Titanium(IV) tris-catecholate complex – a low-cost anode material for redox flow batteries

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1. INTRODUCTION

Alkaline redox flow batteries (RFB) have become of significant interest for energy storage due to their low cost, high efficiency, and long cycle life. The all-vanadium redox flow battery (VRFB) in strongly acidic solutions is the most extensively explored and commercialised type of RFBs. However, numerous studies have been conducted to demonstrate the advantages and applications of alkaline RFBs. While potassium ferrocyanide is commonly used as the posolyte, various candidates for the negolyte have been examined in different studies. In this study, the metal-complex titanium(IV) tris-catecholate ($Ti(cat)_3$) was investigated as a promising negolyte for alkaline RFBs.

2. SYNTHESIS

- Titanyl sulfate ($TiOSO_4$) is mixed with catechol in a 1:3 molar ratio
- The complex is synthesized in a strong acid (pH below 2) to avoid insoluble titanium oxides [1]
- The solution must be rapidly neutralised with a strong base (6.5 M NaOH) to avoid precipitation
- The solution is bobbled with nitrogen gas through the whole synthesis to prevent catechol from reacting with oxygen

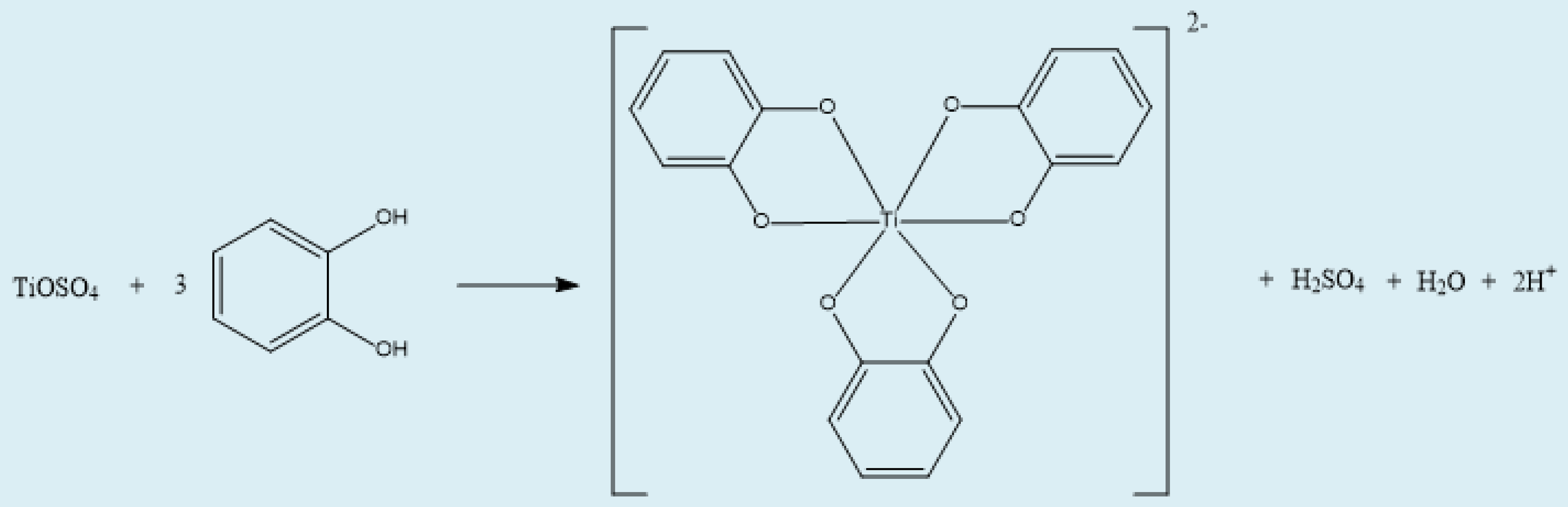

Figure 1: The proposed complexation reaction between catechol and Ti(IV).

3. CHARACTERIZATION

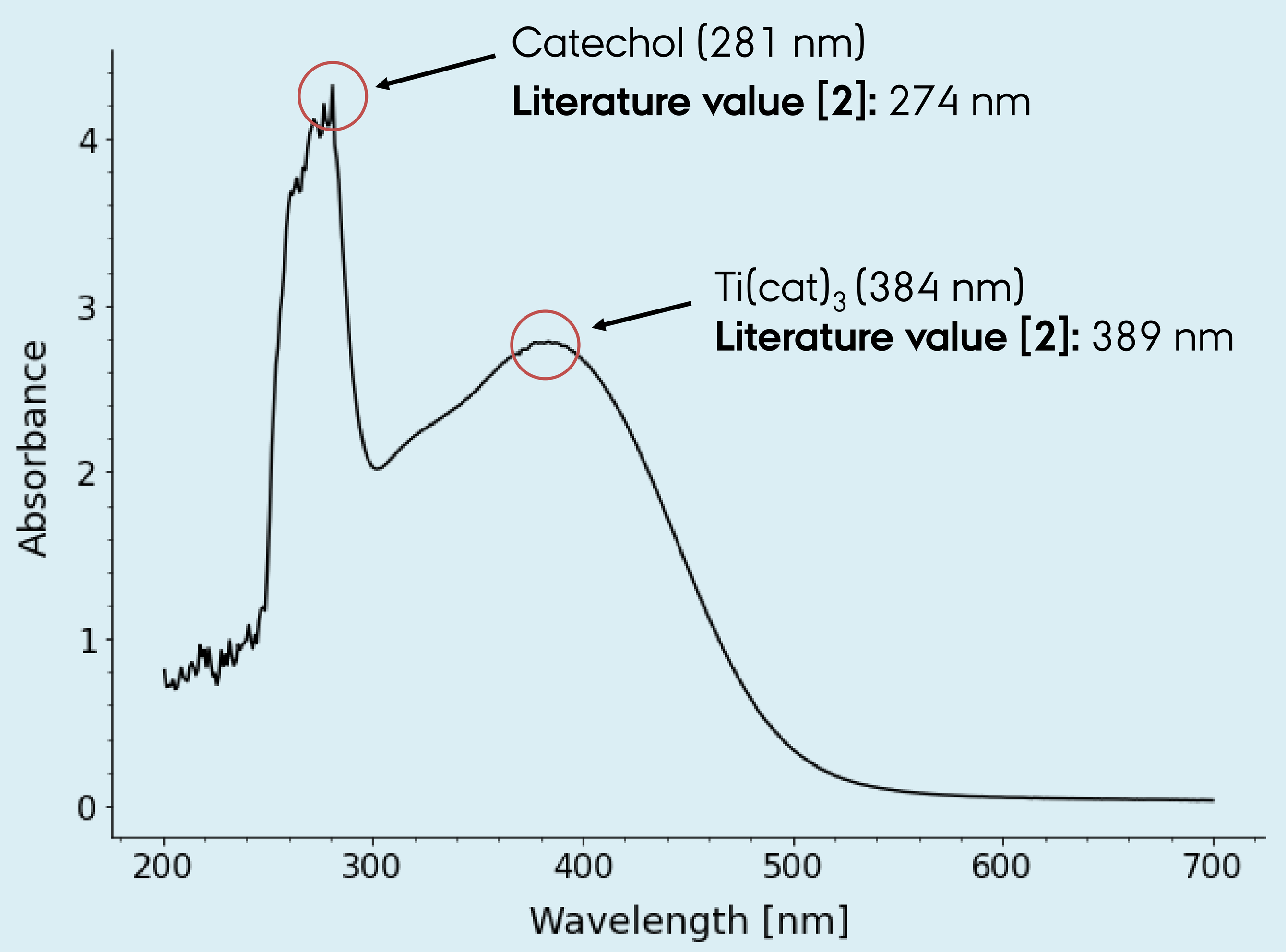

Figure 2: UV-vis spectrum of the $Ti(cat)_3$ complex. The concentration and pH value of the complex were 0.17 mM and 6.76, respectively.

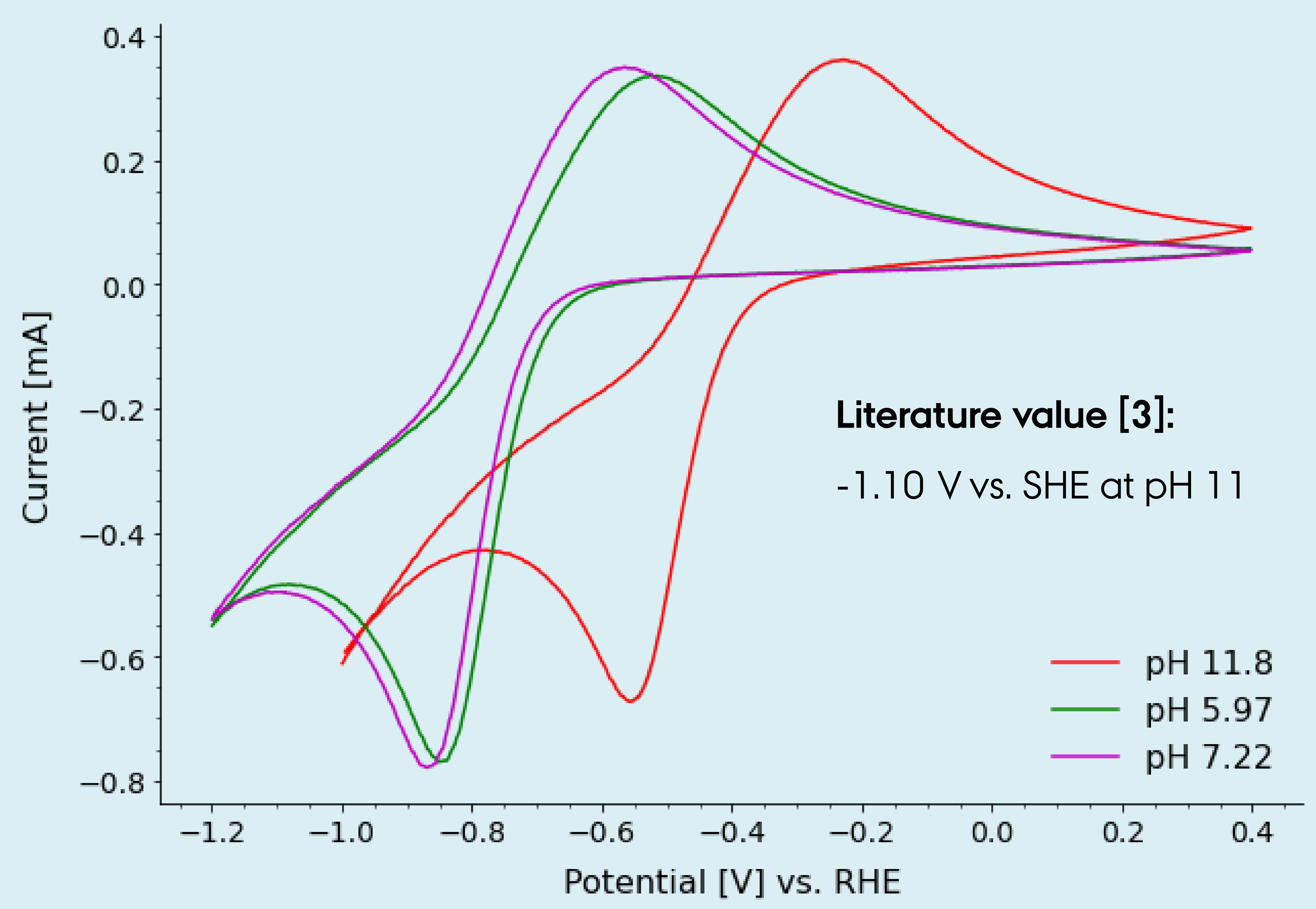

Figure 3: The voltammogram of the $Ti(cat)_3$ complex. The concentration of the complex was 0.08 M and the scan rate used was 100 mV/s.

4. BATTERY PERFORMANCE

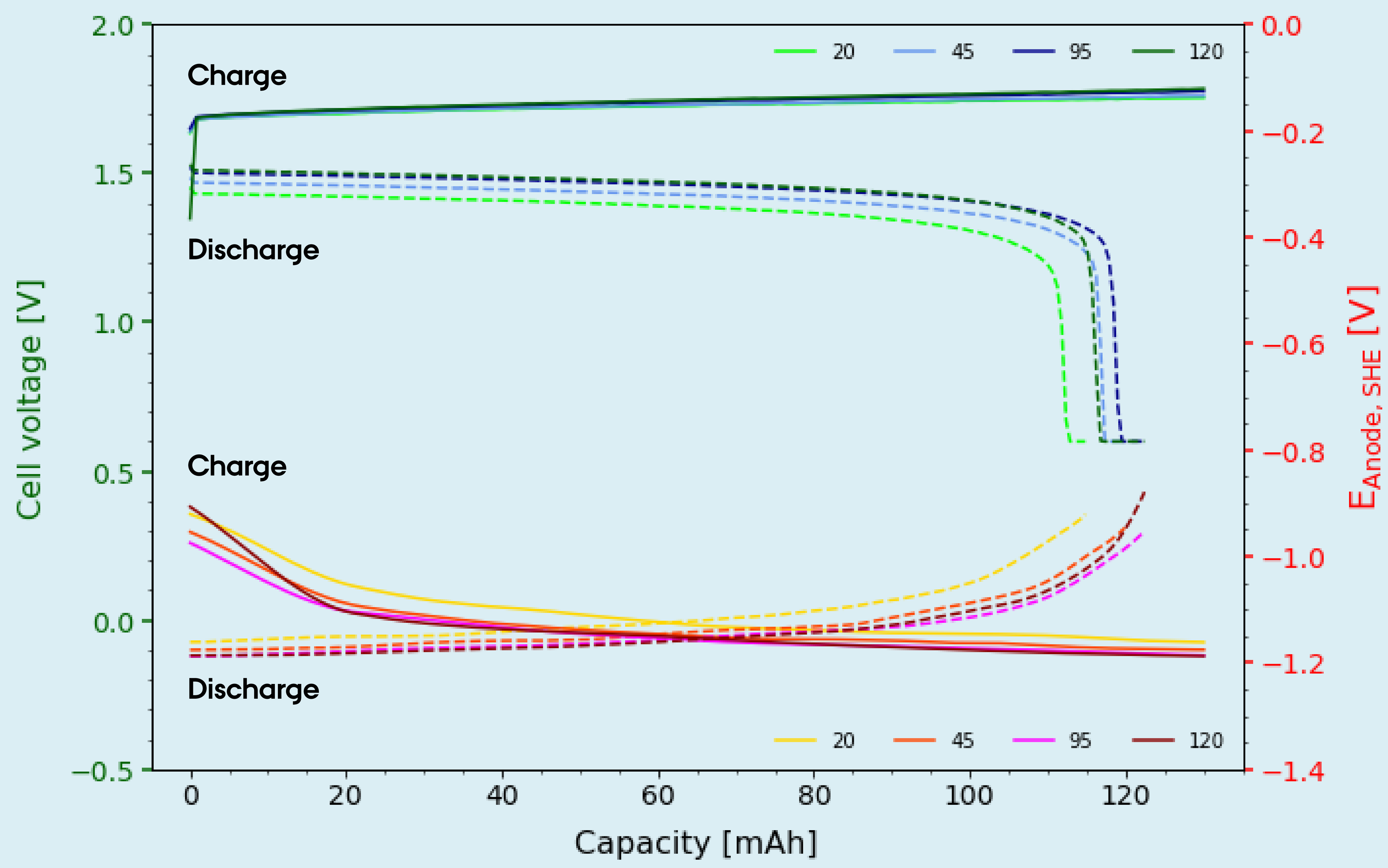

Figure 3: The charge-discharge cycling of the RFB with the $Ti(cat)_3$ complex as the negolyte and ferrocyanide as the posolyte. A Capacity cut-off at 130 mAh was applied from cycle 20 to cycle 120.

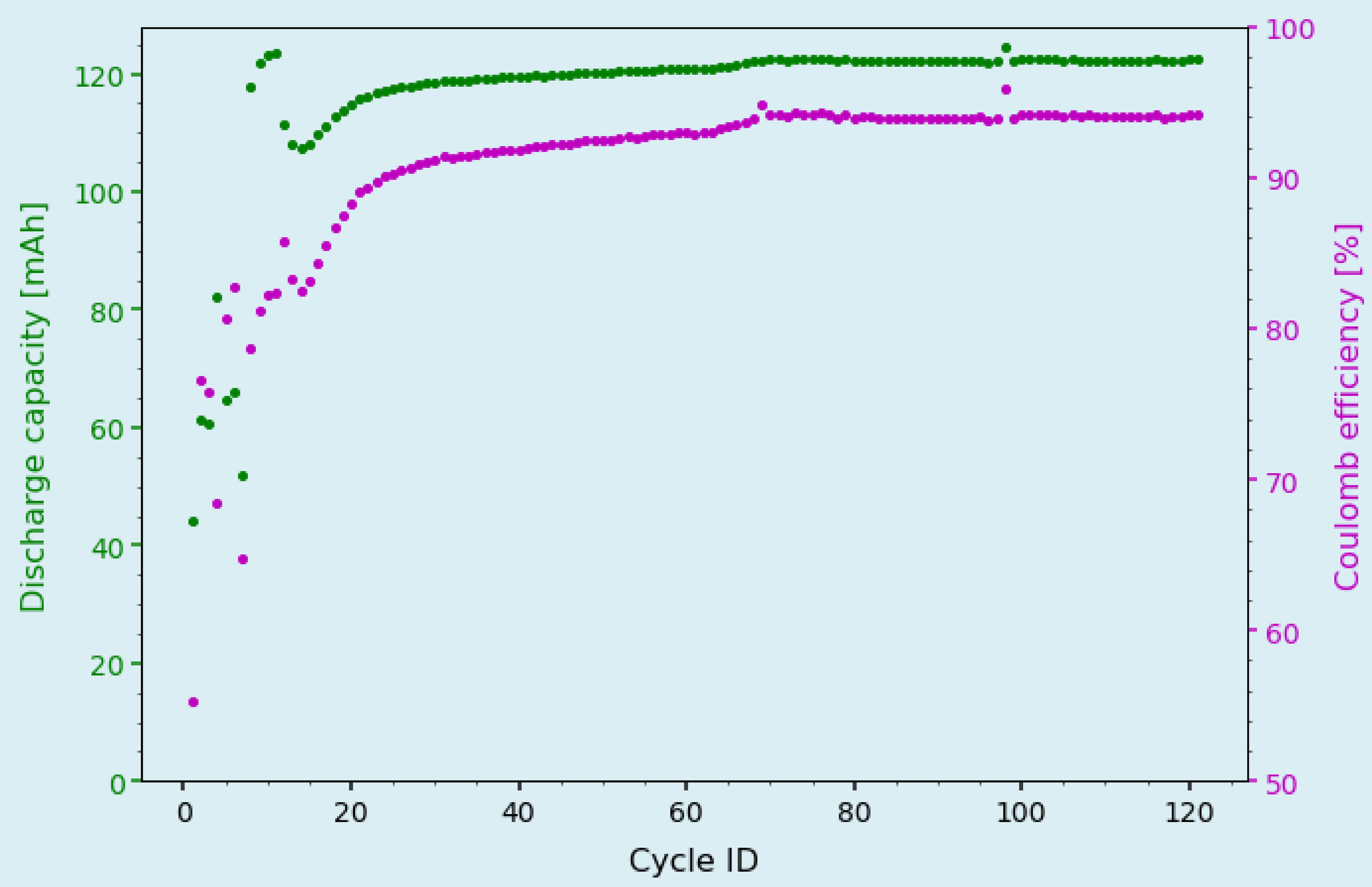

Figure 4: The discharge capacity and the coulombic efficiency of the RFB. The following capacity cut-offs were used: 1) ID 1-3: 80 mAh, 2) ID 4: 120 mAh, 3) ID 5-7: 80 mAh, 4) ID 8-11: 150 mAh, and 5) ID 12-120: 130 mAh.

5. CONCLUSION & OUTLOOK

The complexation reaction between catechol and Ti(IV) was confirmed by using ultraviolet-visible spectroscopy and cyclic voltammetry. The results were compared with the literature and found to be similar. The $Ti(cat)_3$ complex has been confirmed to be extremely air sensitive due to the high reactivity of the catechol ligands. The charge-discharge cycling of the RFB with the $Ti(cat)_3$ complex as the negolyte and ferrocyanide as the posolyte provided a coulombic efficiency of 94%. However, all the battery testing was performed by using a cut-off capacity. Therefore, further studies of the complex include:

- Optimisation of the $Ti(cat)_3$ electrolyte
- Optimisation of the operating conditions of the RFB
- Longer cycling without cut-off capacity
- Degradation study of the $Ti(cat)_3$ complex

REFERENCES

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