



## Searching for new redox-complexes in organic flow batteries

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### ABSTRACT

The study of redox couples based on Fe(III)/(II) and Co(II)/(I) organic complexes has demonstrated chemically reversible redox processes as well as good stability in organic solvents. These active complexes, obtained with polypyridine ligands, present low cost, low toxicity and good chemical stability. Moreover, they demonstrated fast redox kinetics and for that, they are candidate for active species in redox flow cells. A wide library of polypyridine complexes have been prepared and tested as acceptor ligands to reach an open circuit voltage up to 2 V, in a mixture of ethylene carbonate and propylene carbonate (EC/PC) chosen for their low volatility and electrochemical stability. Solubility data are presented after tuning ligand design to optimize metal-complex solubility. The best compounds were  $[\text{Fe}(\text{bpy})_3]\text{Tf}_2$  ( $\text{Tf} = \text{CF}_3\text{SO}_3^-$ ,  $\text{bpy} = 2,2'$ -bipyridine) and  $[\text{Co}(\text{bpy})_3]\text{Tf}_2$  which generated current densities of the order of  $30 \text{ mA/cm}^2$  in thin layer static cells. These complexes were also preliminary tested in a complete flow cell equipped with a Nafion membrane, with LiTf electrolyte, and ca. 90% coulombic efficiency was observed. The decrease of performance observed after 8 h is under investigation and assigned, for now, to membrane degradation. A change of membrane characteristics should be considered to exploit the full potentiality of these redox mediators.

### 1. Introduction

The stationary electrochemical energy storage is an interesting field for renewable energy development. In this aim, liquid flow-batteries look promising for deployment. Among them vanadium redox flow-batteries are presently the most promising prototype with the best performance/cost ratio [1]. However, many efforts have undertaken to improve flow cells energy density and the development of new redox couples is nowadays an active field of research. The redox-flow battery (RFB) architecture offers the advantage to decouple the power rating (reactor size) from the energy capacity (tank size) [2]. Because of their low energy density, RFBs are best suited for stationary storage, on kW - MW scale, with long charge/discharge duration (several hours) [3]. Since 1980s vanadium-based RFB have been explored [4–6] and nowadays it is the benchmark for market penetration [7]. On the other hand, large scale-up of aqueous batteries is contrasted by limited energy density, due to the small potential window (1.23 V) for water stability and by the employment of strongly acidic media (typically sulfuric acid > 1 M) and vanadium in the  $\text{V}^{5+}$  state that is a carcinogenic agent [8]. More recently, first row transition metal complexes have been considered as redox active species in non-aqueous redox flow batteries (NA-RFB) with encouraging results [9–16]. The advantages, in employing transition complexes in NA-RFB, are many: available broader

array of redox-active organic molecules for new redox couples, possibility of easily modify complexes for tailoring electrochemical properties, existence of wider stability windows in NA solvents, possibility to reach higher energy density and multiple electron transfer, Earth-abundant metals available at relatively low cost [17–18]. In the present state metal-complexes in NA-RFBs do not compete with vanadium RFBs in term of long-term performance and additional work should be carried out to individuate viable alternatives. For what concerns cost, a combination of factors must be satisfied, such as: cell voltage towards 3 V, electrolyte cost below 5 \$/kg, molecular weights of complexes below 200 g/mol, as suggested by ref. [19]. In this study we have explored the electrochemical properties of couples based on cobalt (Co (II)/(I)) and iron (Fe(III)/(II)) complexes, in the effort of coupling solubility and reversible electrochemistry to the possibility of extracting large cell voltages. Synthetic simplicity and chemical stability have oriented us towards the preparation of polypyridine chelates derived by pyridine condensation. A wide library of polypyridine complexes have been considered as bidentate or tridentate ligands for Co(II) and Fe(II) (see Fig. 1) [22–23].

Among the multitude of possibilities offered by these species those with bipyridine ligand were selected and substituted by alkyl-groups (see Fig. 2).

Bipyridine based ligands were chosen for synthetic simplicity

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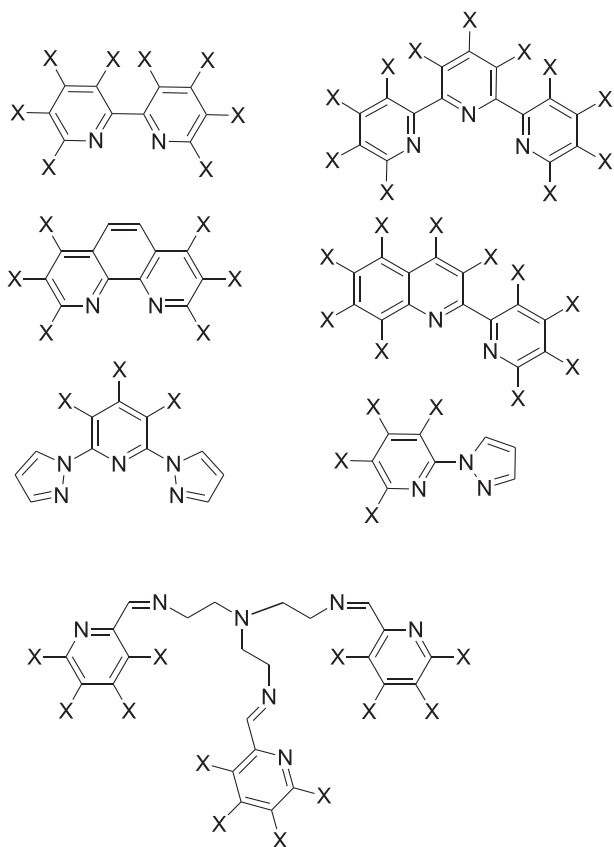


Fig. 1. Some of poly-pyridines considered as ligands.

reasons. Indeed, Co (II) or Fe (II) complexes reported in Fig. 2 can be easily generated by mixing appropriate Co (II) or Fe (II) salts with stoichiometric ratios of bidentate ligands [20–21]. Moreover, the thermodynamics for Fe(III)/(II) and Co(II)/(I) processes is compatible with the delivery of high open circuit voltage.

## 2. Experimental

### 2.1. Materials & methods

All chemicals were Sigma Aldrich products and were used as received: Iron (II) triflate (FeTf,  $\geq 85\%$ ), 2,2'-bipyridine (bpy,  $\geq 99\%$ ), lithium triflate (LiTf, 99.9%), 4,4'-dimethyl-2,2'-bipyridine (dmb,

99%), 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtb, 98%), ammonium Iron(II) sulfate hexahydrate ( $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \times 6(\text{H}_2\text{O})$ , 99.9%), tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>,  $\geq 99\%$ ), bis(trifluoromethane)sulfonamide lithium salt (LiTFSI  $\geq 95\%$ ), 3,4-ethylenedioxythiophene (EDOT, 97%). Except Cobalt(II) triflate which was purchased from AMERICAN ELEMENTS® (CoTf, 99%). The following solvents were Sigma-Aldrich and were used as received: acetonitrile (ACN, for HPLC, gradient grade  $\geq 99.9\%$ ), methanol (MeOH, anhydrous, 99.8%), propylene carbonate (PC, reagent grade, 99%), ethylene carbonate (EC, anhydrous, 99%).

Cyclic Voltammeteries (CVs) were collected in a nitrogen-purged standard three-electrode cell with an Autolab PGSTAT 302/N potentiostat and with a glassy carbon (0.07 cm<sup>2</sup> Area) (Amel) as working electrode, a saturated calomel electrode (SCE) (Amel) as reference and a Pt-wire (Sigma-Aldrich) as auxiliary electrode.

Electrochemical characterization was carried out by Linear Sweep Voltammetry (LSV) at a scan rate of 10 mV/s and by Electronic Impedance Spectroscopy (EIS) with an Autolab PGSTAT 302/N potentiostat, by employing two different kind of electrodes to study Fe (III)/(II) and Co(II)/(I) complexes in symmetric (i.e. two identical electrodes) thin layer cell, having active area of 0.25 cm<sup>2</sup> sealed with a 25  $\mu\text{m}$  inter-electrode spacing (Surlyn®-DuPont). PEDOT (Poly(3,4-ethylenedioxythiophene)) films were electrodeposited [22] on FTO (fluorine-doped tin oxide) (Pilkington) glass to study Fe(III)/Fe(II) couple while carbon nanohorn (CNH) electrodes were spray deposited [23] on FTO glass to study Co(II)/Co(I). Contrary to PEDOT, which is insulating at cathodic voltages, nanohorn films present a large electroactivity window, which allows to intercept the Co(I)/Co(II) couple. EIS experiments were carried out at the equilibrium voltage potential (0 V) of the Fe(III)/(II) couple and at the half wave potential ( $-1.25$  V) of the Co(II)/(I) couple.

A flow cell was assembled to obtain charge/discharge cycles, after purging both compartments under nitrogen flux; with liquid flow rates of 45 mL/min; electrodes employed were two carbon-felts Sigracell® GFD4.6 EA and a Nafion 115 membrane has been used for separation. Before the tests in flow cell, the membrane was wetted with PC for 24 h, followed by 30 min of ultrasonic treatment.

The XPS analysis was carried out with a PHI-5500 spectrometer with monochromator (Pass Energy = 58.7 eV; Step = 0.5 eV; Time x step = 0.10 s). Small membrane samples were inserted in a high vacuum ( $10^{-9}$  Torr) chamber and an electron gun was used as a neutralizer.

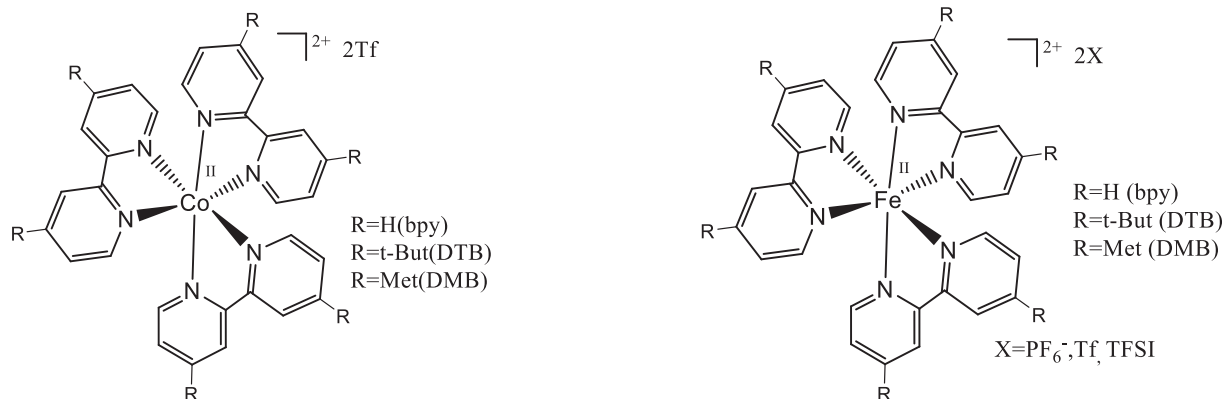


Fig. 2. Co(II) and Fe(II) complexes chosen for electrochemical testing (where TFSI = Bis(trifluoromethane)sulfonamide anion, Tf = triflate anion, bpy = 2,2'-bipyridine, DMB = 4,4'-dimethyl-2,2'-bipyridine, DTB = 4,4'-di-*tert*-butyl-2,2'-bipyridine).

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