

Organic Electrolytes for Redox Flow Batteries

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Summary: Several organic redox systems were investigated as they represent possible 'better' systems for redox flow battery characterisation than aqueous redox couples. All experiments in this work were performed with cyclic voltammetry at room temperature (20 °C) and pressure. Rubrene, Ru(acac)₃ and [Fe(bpy)₃](ClO₄)₂ in acetonitrile were found to exhibit wider potential windows of operation, respectively than aqueous based redox systems (for example the all-vanadium redox flow electrolytes), thereby promising a greater energy output. Due to poor solubility of rubrene in acetonitrile, it has not been found to be a viable redox species for redox flow battery applications. The other organo-metallic redox species were promising to be recommended for further evaluation. Experiments with a stationary H-type cell have been reported in the literature but so far no tests have been conducted with redox flow batteries as yet.

Introduction

The use of organic solvents for electrochemical engineering was reviewed thoroughly by Gores and Barthel [1]. Mann [2] described the properties of various organic solvents and discussed their purification and use in detail for electrochemical tests. The purification process is very important as Corrigan and Evans [3] found that the presence of water in organic solvents decrease the electrode reaction rates of the redox species considerably.

The organic solvents proposed in general for electrochemical batteries include acetonitrile, propylene carbonate, 1,2-dimethoxyethane and tetrahydrofuran [4-6]. Acetonitrile is considered to be a "better" solvent due to lower cost as well as its ability to dissolve a greater number of organo-metallic compounds than its other counterparts [7]. Organic redox species of interest in redox flow batteries have also been found to exhibit superior electrochemical characteristics in acetonitrile than in other solvents [8].

For the purposes of this research, it was more important to compare the performance of different species in the same organic solvent rather than compare the performance of the same species in different organic solvents. The redox species

investigated by Morita and co-workers [9] were investigated here with acetonitrile as the solvent. The species studied had one thing in common; they all could exhibit at least three redox states in solution.

Rubrene (Fig. 1) was also investigated in this work due to its ability to exhibit three oxidation states in organic solutions. The electrochemistry of this aromatic compound has been studied quite extensively in the literature [10-15]. Once again, the compound was found to exhibit superior electrochemical characteristics in acetonitrile [16-19] in comparison to other organic solvents.

Results and Discussion

A series of redox species were investigated using acetonitrile as the solvent [20]. Table- 1 compares the species against each other based on their solubility, electrochemical reaction kinetics [21], the potential window of operation (equilibrium potential), cost and the number of redox states each species could be oxidised/reduced to in solution. For a possible application in the redox flow battery system, the species required to have at least three oxidation states in solution.

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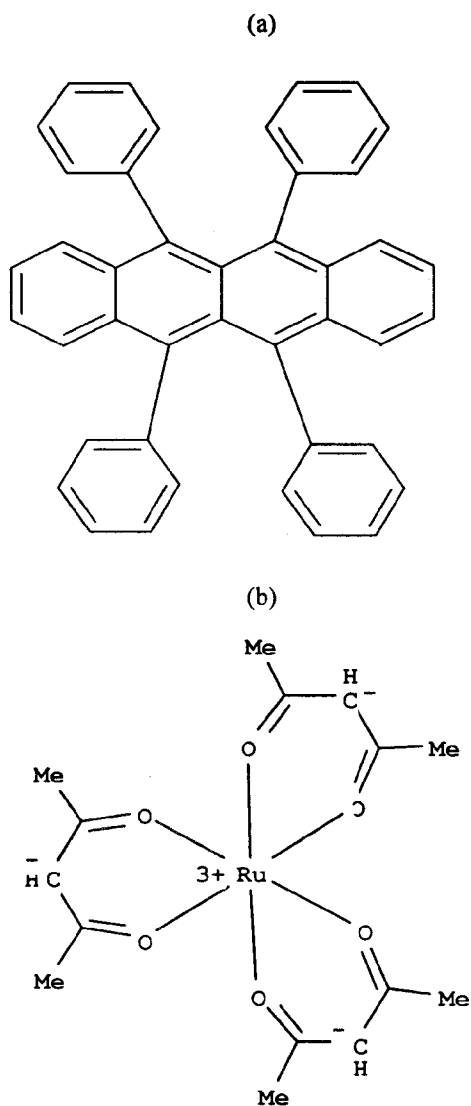


Fig. 1: Chemical structures of (a) Ruthenium Acetylacetonate $[\text{Ru}(\text{acac})_3]$ and (b) Rubrene ($\text{C}_{42}\text{H}_{28}$).

The following systems were rejected after thorough investigation:

$[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$: $\text{Ru}(\text{bpy})_3^{2+}$ ions were not available commercially except as a chloride salt. As chloride ions were found to interfere with the kinetics of the ruthenium redox couples [22], this chemical was not considered for further investigation. High costs, poor solubility in acetonitrile and quasi-reversible kinetics also had a significant influence on this decision even though the electrolyte provided the highest potential window of operation than any other redox species tested in this work. The cyclic voltammogram of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ with an excess of NaBF_4 in solution is shown in Fig. 2. The voltammogram on the positive side of the graph shows the redox reaction between $[\text{Ru}(\text{bpy})](\text{III})$ and $[\text{Ru}(\text{bpy})](\text{II})$ while the negative side shows the redox reaction between $[\text{Ru}(\text{bpy})](\text{II})$ and $[\text{Ru}(\text{bpy})](\text{I})$ with possible interference from chloride ions present in solution

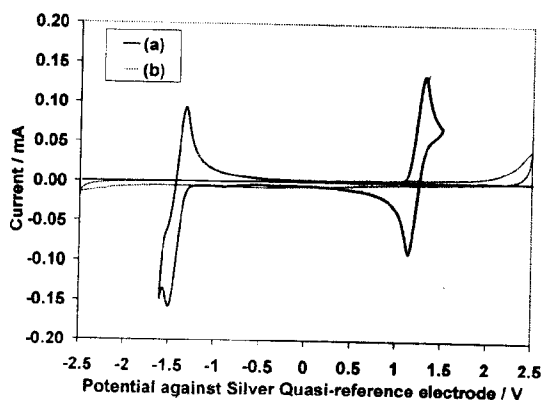


Fig. 2: Cyclic voltammogram recorded at 0.1 V/s at a glassy carbon electrode in (a) 10 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ and 0.05 M NaBF_4 in acetonitrile; and (b) 0.05 M NaBF_4 in acetonitrile.

Table- 1: Characteristics of redox species determined using cyclic voltammetry in this research

Chemical	Equilibrium Potential (V)	Solubility in solvent	Reaction Kinetics	Cost per gram (Sigma-Aldrich, UK, 2003)	Number of redox states
$\text{Ru}(\text{acac})_3$	1.77	High	Reversible	£ 35	Three
$[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ with excess NaBF_4	2.62	Poor	Quasi-reversible	£ 22.20	Three
$[\text{Fe}(\text{bpy})_3](\text{ClO}_4)_2$	2.41	Good	Reversible	£ 2.30	Three
Rubrene	2.33	Poor	Reversible	£ 46.93	Three

beyond -1.5 V [23]. The cyclic voltammogram of NaBF_4 (background electrolyte) in acetonitrile is also shown in Fig. 2.

Rubrene

High costs and poor solubility in acetonitrile were the major reasons behind the exclusion of this chemical. Other factors made it favourable (such as a high potential window of operation) but were not good enough to make up for these two major deficiencies [24]. The cyclic voltammogram of this species is shown in Figure 3. The voltammogram on the positive side of the graph shows the redox reaction between rubrene positive radicals (R^+) and rubrene neutral molecules (R). Similarly the voltammogram on the negative side of the graph shows the redox reaction between rubrene neutral molecules (R) and rubrene negative radicals (R^-). The voltammogram of the background electrolyte (Tetrabutyl-ammonium perchlorate or TBAP) is also shown in Figure 3. The slight hump on the positive side of the graph may be due to impurities generated in solution due to subjecting the species to a high potential (2.2 V) during the cyclic voltammetric scan.

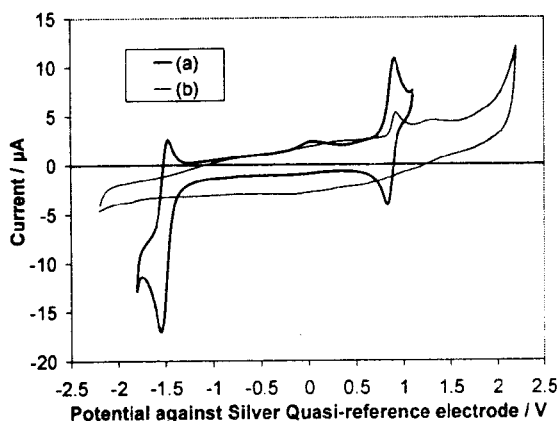


Fig. 3: Cyclic voltammogram recorded at 0.1 V/s at a glassy carbon electrode in (a) 0.25 mM rubrene and 0.05 M TBAP in 3:1 mixture of acetonitrile and toluene; and (b) 0.05 M TBAP in a 3:1 mixture of acetonitrile and toluene.

The redox species considered promising for further study were thus $\text{Ru}(\text{acac})_3$ and

$[\text{Fe}(\text{bpy})_3](\text{ClO}_4)_2$. $\text{Ru}(\text{acac})_3$ was soluble in acetonitrile, showed reversible kinetics and had a reasonable open circuit potential (OCP). These factors were considered over and above the high price of the compound.

Finally, $[\text{Fe}(\text{bpy})_3](\text{ClO}_4)_2$ showed desirable characteristics for a possible application in a redox flow battery as shown in Table- 1. The cyclic voltammogram of $\text{Ru}(\text{acac})_3$ is shown in Fig. 4. The voltammogram on the positive side of the graph depicts the redox reaction shown in Equation 1.

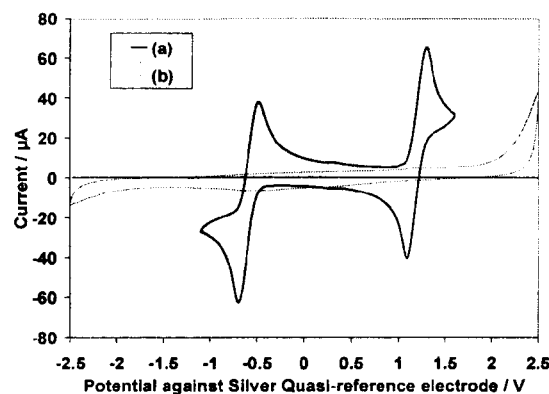
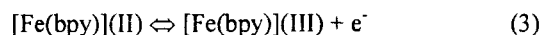


Fig. 4: Cyclic voltammogram recorded at 0.1 V/s at a glassy carbon electrode in (a) 2 mM $\text{Ru}(\text{acac})_3$ and 0.05 M TEABF₄ (tetraethyl ammonium tetrafluoroborate) in acetonitrile; and (b) 0.05 M TEABF₄ in acetonitrile.

The voltammogram on the negative side of the graph depicts the redox reaction shown in Equation 2.



The cyclic voltammogram of $[\text{Fe}(\text{bpy})_3](\text{ClO}_4)_2$ is shown in Figure 5. The voltammogram on the positive side of the graph depicts the redox reaction shown in Equation 3.



The voltammograms on the negative side of the graph depict the redox reactions shown in Equations 4a and 4b.

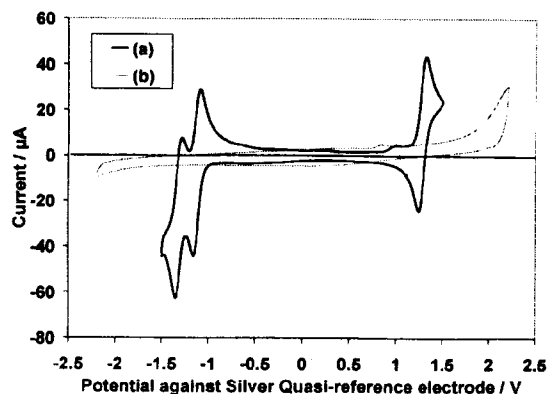
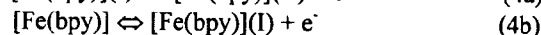
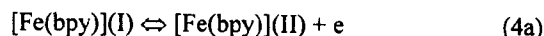


Fig. 5: Cyclic voltammogram recorded at 0.1 V/s at a glassy carbon electrode in (a) 2 mM $[\text{Fe}(\text{bpy})_3](\text{ClO}_4)_2$ and 0.1 M TEAP (tetraethyl ammonium perchlorate) in acetonitrile; and (b) 0.1 M TEAP in acetonitrile.



The results obtained in this work with cyclic voltammetry at a glassy carbon (GC)

electrode were in accordance with the literature [25-26]. Results of charge-discharge experiments with selected species in a stationary H-type cell have been reported elsewhere [26]. Tests with an actual redox flow battery are yet to be performed.

Experimental

The chemicals investigated in this work are shown in Table- 2. To remove dissolved oxygen, oxygen-free dry nitrogen (BOC, UK) was sparged through all electrolyte solutions for at least ten minutes prior to use. The removal of trace quantities of water (0.03 % w/w) from the solvent (acetonitrile – Merck, HPLC Grade) required a number of steps to be followed:

1. Zeolite 4A (molecular sieves from Aldrich) was dried in a Gallenkamp Muffle furnace at 400 °C for 12 hours.
2. The zeolite was then placed inside a vacuum desiccator (Merck) containing anhydrous P_2O_5 (Merck) to allow the zeolite to cool to room temperature without absorbing atmospheric moisture.
3. Once at room temperature, the dried zeolite was mixed with the HPLC grade acetonitrile

Table- 2: Chemicals employed for preparing electrolytes for organic redox tests.

Chemical Name	Formula	Use of Chemical	Supplier and Grade/Purity
Tris (2,2'-bipyridine) ruthenium(II) chloride hexahydrate	$\text{C}_{30}\text{H}_{24}\text{Cl}_2\text{N}_6\text{Ru} \cdot 6\text{H}_2\text{O}$	Used to prepare tris(2,2'-bipyridine) ruthenium(II) tetrafluoroborate, $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$ (redox species).	Aldrich, Reagent (UK)
Sodium tetrafluoroborate	NaBF_4	Reagent for preparing tris(2,2'-bipyridine) ruthenium(II) tetrafluoroborate.	Aldrich, Technical (UK)
Ruthenium acetylacetonate	$\text{C}_{12}\text{H}_{21}\text{O}_6\text{Ru}$	Active species for testing potential redox couples $[\text{Ru}(\text{acac})_3]$.	Aldrich, 97 % (UK)
Tetraethyl-ammonium tetrafluoroborate	$(\text{C}_2\text{H}_5)_4\text{NBF}_4$	Background electrolyte for providing conductivity (TEABF ₄).	Aldrich, 99 % (UK)
Tris(2,2'-bipyridine) iron(II) perchlorate	$(\text{C}_{10}\text{H}_8\text{N}_2)_3\text{Fe}(\text{ClO}_4)_2$	Potential redox species $[\text{Fe}(\text{bpy})_3](\text{ClO}_4)_2$	GFS, Reagent (USA)
Tetraethyl-ammonium perchlorate	$\text{C}_8\text{H}_{20}\text{ClNO}_4$	Background electrolyte to provide conductivity (TEAP).	Fluka, Puriss (USA)
Tetrabutyl-ammonium perchlorate	$\text{C}_{16}\text{H}_{36}\text{ClNO}_4$	Background electrolyte to provide conductivity (TBAP) – used only for rubrene experiments.	Fluka, Puriss (USA)
Rubrene	$\text{C}_{42}\text{H}_{28}$	Active species (R) for testing potential redox couples.	Aldrich, Reagent (UK)
Toluene	C_7H_8	Solvent to enhance the solubility of rubrene in acetonitrile	Aldrich, HPLC (UK)

(Merck) and left for 24 hours to absorb the moisture from the organic liquid in the vacuum desiccator.

4. Dried acetonitrile samples were titrated using the Karl-Fischer method (equipment supplied by Aquapal) to detect moisture levels.

Drying with zeolites was repeated several times until the moisture level in the organic chemical was below 0.005 % w/w.

The preparation of tris(2,2'-bipyridine) ruthenium (II) tetrafluoroborate was adapted from the procedure used by Tokel-Takvoryan and co-workers. Bright orange crystals of tris(2,2'-bipyridine) ruthenium (II) chloride were dissolved in dried acetonitrile to which 0.07 M sodium tetrafluoroborate was added. The solution was then filtered giving a white precipitate and a bright orange filtrate. The precipitate was analysed by a chloride ion selective electrode to quantify the presence of chloride ions and atomic emission spectroscopy was used to determine the presence of sodium ions in the precipitate. Both these analytical methods confirmed the presence of sodium and chloride ions in the precipitate affirming that the filtrate was tris(2,2'-bipyridine) ruthenium(II) tetrafluoroborate. However, it was obvious from cyclic voltammetric tests that all chloride ions could not be removed through this ion exchange procedure.

Three electrodes were used for cyclic voltammetry (Fig. 6). A glassy-carbon (GC) electrode (IJ Cambria Scientific, UK) of surface area 0.07 cm² was used as a working electrode for cyclic voltammetry in organic media. The glassy carbon electrode was pre-treated prior to experiments. Organic media required the use of a silver wire (Advent Research Materials, UK) quasi-

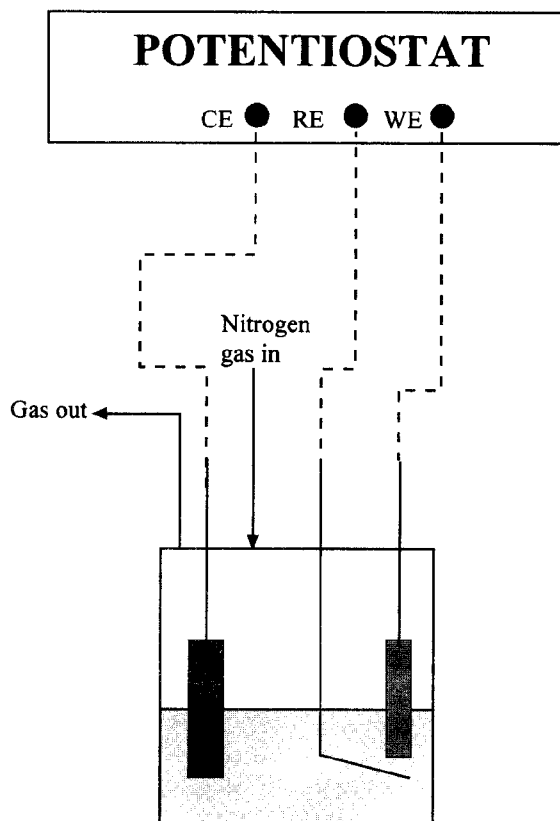


Fig. 6: Schematic diagram of the electrochemical beaker cell and instrumentation for electrolytes using acetonitrile as the solvent. WE = working electrode, CE = counter electrode and RE = reference electrode.

reference electrode (*AgQRE*) instead of the usual saturated calomel electrode (employed for aqueous tests). The reason for this was to minimise the development of potential junctions between

Table- 3: Experimental conditions for cyclic voltammetry.

Redox species and concentration	Ionic Form	Redox Couples Investigated	Background electrolyte and concentration	Colour of solution	Scan range used (V)
2 mM Ru(acac) ₃	Ru ³⁺ (acac) ₃ ⁻	Ru(III)/Ru(IV) and Ru(II)/Ru(III)	0.05 M TEABF ₄	Blood-red	-1.1 to 1.6
10 mM [Ru(bpy) ₃](BF ₄) ₂	[Ru(bpy) ₃] ²⁺ [BF ₄] ⁻	Ru(II)/Ru(III) and Ru(II)/Ru(I)	0.05 M NaBF ₄	Bright orange	-1.6 to 1.5
2 mM [Fe(bpy) ₃](ClO ₄) ₂	[Fe(bpy) ₃] ²⁺ [ClO ₄] ⁻	Fe(II)/Fe(III) and Fe(II)/Fe(I)	0.1 M TEAP	Deep red	-1.5 to 1.5
0.25 mM Rubrene	Neutral species	R/R ⁺ and R/R ⁻	0.05 M TBAP	Light orange	-1.8 to 1.1

aqueous and organic electrolyte interfaces. Platinum disc was used as the counter electrode.

Cyclic voltammetry was conducted using a standard electrochemical beaker cell at room temperature (20 °C) and pressure (three electrode arrangement shown in Fig. 6). The experimental conditions employed for redox tests are shown in Table- 3. The total volume of the test vessel (Kilner jar) was approximately 275 ml. The cell had a flask cover with five ports attached to screw fittings.

A gas sparging tube with a sintered glass end-piece was fitted through the central port. Three further ports were used to fit the working, counter and reference electrodes, respectively. The final port was used as a gas vent.

All experiments used 250 ml of electrolyte solution. An Autolab/ PGSTAT30 (Windsor Scientific, UK) was used as a potentiostat. The unit was computer-controlled using software (General Purpose Electrochemical System, GPES) for performing electrochemical experiments and data logging. All solutions were de-aerated for at least 10 min with inert gas prior to experiments. After 10 min the solution headspace was purged with inert gas for the duration of experiments.

Rubrene was dissolved with difficulty to a maximum concentration of 1 mM with 0.05 M tetrabutylammonium perchlorate in a 3: 1 mixture of acetonitrile and toluene (HPLC grade, Aldrich).

Conclusions

Cyclic voltammetry with selected organo-metallic species provided results consistent with those reported in the literature [26]. Several potential redox systems were rejected on the basis of cost and poor solubility in the organic solvent of interest (acetonitrile). The ones selected for further work were Ru(acac)₃ and [Fe(bpy)₃](ClO₄)₂ [26]. Although charge-discharge experiments with a stationary H-type cell has been reported [26], experiments with a suitable redox flow battery is required to draw meaningful conclusions.

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