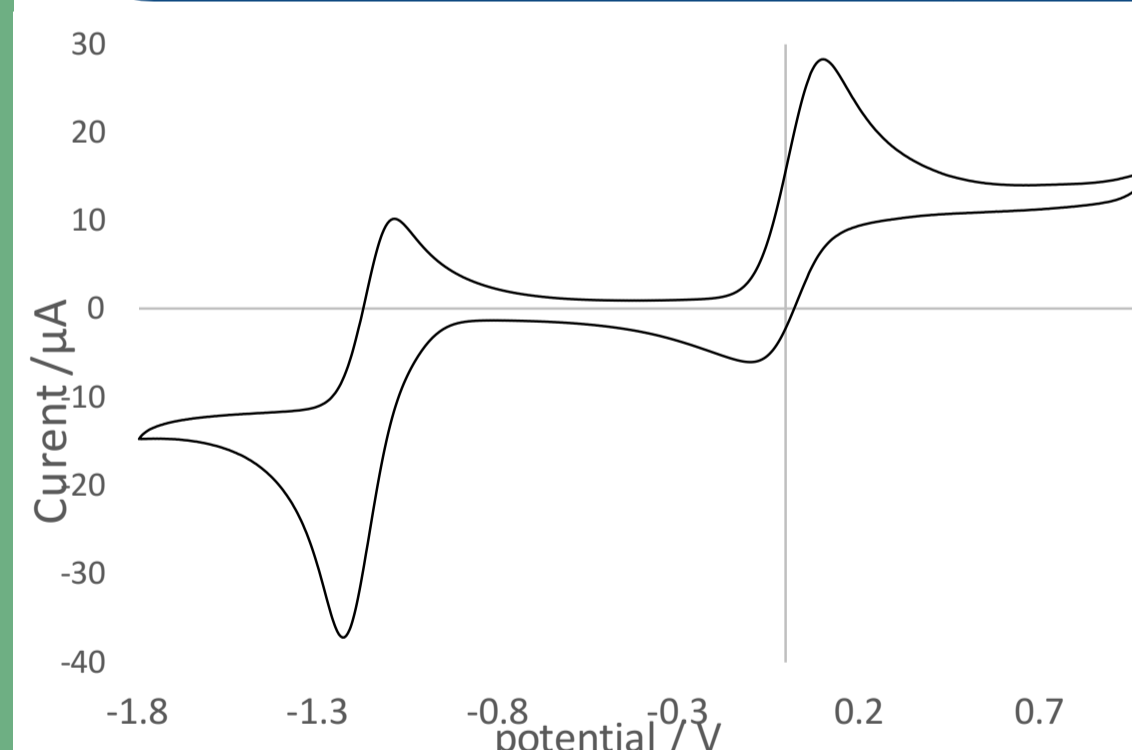


Figure 4: Complex 1 cyclic voltammogram

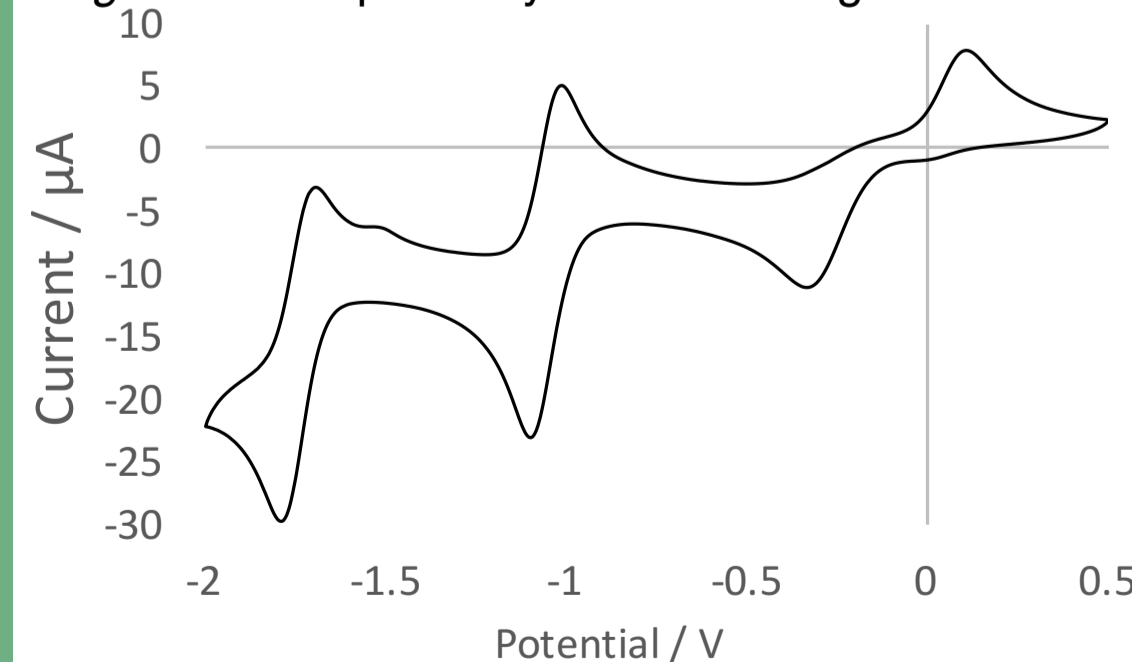


Figure 5: Complex 7 cyclic voltammogram

Each run was taken at a scan rate of 100mV/s. The cyclic voltammograms from the complexes all show that they can successfully be oxidised and reduced. Some of the complexes show more prominent peaks than others which means they can be oxidised and reduced more easily. Figure 4 shows two distinct peaks for the oxidation and reduction between Co(I), Co(II) and Co(III). The smaller reduction peak at -0.1V shows that the Co(III) oxidation state was more stable for this complex so less of it reduced back to Co(II). In figure 5 there are multiple peaks, so this complex was very easy to oxidise and reduce to multiple states, therefore there was not a more stable oxidation state for it.

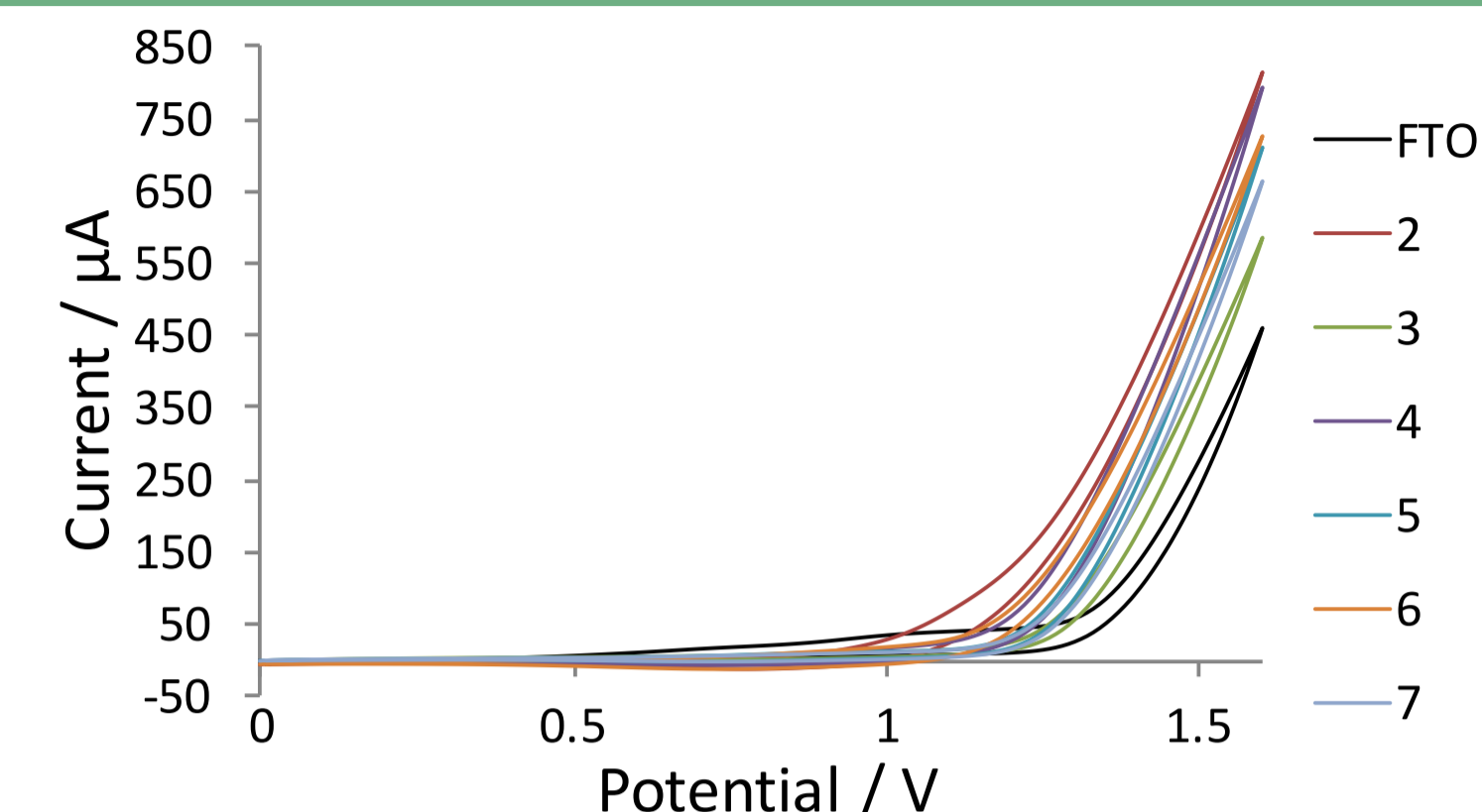


Figure 6: Electrochemical water oxidation in phosphate buffer pH7

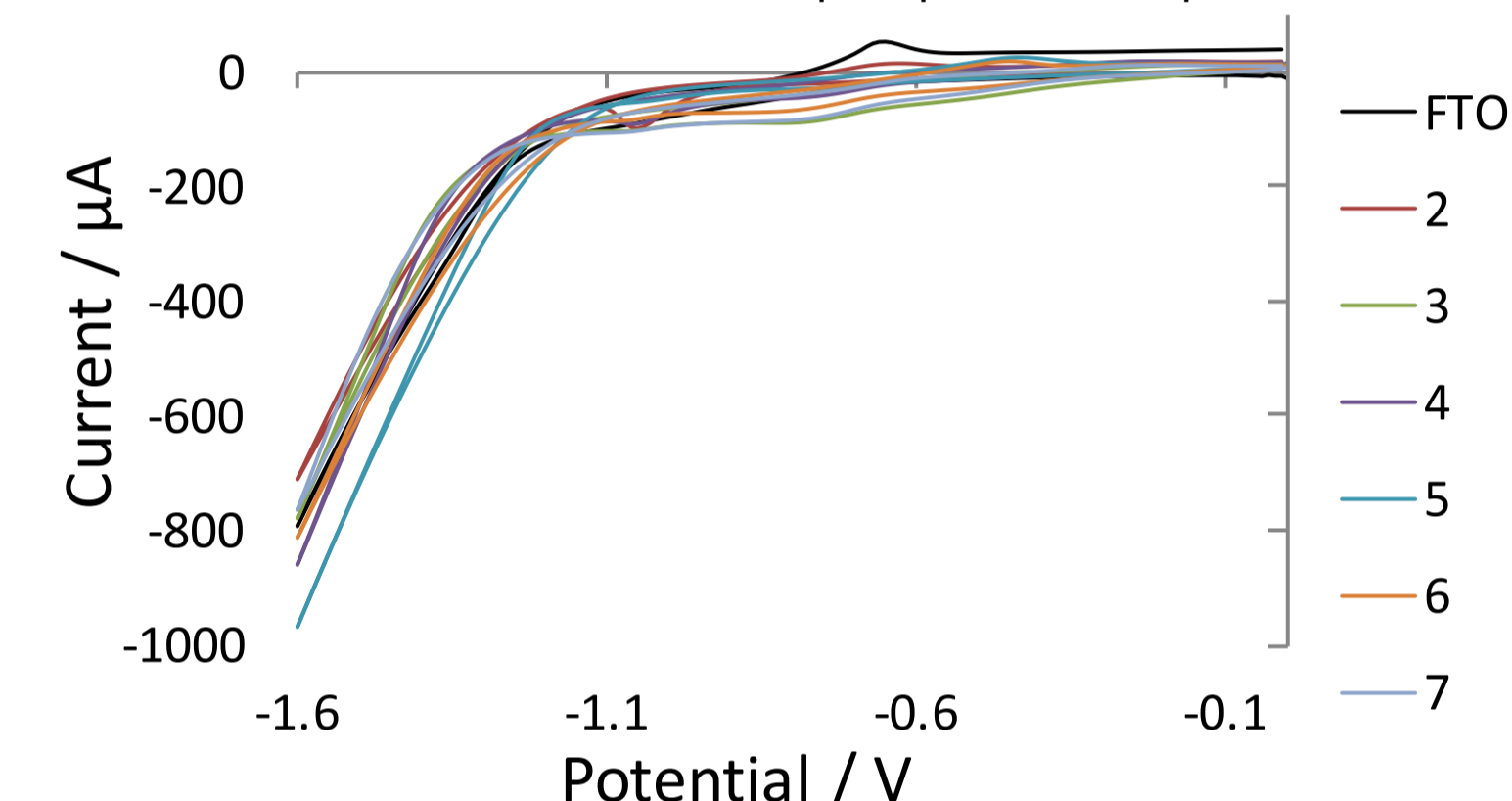


Figure 7: Electrochemical water reduction in phosphate buffer pH7

Figures 6 and 7 show the results from the electrochemical water oxidation and reduction which gave significant readings. Each complex successfully catalysed the water oxidation and reduction as aimed. The graphs show that the Co(III) was much better at oxidising the water however the Co(II) was better at reducing it. The complexes with the bulkier groups act as the best catalysts in this test.

Discussion

Overall the results obtained showed that each cobalt salen tested was better at oxidising the water than the plain FTO plate. Some complexes (1,3 and 7) show not to reduce water as well as the plain FTO plate, this means that these complexes are more stable in lower oxidation states so therefore less likely to oxidise the water. Complex 4 showed the most promising results, its data from the electrochemical testing gave the most even results. This complex oxidised as much as it reduced the water. In water splitting, for the production and storage of hydrogen, it's important that the catalyst can both oxidise and reduce.

The next step on from this would be to test the same complexes photochemically to see if the catalysts still work in the more realistic conditions for light driven water oxidation.

Acknowledgements

- Elizabeth Gibson and her team of PHD students for the opportunity and all the help with the project
- Funding from Newcastle University summer vacation scholarship

- Haiyan Chen, Zijun Sun, Sheng Ye, Dapeng Lu and Pingwu Du, *J. Mater. Chem. A*, 2015, 3, 15729-15737
- Bertha Ortiz and Su-Moon Park, *Bull. Korean Chem. Soc.* 2000, 21, 405
- Md. Ali Asraf, Hussein A. Younus, Chizoba I. Ezugwu, Akshay Mehta and Francis Verpoort, *Catal. Sci. Technol.*, 2016, 6, 427