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## Mechanistic Insights of Cycling Stability of Ferrocene Catholytes in Aqueous Redox Flow Batteries

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**Abstract:** Water soluble ferrocene (Fc) derivatives are promising cathode materials for aqueous organic redox flow batteries (AORFBs) towards scalable energy storage. However, their structure-performance relationship and degradation mechanism in aqueous electrolytes remain unclear. Herein, physicochemical and electrochemical properties, battery performance, and degradation mechanisms of three Fc catholytes, (ferrocenylmethyl)trimethylammonium chloride (**C<sub>1</sub>-FcNCl**), (2-ferrocenyl-ethyl)trimethylammonium chloride (**C<sub>2</sub>-FcNCl**), and (3-ferrocenyl-propyl)trimethylammonium chloride (**C<sub>3</sub>-FcNCl**) in pH neutral aqueous electrolytes were systemically investigated. UV-Vis and gas chromatography (GC) studies confirmed the thermal and photolytic C<sub>x</sub>-Cp ligand dissociation decomposition pathways of both discharged and charged states of **C<sub>1</sub>-FcNCl** and **C<sub>2</sub>-FcNCl** catholytes. In contrast, in the case of the **C<sub>3</sub>-FcNCl** catholyte, the electron-donating 3-(trimethylammonium)propyl group strengthens the coordination between the C<sub>3</sub>-Cp<sup>-</sup> ligand and the Fe<sup>3+</sup> or Fe<sup>2+</sup> center and thus mitigates the ligand-dissociation degradation. Consistently, the Fc electrolytes displayed cycling stability in both half-cell and full-cell flow batteries in the order of **C<sub>1</sub>-FcNCl** < **C<sub>2</sub>-FcNCl** < **C<sub>3</sub>-FcNCl**.

### Broader Context

Redox flow batteries (RFBs) are positioned to integrate renewable energy into existing electricity grids. A new generation of aqueous organic RFBs (AORFBs) using sustainable and tunable redox organic molecules holds excellent promise to penetrate scalable energy storage applications. However, the performance of AORFBs is typically limited by the lack of high-performance cathode electrolytes (called catholytes). Thus, it is highly critical to conduct mechanistic studies of catholyte molecules. In-depth understandings of their degradation pathways

are essential to developing more robust, energy dense catholyte molecules, paving the road to resilient energy storage performance. We present a comprehensively mechanistic study of water-soluble ferrocene catholytes. This work discloses their thermal and photolytic degradation pathways and molecular engineering solutions for developing stable coordination complex redox active electrolytes. Presented results enlighten valuable design principles to develop advanced coordination complex redox active electrolytes for scalable, long-duration energy storage.

## Introduction

Advanced technologies for grid-scale energy storage are broadly demanded to efficiently utilize intermittently available, fluctuating renewable energies such as solar and wind and ensure stable, secured power supply of the electricity grid.<sup>1</sup> Among various electrochemical energy storage technologies, aqueous redox flow batteries (ARFB) have been recognized as a viable technology for renewable energy integration and electricity grid balancing because of their technologic advantages, including decoupled energy and power, high power and energy performance, excellent modularity and scalability, and environmentally friendly aqueous electrolytes.<sup>1,2</sup>

Sustainable and tunable organic and organometallic redox-active molecules have become increasingly attractive to serve as charge storage materials in ARFBs. In the past ten years, significant progress has been made in the aqueous organic redox flow battery (AORFB) technology.<sup>13-5</sup> Water-soluble viologen (anolyte),<sup>6-10</sup> quinone (anolyte and catholyte),<sup>11-16</sup> phenazine (anolyte),<sup>17-20</sup> TEMPO (catholyte),<sup>21-25</sup> and ferrocene (catholyte)<sup>7,10,26,27</sup> compounds were developed for AORFB demonstration. However, the most critical roadblock to further boost the energy storage performance of AORFBs lies in the lack of stable catholyte materials.<sup>28</sup> So far, ferrocene and TEMPO derivatives are common catholyte materials for AORFBs. Despite being extensively used in flow batteries, there are very few mechanistic studies to gain insightful understandings of the chemical stability of catholyte molecules, which is key to developing more advanced catholyte materials.<sup>1</sup>

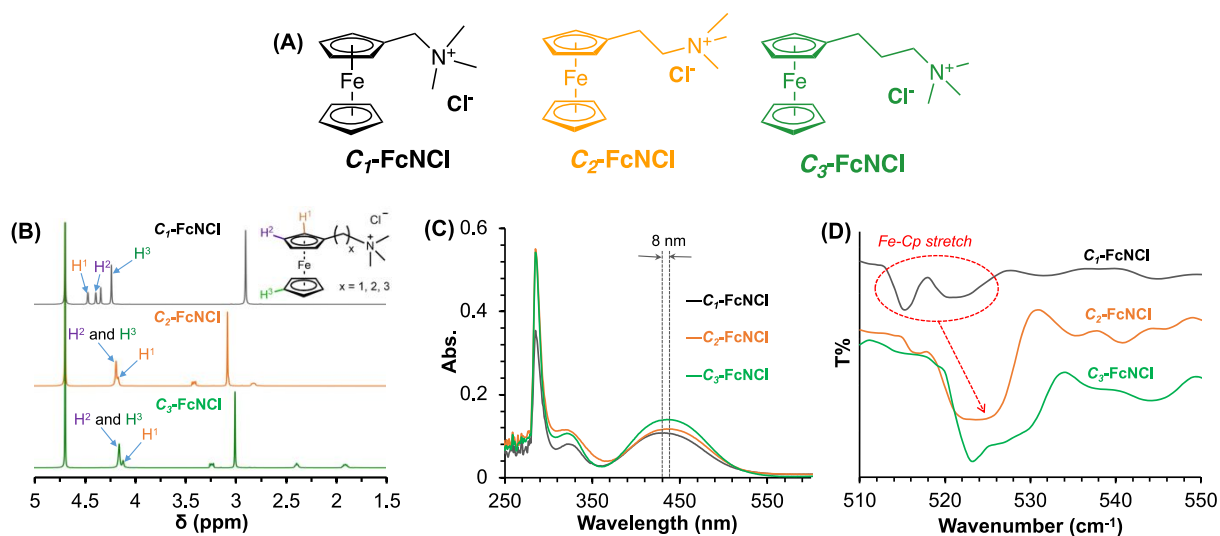
In our previous work, we reported a highly water-soluble (ferrocenylmethyl)trimethylammonium chloride ( $C_1$ -FcNCl, Figure 1A) as a catholyte (4.00 M solubility in water at room temperature) for AORFB applications.<sup>7</sup> Paired with methyl viologen (MV) anolyte, the  $C_1$ -FcNCl/MV AORFB delivered reliable cycling performance and battery

efficiency. However, in long-term cycling tests, capacity fading was still observed, specifically, ca. 9.0% capacity decay in 700 charge/discharge cycles at 60 mA/cm<sup>2</sup> current density.<sup>7</sup> Subsequent studies revealed that the derivatives of **C<sub>1</sub>-FcNCl** with a longer methylene chain between the Fc and ammonium groups displayed improved cycling performance.<sup>10,27</sup> One argument was that **C<sub>1</sub>-FcNCl** might undergo a dimerization decomposition mechanism.<sup>10</sup> Instead, Cp<sup>-</sup> ligand exchange with an external ligand such as Cl<sup>-</sup> was proposed as a possible degradation pathway for ferrocenium cation (Fc<sup>+</sup>) in organic solutions in 1972.<sup>29</sup> Our recent work also suggested that the ligand dissociation commences the decomposition of ferrocyanide in alkaline solutions.<sup>30</sup> Thus, we hypothesize that the Cp<sup>-</sup> ligand dissociation initiates the degradation of ferrocene in organic solutions. We further infer that the charged state, [**C<sub>1</sub>-FcN**]<sup>2+</sup>, of **C<sub>1</sub>-FcNCl** might follow a similar decomposition mechanism. Furthermore, we envision that ferrocene catholytes can be stabilized by the +I inductive effect of substituted groups of the Cp<sup>-</sup> ligand. The electron-donating functional groups can increase the binding strength of a Cp<sup>-</sup> ligand and a Fe<sup>3+</sup> center and lower the possibility of dissociation of the Cp<sup>-</sup> ligand, thereby suppressing subsequent ligand exchange reactions.

To elucidate the donation effect of the Cp<sup>-</sup> ligand, we report a systematic study of physiochemical properties, chemical stability, and battery performance of a series of (trimethylammonium)alkyl functionalized ferrocene molecules, **C<sub>1</sub>-FcNCl**, and two derivatives with a purposely designed longer (trimethylammonium)alkyl pendant, (2-ferrocenylethyl)trimethylammonium chloride (**C<sub>2</sub>-FcNCl**) and (3-ferrocenylpropyl)trimethylammonium chloride (**C<sub>3</sub>-FcNCl**) (Figure 1A). Our results revealed that the series displayed increased chemical stability and cycling stability with the increased length of the (trimethylammonium)alkyl pendant and thus the donation strength of the substituted Cp<sup>-</sup> ligand by avoiding the ligand exchange side reaction of the Cp<sup>-</sup> ligand (Figure 1). Specifically, a suit of spectroscopic studies elucidated that both thermally and photolytically induced ligand dissociation triggered the chemical decomposition of electron deficient ferrocene electrolytes to iron hydroxide precipitates in the presence of water. The present results highlight the importance of the ligand coordination sphere of the coordination compound based redox active electrolytes regarding their energy storage performance. Paired with a viologen anolyte under pH-neutral conditions, the most stable **C<sub>3</sub>-FcNCl** catholyte in a 0.50 M AORFB delivered up to an energy efficiency of 91% at 10 mA/cm<sup>2</sup> and capacity retention of 99.998% per cycle or 99.927% per day in 500 cycles.

## Results

Hydrophilic (trimethylammonium)alkyl group functionalized Fc derivatives ( $C_x\text{-FcNCl}$ ,  $x = 1, 2, \text{ and } 3$ , Figure 1A), (ferrocenylmethyl)trimethylammonium chloride ( $C_1\text{-FcNCl}$ ), (2-ferrocenyl-ethyl)trimethylammonium chloride ( $C_2\text{-FcNCl}$ ), and (3-ferrocenyl-propyl)trimethylammonium chloride ( $C_3\text{-FcNCl}$ ) were synthesized (Scheme S1) and fully characterized by  $^1\text{H-NMR}$ , elemental analysis, UV-Vis, IR, and cyclic voltammetry (CV). Figure 1B exhibits the  $^1\text{H-NMR}$  spectra of the  $C_x\text{-FcNCl}$  compounds. For  $C_1\text{-FcNCl}$ , the proton signals of the (trimethylammonium)methyl group modified Cp ligand possessed much larger chemical shifts than those of the pristine Cp ligand ( $\delta$ :  $\text{H}^1\text{-}4.47$  and  $\text{H}^2\text{-}4.39$  ( $\text{H}^2$ ) vs.  $\text{H}^3\text{-}4.24$  in Figure 1B), which suggests the strong electron-withdrawing effect of the (trimethylammonium)methyl group. In contrast, in  $C_2\text{-FcNCl}$  and  $C_3\text{-FcNCl}$  compounds, the signal of proton near the (trimethylammonium)alkyl functional groups ( $\text{H}^1$ ) shifted to a higher field than those of the pristine Cp ligand ( $\text{H}^3$ ), indicating 2-(trimethylammonium)ethyl and 3-(trimethylammonium)propyl are electron-donating groups. Smaller chemical shifts of protons on Cp ligands of  $C_3\text{-FcNCl}$  (4.14 ( $\text{H}^1$ ) and 4.18 ppm ( $\text{H}^2$  and  $\text{H}^3$ )) than those of  $C_2\text{-FcNCl}$  (4.17 ( $\text{H}^1$ ) and 4.20 ( $\text{H}^2$  and  $\text{H}^3$ )) indicates the stronger electron-donating capability of 3-(trimethylammonium)propyl group than 2-(trimethylammonium)ethyl group. Figure 1C shows the UV-Vis absorption of  $C_x\text{-FcNCl}$  compounds. Three compounds displayed two spin-allowed d-d transitions: 323 and 430 nm for  $C_1\text{-FcNCl}$ , 321 and 438 nm for  $C_2\text{-FcNCl}$ , and 323 and 438 nm for  $C_3\text{-FcNCl}$ . The strong absorption around 285 nm is assigned as the overlapped metal-to-ligand charge transfer (MLCT) and ligand-to-metal charge transfer (LMCT).<sup>31</sup> As shown in the IR spectra of  $C_1\text{-FcNCl}$  (Figure 1D, gray curve), two divided  $\text{Fe}^{\text{II}}\text{-Cp}$  stretch absorption were observed at 515  $\text{cm}^{-1}$  and 521  $\text{cm}^{-1}$  wavenumbers, corresponding to those two different Cp ligands.<sup>32</sup> However, the same absorption signals were shifted to larger wavenumbers, a broad peak centered on 524  $\text{cm}^{-1}$  for  $C_2\text{-FcNCl}$  and 523  $\text{cm}^{-1}$  and 527  $\text{cm}^{-1}$  for  $C_3\text{-FcNCl}$ , which indicates the stronger coordination between  $\text{Fe}^{\text{II}}$  center and substituted Cp ligands in  $C_2\text{-FcNCl}$  and  $C_3\text{-FcNCl}$  than that of  $C_1\text{-FcNCl}$ .



**Figure 1.** Spectroscopic studies of the Fc derivatives,  $C_1$ -FcNCl (black),  $C_2$ -FcNCl (orange),  $C_3$ -FcNCl (green). (A) Structures of the Fc derivatives; (B)  $^1\text{H}$ -NMR in  $\text{D}_2\text{O}$ ; (C) UV-vis absorption; and (D) ATR-IR spectra.

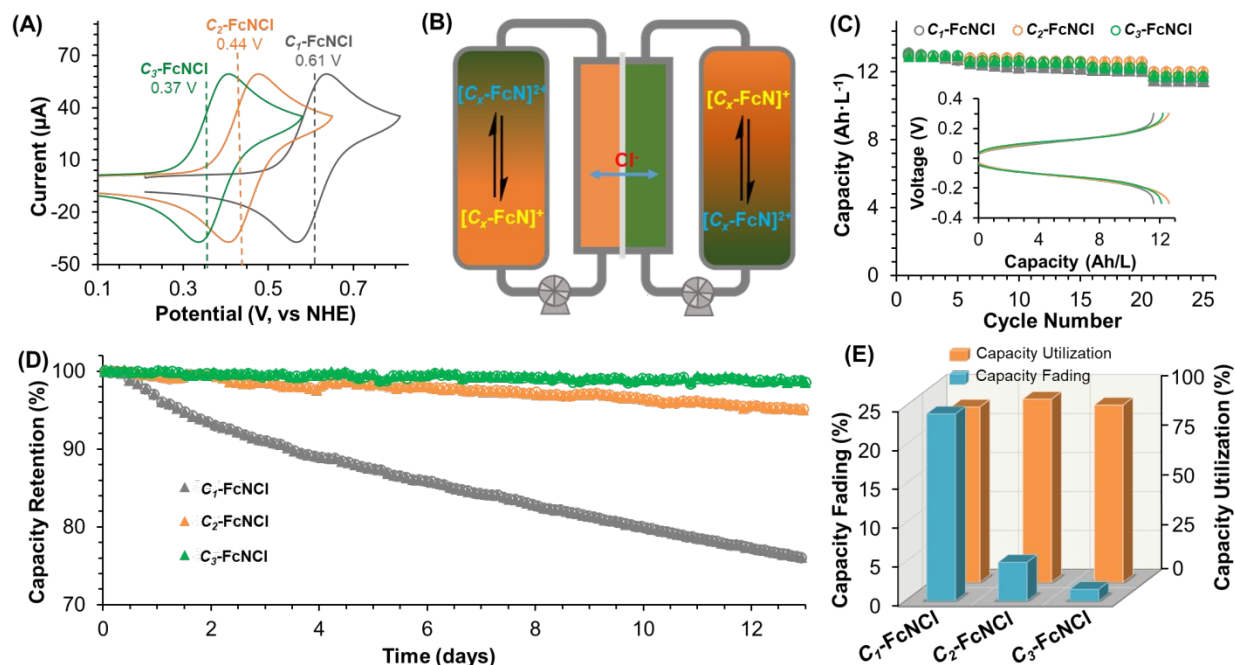
Physicochemical properties of the  $C_x$ -FcNCl compounds regarding flow battery performance were systemically investigated. With the extension of the alkyl chain between the Fc redox center and trimethylammonium functional group, water solubility gradually decreased from 4.00 M (i.e., a capacity of 107.2 Ah/L) of  $C_1$ -FcNCl to 2.60 M (69.7 Ah/L) of  $C_2$ -FcNCl and 2.30 M (61.6 Ah/L) of  $C_3$ -FcNCl at room temperature. Ion conductivities of the Fc derivatives in water were measured at a concentration range from 0.01 M to 2.00 M (Figure S1A). Even in the absence of a supporting electrolyte, aqueous solutions of  $C_x$ -FcNCl demonstrated high conductivities of up to 50.0 mS/cm at room temperature. Liner relationship between conductivity and concentration was observed in the 0.01 M to 0.20 M concentration range. The slope of conductivity versus concentration plot is calculated as molar ion conductivity of the  $C_x$ -FcNCl compounds (Figure S1B). These three Fc derivatives displayed comparable molar ion conductivity ( $63.0 \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$  for  $C_1$ -FcNCl,  $63.7 \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$  for  $C_2$ -FcNCl, and  $61.4 \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$  for  $C_3$ -FcNCl, Table 1). The high ion conductivities of  $C_x$ -FcNCl compounds are beneficial for boosting the energy and power performance of related AORFBs.

**Table 1.** Solubility, Charge Capacity, Molar Ion Conductivity, Reduction Potentials, and Electrochemical Kinetics Data of  $C_x$ -FcNCl in Aqueous Solutions at Room Temperature.

Compound	Solubility, M (Capacity, Ah/L)	Molar Ion Conductivity ( $\Lambda_m$ , $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ )	$E_{1/2}$ , V (vs. NHE)	$k^0$ , $\text{cm}\cdot\text{s}^{-1}$	$D$ , $\text{cm}^2\cdot\text{s}^{-1}$
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$C_1$ -FcNCl	4.00 (107.2)	63.0	0.61	0.126	$6.80 \times 10^{-6}$
$C_2$ -FcNCl	2.60 (69.7)	63.7	0.44	0.288	$6.10 \times 10^{-6}$
$C_3$ -FcNCl	2.30 (61.6)	61.4	0.37	0.193	$5.78 \times 10^{-6}$

\*Redox potentials and electrochemical kinetics were tested in 0.50 M  $\text{NH}_4\text{Cl}$  aqueous solution.



**Figure 2.** Cyclic voltammograms and half-cell RFB studies of the  $C_x$ -FcNCl catholytes. (A) Cyclic voltammograms of the Fc derivatives; (B) The scheme of  $C_x$ -FcNCl half-cell RFBs; (C) Charge ( $\circ$ ) and discharge ( $\blacktriangle$ ) capacity versus cycling number at from 10 to 50  $\text{mA}/\text{cm}^2$  current densities for 0.50 M  $C_1$ -FcNCl (gray),  $C_2$ -FcNCl (orange), and  $C_3$ -FcNCl (green) half-cell RFBs; Inset: representative charge and discharge profiles at  $40 \text{ mA}/\text{cm}^2$ ; (D) Capacity retention of 0.50 M  $C_x$ -FcNCl half-cell RFBs at  $40 \text{ mA}/\text{cm}^2$  during 13 testing days:  $C_1$ -FcNCl (gray),  $C_2$ -FcNCl (orange), and  $C_3$ -FcNCl (green); (E) Comparison of initial capacity utilization (orange) and capacity fading percentages (blue) of the  $C_x$ -FcNCl half-cell RFBs at  $40 \text{ mA}/\text{cm}^2$  in 13 testing days. CV conditions: 2 mM  $C_x$ -FcNCl in 0.50 M  $\text{NH}_4\text{Cl}$  aqueous solution, 100  $\text{mV}/\text{s}$  scan rate, glassy carbon working and counter electrodes, Ag/AgCl reference electrode. RFB conditions: catholyte, 0.50 M  $C_x$ -FcNCl in 1.00 M.

Electrochemical studies of the Fc derivatives were conducted in a 0.50 M  $\text{NH}_4\text{Cl}$  supporting electrolyte. As shown in Figure 2A, three compounds exhibited a reversible  $\text{Fe}^{3+/2+}$  redox wave in their cyclic voltammetry, i.e., 0.61 V (vs. NHE) for  $C_1$ -FcNCl, 0.44 V for  $C_2$ -FcNCl, and 0.37 V for  $C_3$ -FcNCl. CV scan rate dependence studies indicate that the reversible  $\text{Fe}^{3+/2+}$  redox process is a diffusion-controlled process (Figure S2A). The heterogeneous standard electron transfer rate constants  $k^0$  of  $C_x$ -FcNCl compounds were determined by Nicholson's method (Figure S2).<sup>33</sup> Fast electron transfer rate constants ( $k^0$ ) were calculated (0.126  $\text{cm}/\text{s}$  for  $C_1$ -FcNCl, 0.288  $\text{cm}/\text{s}$  for  $C_2$ -

**FcNCl**, and 0.193 cm/s for **C<sub>3</sub>-FcNCl**, respectively). Linear sweep voltammetry (LSV) studies using a glassy carbon rotation disc electrode were performed to measure the diffusion coefficients (*D*) of **C<sub>x</sub>-FcNCl** compounds (Figure S3). The diffusion coefficients (*D*) were calculated by Levich equation as  $6.80 \times 10^{-6}$  cm<sup>2</sup>/s for **C<sub>1</sub>-FcNCl**,  $6.10 \times 10^{-6}$  cm<sup>2</sup>/s for **C<sub>2</sub>-FcNCl**, and  $5.78 \times 10^{-6}$  cm<sup>2</sup>/s for **C<sub>3</sub>-FcNCl** in 0.50 M NH<sub>4</sub>Cl aqueous solution, respectively. The gradual decrease of diffusion coefficients (*D*) from **C<sub>1</sub>-FcNCl** to **C<sub>2</sub>-FcNCl** and **C<sub>3</sub>-FcNCl** is likely due to the increase of Fc molecular size with the extension of the alkyl chain.

Battery performance of the **C<sub>x</sub>-FcNCl** catholytes in AORFB was evaluated using a half-cell RFB approach, which has been confirmed as an efficient method for assessing the performance of a redox active electrolyte.<sup>30</sup> The battery studies were conducted in the dark to avoid the possible negative impacts of light exposure. As shown in Figure 2B, the half-cell RFBs were tested using 0.50 M discharged state, [**C<sub>x</sub>-FcN**]<sup>+</sup>, and 0.5 M charged state, [**C<sub>x</sub>-FcN**]<sup>2+</sup>, in a 1.0 M NH<sub>4</sub>Cl supporting electrolyte as a catholyte and an anolyte, respectively. The RFBs were performed at a current density from 10 mA/cm<sup>2</sup> to 50 mA/cm<sup>2</sup> with  $\pm 0.30$  V cutoff voltage. As shown in Figure 2C, **C<sub>1</sub>-FcNCl** half-cell RFB showed slight capacity decay over 5 continuous cycles at 10 and 20 mA/cm<sup>2</sup> current densities. However, stable capacity retention was observed in **C<sub>2</sub>-FcNCl** and **C<sub>3</sub>-FcNCl** half-cell RFBs at each current density from 10 mA/cm<sup>2</sup> to 50 mA/cm<sup>2</sup>. In addition, as seen in Figure 2C, it was observed that the capacity utilization of these ferrocene catholytes was in the order of **C<sub>1</sub>-FcNCl** (e.g., 11.6 Wh/L at 40 mA/cm<sup>2</sup>) < **C<sub>3</sub>-FcNCl** (12.1 Wh/L) < **C<sub>2</sub>-FcNCl** (12.6 Wh/L). We interpreted that the charge transfer resistance becomes impactful with the increased operational current as the charge transfer rate constants of these ferrocene catholytes are in the order of C1- **C<sub>1</sub>-FcNCl** < **C<sub>3</sub>-FcNCl** < **C<sub>2</sub>-FcNCl** (see table 1). The coulombic efficiencies of all the three half-cell RFBs at each current density were nearly 100%.

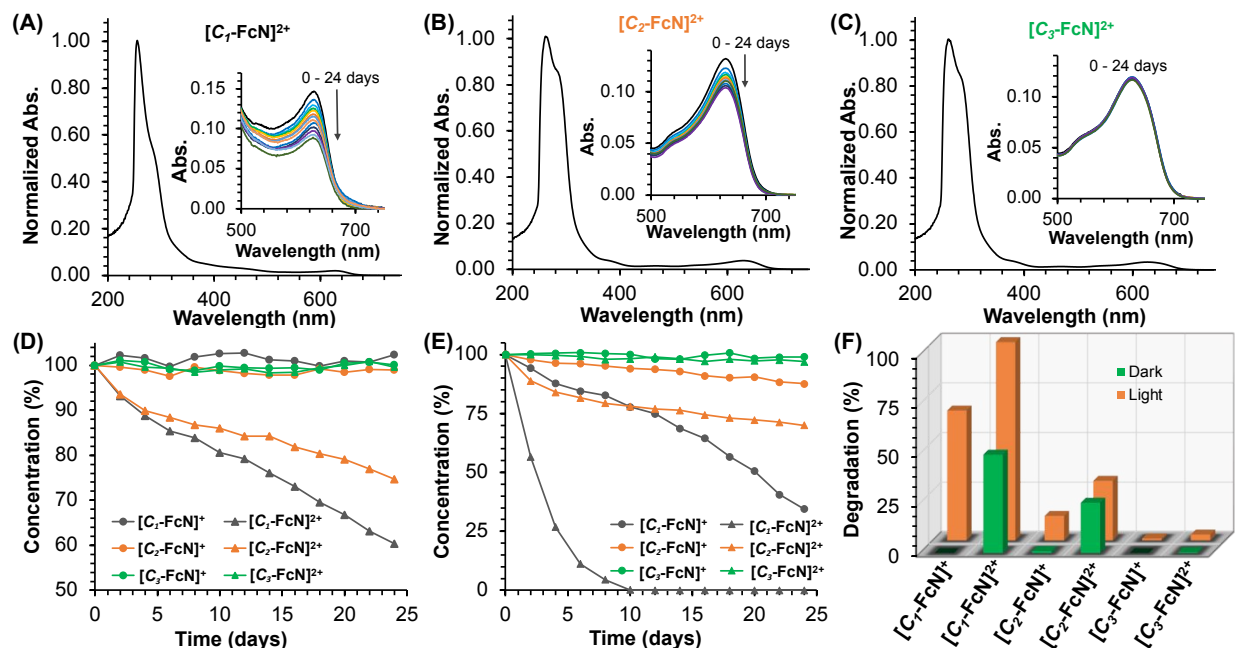
**Table 2.** Long-term Cycling Performance of the **C<sub>x</sub>-FcNCl** Half-cell RFBs and **C<sub>x</sub>-FcNCl/(NPr)<sub>2</sub>VCl<sub>4</sub>** Full-cell AORFBs at 40 mA·cm<sup>-2</sup>.

Material	Cycle Number	Capacity Fading (%)	Fading Rate	
			%/day	%/cycle
<b>C<sub>1</sub>-FcNCl</b>	585	23.99	1.85	0.041
<b>C<sub>2</sub>-FcNCl</b>	527	4.95	0.38	0.009
<b>C<sub>3</sub>-FcNCl</b>	508	1.85	0.14	0.004



<b>C<sub>1</sub>-FcNCl/</b> (NPr) <sub>2</sub> VCl <sub>4</sub>	500	13.53	1.03	0.027
<b>C<sub>2</sub>-FcNCl/</b> (NPr) <sub>2</sub> VCl <sub>4</sub>	500	2.57	0.18	0.005
<b>C<sub>3</sub>-FcNCl/</b> (NPr) <sub>2</sub> VCl <sub>4</sub>	500	1.03	0.07	0.002

Cycling stability is one of the most essential properties of a redox active electrolyte, as it directly determines the lifetime and energy storage cost of RFBs. To validate the cycling stability of the **C<sub>x</sub>-FcNCl** catholytes, the half-cell RFBs were continually operated at 40 mA/cm<sup>2</sup> for 13 days (Figure 2D and Figure S4 – S6 for detail). Initial capacity utilization of the half-cell RFBs was 90.3% for **C<sub>1</sub>-FcNCl**, 94.1% for **C<sub>2</sub>-FcNCl**, and 91.4% for **C<sub>3</sub>-FcNCl**, respectively (Figure 2E). In 13 testing days, **C<sub>2</sub>-FcNCl** and **C<sub>3</sub>-FcNCl** half-cell RFBs delivered excellent cycling stability; specifically, only 4.95% and 1.85% capacity fading was observed, equivalent to 0.381% and 0.14% per day capacity fading rate, respectively. However, significant capacity decay was observed in the **C<sub>1</sub>-FcNCl** half-cell RFB (23.99% capacity fading, equivalent to 1.85% per day fading rate). CV and <sup>1</sup>H-NMR post-cycling analyses were conducted to understand the possible chemical degradation of the **C<sub>x</sub>-FcNCl** electrolytes in the cycling process. As shown in Figure S8 – S10, <sup>1</sup>H-NMR spectra and CV curves of cycled **C<sub>2</sub>-FcNCl** and **C<sub>3</sub>-FcNCl** remained unchanged. However, a new peak at  $\delta = 2.81$  ppm was observed in the <sup>1</sup>H-NMR spectrum of cycled **C<sub>1</sub>-FcNCl electrolyte** (Figure S7), which is assigned to the dissociated (2, 4-cyclopentadiene-1-methyl)trimethylammonium ligand. Decomposition of the **C<sub>1</sub>-FcNCl** electrolyte was further confirmed by the remarkable peak intensity decrease in the post-cycling CV analysis (Figure S10A). Noticeably, Fe(OH)<sub>3</sub> was identified as an orange solid on the surface of electrodes and separator of the **C<sub>1</sub>-FcNCl** half-cell RFB after long-term cycling and confirmed by EDS tests (Figure S11). However, no apparent Fe(OH)<sub>3</sub> was observed in the cycled **C<sub>2</sub>-FcNCl** and **C<sub>3</sub>-FcNCl** half-cell RFBs (Figure S12), consistent with the half-cell RFB results.

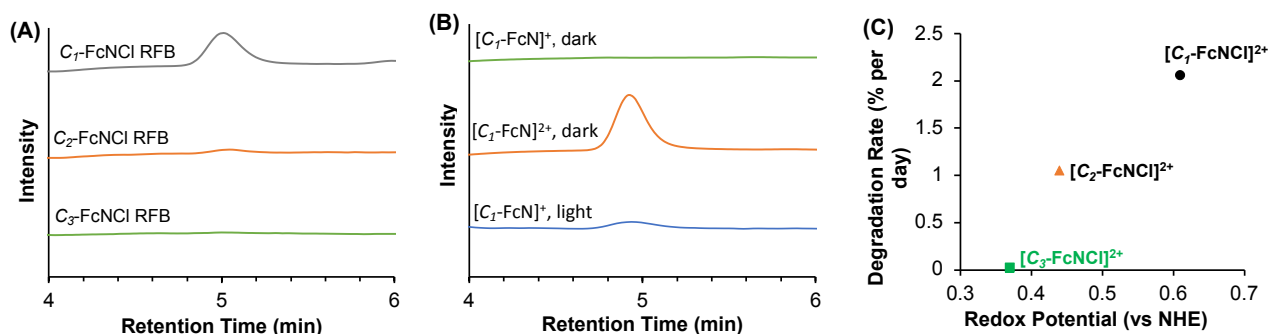


**Figure 3.** UV-Vis stability studies of the  $C_x$ -FcNCl catholytes in  $N_2$  atmosphere for 24 days. (A) Charged state  $[C_7-FcN]^{2+}$  under dark; (B) Charged state  $[C_2-FcN]^{2+}$  under dark; (C) Charged state  $[C_3-FcN]^{2+}$  under dark; (D) Concentration change of charged state and discharged state  $C_x$ -FcNCl catholytes under dark; (E) Concentration change of charged state and discharged state  $C_x$ -FcNCl catholytes under light; (F) Comparison of the degradation percentages.

We also performed full-cell AORFB studies of the  $C_x$ -FcNCl catholytes by pairing with 1,1'-di(trimethylammonium-propyl) 4,4'-bipyridium tetrachloride,  $[(NPr)_2V]Cl_4$  ( $E_{1/2} = -0.38$  V versus NHE), which has been reported as a robust viologen anolyte in viologen/ferrocene and viologen/TEMPO AORFBs.<sup>6,8,10</sup> The same trend of cycling stability as the half-cell RFBs was observed; specifically,  $C_7$ -FcNCl/ $(NPr)_2VCl_4$  AORFB showed much poorer stability than  $C_2$ -FcNCl/ $(NPr)_2VCl_4$  and  $C_3$ -FcNCl/ $(NPr)_2VCl_4$  AORFBs (see SI for detail). In 500 charge/discharge cycles at 40 mA/cm<sup>2</sup>, capacity fading of 13.53% was obtained in  $C_7$ -FcNCl/ $(NPr)_2VCl_4$  AORFB. However, only 2.57% and 1.03% capacity fading was observed in the  $C_2$ -FcNCl/ $(NPr)_2VCl_4$  and  $C_3$ -FcNCl/ $(NPr)_2VCl_4$  AORFBs, respectively (Figure S13 – S15). The capacity fading rate is equivalent to 1.03% per day for  $C_7$ -FcNCl/ $(NPr)_2VCl_4$  AORFB. However, only 0.18% per day for the  $C_2$ -FcNCl/ $(NPr)_2VCl_4$  AORFB and 0.073% per day for the  $C_3$ -FcNCl/ $(NPr)_2VCl_4$  AORFB.

Based on the battery testing results, the stability of  $C_x$ -FcNCl catholytes and their charged states in aqueous solutions was further investigated with UV-Vis measurements (Figures 3A – 3C

and Figures S23 – S25). Three absorptions were observed for the discharged state,  $[C_x\text{-FcN}]^{2+}$ , 259 nm (MLCT), 295 nm (LMCT), 653 (d-d) for  $[C_1\text{-FcN}]^{2+}$  (Figure 3A), 274 nm (MLCT), 291 nm (LMCT), 357 (d-d), 647 (d-d) for  $[C_2\text{-FcN}]^{2+}$  (Figure 3B), and 259 nm (MLCT), 295 nm (LMCT), 639 (d-d) for  $[C_3\text{-FcN}]^{2+}$  (Figure 3C). As shown in Figures 3D, 3F, S23A, S24A, and S25A, the discharged states,  $[C_x\text{-FcN}]^+$ , are highly stable, as minor decomposition was detected after standing for 24 days under dark in an  $N_2$  atmosphere. However, by monitoring the d-d transition absorption, the charged state  $[C_1\text{-FcN}]^{2+}$  and  $[C_2\text{-FcN}]^{2+}$  showed 49.6% or 2.06% per day and 25.4% or 1.05% per day decomposition in 24 days, respectively. In stark contrast, the charged state,  $[C_3\text{-FcN}]^{2+}$ , is significantly more stable (only 0.5% or 0.02% per day) (Figures 3A – 3D). It is noted that the degradation rates measured in the UV-Vis studies are consistent with the capacity fading rates obtained by the half-cell studies. The influence of light on the stability of  $C_x\text{-FcNCl}$  catholytes was also studied by UV-Vis tests. As shown in Figures 3E and 3F, the degradation of the charged state  $[C_x\text{-FcN}]^{2+}$  species was even accelerated by ambient light exposure. Specifically,  $[C_1\text{-FcN}]^{2+}$  was fully decomposed in 10 days, 30.1% and 3.0% decomposition were detected for  $[C_2\text{-FcN}]^{2+}$  and  $[C_3\text{-FcN}]^{2+}$  species, respectively. To our surprise, the discharged state  $[C_1\text{-FcN}]^+$  and  $[C_2\text{-FcN}]^+$  species are also light-sensitive, as 65.5% and 12.4% decomposition were observed, respectively, after 24 days of light exposure while no apparent decomposition was observed for  $C_3\text{-FcNCl}$ . Overall, the  $C_3\text{-FcNCl}$  catholyte delivered the best thermal- and photo-stability under both charged and discharged states among these Fc derivatives.



**Figure 4.** Gas chromatography (GC) studies and correlation of redox potential and stability. (A) GC curves of the gas phase samples collected from electrolyte reservoirs of the  $C_x\text{-FcNCl}$  half-cell RFBs after 13 days of cycling. (B) GC curves of gas phase samples upon keeping 0.50 M discharged state  $[C_1\text{-FcN}]^+$  and charged state  $[C_1\text{-FcN}]^{2+}$  water solutions in sealed vials for 5 days. (C) The correlation of the degradation rate of the charged state  $[C_x\text{-FcN}]^{2+}$  series measured by UV-Vis vs. their redox potential.

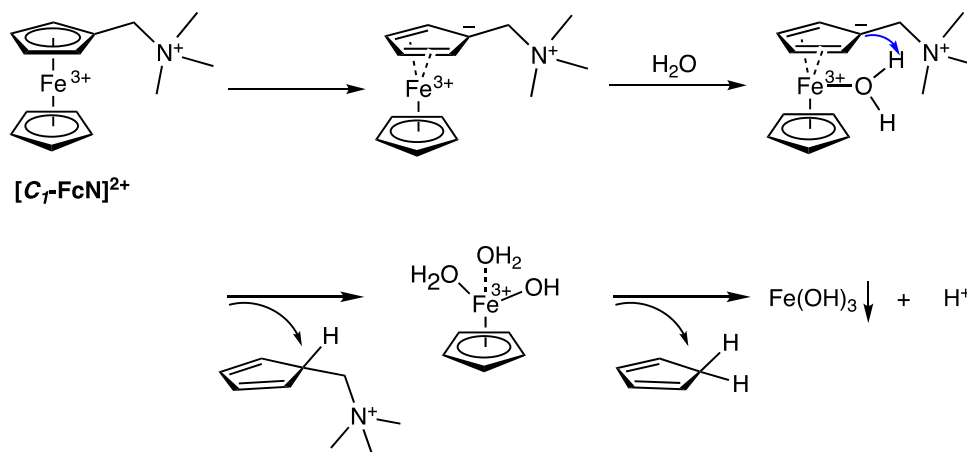
To gain a further understanding of the degradation mechanism of the  $C_x$ -FcNCl catholytes in AORFBs, gas phase samples were collected from the electrolyte reservoirs of the half-cell RFBs after long-term cycling tests for gas chromatography (GC) studies. As shown in Figure 4A, signals with a retention time of 4.98 min were observed in the GC curves of  $C_1$ -FcNCl and  $C_2$ -FcNCl samples. It was further characterized by GC-MS (Figure S26), and a signal of  $m/z = 66.0$  was detected, indicating the formation of free cyclopentadiene ( $C_5H_6$ ). Then, we further conducted GC tests with the gas phase samples collected from vials sealed with discharged state  $[C_1\text{-FcN}]^+$  and charged state  $[C_1\text{-FcN}]^{2+}$ . As shown in Figure 4B, no free  $C_5H_6$  was detected from the  $[C_1\text{-FcN}]^+$  sample after standing in the dark for 5 days (green curve). However,  $C_5H_6$  was detected from the samples of  $[C_1\text{-FcN}]^{2+}$  under dark (orange curve) and  $[C_1\text{-FcN}]^+$  under light (blue curve). These findings are consistent with the results of UV-Vis studies.

Besides the thermal- and photo-induced degradation of  $C_x$ -FcNCl catholytes, we observed that the cycling stability of  $C_1$ -FcNCl half-cell RFB was sensitive to  $O_2$ . As shown in Figure S27, when the environmental  $O_2$  content was increased to 20 ppm, dramatic decay of the battery capacity was observed. UV-Vis studies indicate that  $O_2$  could accelerate the degradation of the charged state  $[C_1\text{-FcN}]^{2+}$  (Figure S28). It was also found that the electron-rich discharged states,  $[C_2\text{-FcN}]^+$  and  $[C_3\text{-FcN}]^+$ , can be partially oxidized by  $O_2$ . However, the discharged state  $[C_1\text{-FcN}]^+$  and charged state  $[C_2\text{-FcN}]^{2+}$  and  $[C_3\text{-FcN}]^{2+}$  were not sensitive to  $O_2$  (Figure S28 – S30).

## Discussion

According to the above experimental results, it is reasonable to conclude that thermal-induced  $Cp^-$  ligand dissociation of the charged state  $Fc^+$  is a possible degradation pathway under the dark conditions for the Fc catholytes in AORFBs. It is also reasonable to argue that the 18-electron configuration of the discharged state, Fc, is much more stable than the 17-electron configuration of  $Fc^+$ . Within the  $C_x$ -FcNCl series, thermal ligand dissociation takes place in the order of  $[C_1\text{-FcN}]^{2+} > [C_2\text{-FcN}]^{2+} > [C_3\text{-FcN}]^{2+}$ , consistent with the ligand strength order of  $C_1\text{-Cp}^- < C_2\text{-Cp}^- < C_3\text{-Cp}^-$ . The degradation mechanism in the case of  $C_1$ -FcNCl is proposed in Scheme 1. After the dissociation of the  $C_1\text{-Cp}^-$  ligand, the open site of the electrophilic  $Fe^{3+}$  center of  $Fc^+$  can be attacked by  $H_2O$  in an aqueous solution. The coordinated  $H_2O$  becomes more acidic. It is believed that intramolecular deprotonation by the dissociated  $C_1\text{-Cp}^-$  anion ligand leads to the formation of the protonated product, (trimethylammonium)methyl cyclopentadiene. The other

plain Cp<sup>-</sup> ligand will undergo the same reaction and eventually lead to the formation of the Fe(OH)<sub>3</sub> precipitate. Particularly, C<sub>1</sub>-FcNCl with the least donating C<sub>1</sub>-Cp<sup>-</sup> ligand experienced the fastest degradation. Regarding battery performance, the cycling stability is primarily limited by the charged state.



**Scheme 1.** Proposed thermal degradation mechanism of  $[C_1-FcN]^{2+}$ , the charged state of C<sub>1</sub>-FcNCl.

Under the light condition, it is believed the metal-to-ligand charge transfer (MLCT) activates the bonding between the Fe<sup>2+</sup> or Fe<sup>3+</sup> center and the Cp ligands and triggers the photo-induced ligand dissociation. Photolytic ligand dissociation is greater than the thermal ligand dissociation as even the discharged state (the oxidation state of Fe<sup>2+</sup>) such as  $[C_3-FcN]^+$  becomes unstable. Then subsequent reactions are similar to those in the thermal degradation. Thereby, avoiding light exposure is critical to mitigating the photolytic ligand dissociation and should be aware of in future flow battery studies.

For the future development of coordination compound electrolytes, it is important to develop a strong ligand-metal coordination sphere that could alleviate the performance decay of coordination catholyte molecules. It is also noticed that the redox potential can serve as a reporter for the ligand strength and is consistent with the degradation rate of the C<sub>x</sub>-FcNCl series (Figure 4C) measured by UV-Vis tests. The redox potential and chemical stability of the C<sub>1</sub>-FcNCl series can serve as the benchmark for future coordination compound electrolytes. It is worth noting that within the C<sub>x</sub>-FcNCl series, the increased ligand-metal coordination stability scarifies the oxidation potential, e.g., C<sub>3</sub>-FcNCl (0.37 V, stable) versus C<sub>1</sub>-FcNCl (0.61 V, unstable). In

addition, electron rich  $C_3$ -FcNCl becomes more  $O_2$  sensitive than  $C_7$ -FcNCl. Thus, it is important to exclude  $O_2$  induced side reactions in flow battery studies.

## Conclusions

In summary, we reported the detailed degradation mechanism of Fc catholytes in pH-neutral AORFBs. Thermal- and photo-induced  $C_x$ -Cp<sup>-</sup> ligand dissociation pathways of the charged state ( $Fe^{3+}$ ) and light-excited state ( $Fe^*$ ) species were experimentally confirmed. Electron-withdrawing functional groups weaken the coordination between the  $Fe^{3+}$  or  $Fe^{2+}$  center and the  $C_x$ -Cp<sup>-</sup> ligand of the charged state and light-excited state. Thus, the  $C_x$ -Cp<sup>-</sup> ligands can be irreversibly replaced by nucleophiles. However, electron-donating groups stabilize the  $Fe^{3+}$  or  $Fe^{2+}$  center of the Fc molecules and hinder the thermal- and photo-induced ligand dissociation reactions. This work not only reveals the structure-performance relationship and degradation mechanisms of the Fc catholytes in aqueous electrolytes but also provides important guidance for the design of high-performance Fc and other coordination compound electrolytes and the operation condition of flow batteries.

## Associated Content

**Supporting Information.** The Supporting Information, including the ferrocene compounds synthesis and characterization, electrochemical study and battery test details, post-cell analysis is available free of charge via the Internet at <http://pubs.acs.org>.

## Experimental Section

**Chemicals and Manipulations.** All chemicals were purchased from Sigma-Aldrich, TCI, and Oakwood, stored in an argon filled glove box and used directly. Deionized water was degassed by purging with  $N_2$  before use. All experimental operations were conducted under an  $N_2$  atmosphere. Conductivities and pH values of the electrolytes were measured using a Mettler Toledo conductivity meter or a Mettler Toledo pH meter at room temperature.  $^1H$ -NMR spectra were collected using a Bruker 500 MHz NMR spectrometer. Elemental analysis was performed by Atlantic Microlab. FT-IR spectra were collected on a PerkinElmer Spectrum 100 FT-IR spectrometer with a universal ATR sampling accessory. UV-Vis spectra were collected using an Agilent Cary 100 UV-Vis spectrometer. Gas chromatography (GC) was measured via an SRI gas chromatography system 8610C equipped with a molecular sieve 13x packed column, a HayesSep

D packed column, and a flame ionization detector (FID) using argon as the carrier gas. The GC-MS measurements were conducted in a Shimadzu GCMS-QP5000 system using helium as the carrier gas. Energy dispersive spectroscopy (EDS) measurement was conducted on an FEI Quanta 650 (FEI, USA) at the Microscopy Core Facility of Utah State University (WD 10mm, voltage 10-20 kV). All electrochemical experiments were conducted with Gamry 5000E or 1000E potentiostat. Battery tests were conducted using a Land battery testing system.

**Synthesis of (Ferrocenylmethyl)trimethylammonium Chloride ( $C_1$ -FcNCl).** Iodomethane ( $CH_3I$ , 3.7 mL, 60.0 mmol, 1.2 eq.) in 100.0 mL diethyl ether was added dropwise to a solution of N, N-dimethylaminomethylferrocene (12.2 g, 50.0 mmol, 1.0 eq.) in 300.0 mL diethyl ether under rapid stirring at 0 °C. After stirring the reaction mixture at room temperature for 6 h, the produced orange precipitate was filtered, washed with 3 × 50.0 mL diethyl ether, and dried under vacuum. The iodide salt was converted to chloride salt by anion exchange. The  $C_1$ -FcNCl product was obtained as a bright yellow powder, 14.4 g (98% yield). The  $^1H$ -NMR spectrum and elemental analysis data are the same as previously reported.<sup>7</sup>

**Synthesis of (Ferrocenylethyl)dimethylamine.**  $tBuLi$  (66.0 mL, 1.7 M in hexane, 1.05 eq.) solution was added dropwise into a solution of ferrocene (20.0 g, 107.0 mmol, 1.0 eq.) in 200.0 mL dry THF at 0 °C. The reaction mixture was warmed up to room temperature and stirred for 30 min. And then, a solution of 2-chloro-N, N-dimethylethylamine (13.9 g, 128.0 mmol, 1.2 eq.) in 40.0 mL dry THF was added dropwise at 0 °C. After stirring for another 14 h at room temperature, 5.0 mL  $H_2O$  was carefully added to quench the reaction. The mixture was dried under a vacuum. The residue was dissolved in a 250.0 mL 1.0 M HCl solution and washed with 150.0 mL hexane three times. Then, the pH of the aqueous solution was turned to > 7.0 and extracted with 3 × 200.0 mL  $CH_2Cl_2$ . The organic phase was combined and dried with  $Na_2SO_4$ . The solvent was removed to give the product as a deep brown liquid (18.2 g, 66% yield).  $^1H$ -NMR ( $CDCl_3$ , 500 MHz):  $\delta$  (ppm), 2.35 (s, 6H), 2.49 ~ 2.61 (m, 4H), 4.01 ~ 4.21 (m, 9H).

**Synthesis of (2-Ferrocenyl-ethyl)trimethylammonium Chloride ( $C_2$ -FcNCl).** Iodomethane ( $CH_3I$ , 3.7 mL, 60.0 mmol, 1.2 eq.) in 100.0 mL diethyl ether was added dropwise to a solution of (ferrocenylethyl)dimethylamine (12.9 g, 50.0 mmol, 1.0 eq.) in 300.0 mL diethyl ether under rapid stirring at 0 °C. The reaction mixture was stirred at room temperature for 6 h. The resulting orange precipitate was filtered, washed with 50.0 mL diethyl ether three times, and dried under vacuum. The  $C_2$ -FcNCl product was obtained through anion-exchange as an orange

powder (15.0 g, 98% yield).  $^1\text{H-NMR}$  ( $\text{D}_2\text{O}$ , 500 MHz):  $\delta$  (ppm), 2.41 (m, 4H), 2.83 (t,  $J = 8.0$  Hz, 2H), 3.09 (s, 9H), 3.42 (d,  $J = 8.5$  Hz, 2H), 4.08 ~ 4.27 (m, 9H). Elemental analysis for  $\text{C}_2\text{-FcNCl}$ , Calculated: C 58.56, H 7.21, N 4.55. Found: C 58.48, H 7.47, N 4.46.

**Synthesis of 3-Chloro-propylferrocene.** A solution of 3-chloropropanoyl chloride (13.0 g, 102.0 mmol, 1.02 eq.) in 50.0 mL dry  $\text{CH}_2\text{Cl}_2$  was added into a suspension of  $\text{AlCl}_3$  (14.7 g, 110.0 mmol, 1.1 eq.) in 100.0 mL dry  $\text{CH}_2\text{Cl}_2$ . After stirring at room temperature for 2 h, the mixture was transferred into a solution of ferrocene (18.6 g, 100.0 mmol, 1.0 eq.) in 150.0 mL dry  $\text{CH}_2\text{Cl}_2$  at 0 °C. The reaction mixture was warmed up to room temperature and stirred overnight. Then, the mixture was cooled to 0 °C again, and a solution of  $\text{NaBH}_4$  (3.8 g, 100.0 mmol, 1.0 eq.) in 50.0 mL diglyme was added. After stirring at room temperature for another 4 h, the mixture was quenched with 150.0 mL 1.00 M HCl solution and extracted with 100.0 mL  $\text{CH}_2\text{Cl}_2$  three times. The organic phase was combined and dried with  $\text{Na}_2\text{SO}_4$ . After removal of the solvent, the product was obtained as a deep brown liquid. 21.8 g, 83% yield.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm), 1.78 ~ 2.17 (m, 2H), 2.25 ~ 2.66 (m, 2H), 3.36 ~ 3.76 (m, 2H), 3.91 ~ 4.41 (m, 9H).

**Synthesis of (3-Ferrocenyl-propyl)trimethylammonium Chloride ( $\text{C}_3\text{-FcNCl}$ ).** 3-Chloro-propylferrocene (2.6 g, 10.0 mmol, 1.0 eq.) and  $\text{Me}_3\text{N}$  in THF solution (2.00 M, 25.0 mL, 5.0 eq.) were sealed in an autoclave (8 autoclaves were simultaneously setup). The reactors were kept at 85 °C for 3 days. The  $\text{C}_3\text{-FcNCl}$  product was obtained through filtration as orange powder. 22.7 g, 88% yield.  $^1\text{H-NMR}$  ( $\text{D}_2\text{O}$ , 500 MHz):  $\delta$  (ppm), 1.86 ~ 1.98 (m, 2H), 2.33 ~ 2.47 (m, 2H), 3.02 (m, 9H), 3.25 (t,  $J = 7.5$  Hz, 2H), 3.67 ~ 4.66 (m, 9H). Elemental analysis for  $\text{C}_3\text{-FcNCl}$ , Calculated: C 59.74, H 7.52, N 4.35. Found: C 59.63, H 7.71, N 4.28.

**Cyclic Voltammetry.** All CV measurements were conducted in 0.50 M  $\text{NH}_4\text{Cl}$  electrolyte solutions under  $\text{N}_2$  atmosphere using a Gamry 1000E potentiostat with a three-electrode system: a PEEK-encased 3.0 mm diameter glassy carbon working electrode, a glassy carbon rod counter electrode, and an Ag/AgCl reference electrode. Before each CV scan, the working electrode was cleaned by polishing with 0.05 micron alumina powder and rinsing with deionized water. Potential values were corrected to NHE using a methyl viologen ( $\text{MV}^{2+}$ ) internal standard with a known redox potential at -0.45 V vs. NHE.

**Levich Equation to Measure the Diffusion Coefficient ( $D$ ).** The linear sweep voltammetry (LSV) studies were conducted using a Gamry 5000E potentiostat in a three-electrode configuration, a 5.0 mm Teflon-encased glassy carbon disc working electrode (Pine Research Instrumentation),



a glassy carbon rod counter electrode, and an Ag/AgCl reference electrode. Before each measurement, the working electrode was polished with 0.05 micron alumina powder and rinsed with deionized water. The electrode was rotated from 300 to 2400 rpm with an increment of 300 rpm using a Pine MSR rotation controller. LSV curves were collected at 5 mV·s<sup>-1</sup> scan rate. At each rotation rate, the LSV was recorded three times to ensure repeatability.

Diffusion coefficients ( $D$ ) were obtained from the slopes of Levich plots based on the RDE data of 1.0 mM  $C_x$ -FcNCl in 0.50 M NH<sub>4</sub>Cl. The Levich equation is written as:

$$i = (0.620)nFAC_0D^{2/3}\omega^{1/2}\nu^{-1/6} \quad (1)$$

Where  $i$  is the limiting current density from the RDE tests,  $A$  is the area of the RDE (glassy carbon, 0.196 cm<sup>2</sup>),  $n$  is the number of charges ( $n = 1$ ),  $F$  is 96485 C·mol<sup>-1</sup>,  $C_0$  is the concentration of compounds ( $C_0 = 1.0 \times 10^{-6}$  mol·cm<sup>-3</sup>),  $D$  is the diffusion coefficient (cm<sup>2</sup>/s),  $\omega$  is the angular rotation rate of the electrode, and  $\nu$  is the kinematic viscosity (0.0100 cm<sup>2</sup>·s<sup>-1</sup> for 0.50 M NH<sub>4</sub>Cl solution).

The slope of  $i - \omega^{1/2}$  curve is  $(0.620)nFAC_0D^{2/3}\nu^{-1/6}$ .

**Nicholson's Method to Estimate Electron Transfer Rates Constants ( $k^0$ ).** Following the Nicholson's method, CV curves of 4.0 mM  $C_x$ -FcNCl in 0.50 M NH<sub>4</sub>Cl were collected at a scan rate range of 5 mV·s<sup>-1</sup> - 500 mV·s<sup>-1</sup>. The kinetic parameter,  $\Psi$ , was calculated by the potential gap between reductive and oxidative peaks (peak-to-peak separation,  $\Delta E_p$ ) through Equation 2. And then, based on the relationship between  $\Psi$  and  $\nu^{-1/2}$  (Equation 3),  $k^0$  was calculated using the slope of  $\Psi$  vs.  $\nu^{-1/2}$  plot.

$$\Psi = (-0.6288 + 0.0021\Delta E_p)/(1 - 0.017\Delta E_p) \quad (2)$$

$$\Psi = k^0 [\pi D n F / RT]^{-1/2} \nu^{1/2} \quad (3)$$

where  $F$ ,  $D$ , and  $n$  are defined in equation 1, and  $\nu$  represents the scan rate.

**Half-cell Flow Battery Tests.** The half-cell RFBs were constructed with two carbon electrolyte chambers, two graphite felt electrodes (SGL Carbon Group, Germany), a piece of Selemion AMV anion-exchange membrane sandwiched between the graphite felts. Two copper plates were used as current collectors. Each carbon chamber was connected with an electrolyte reservoir using a piece of Viton tubing. The electrolyte reservoir is home designed and is a 10.0 mL glass tube (2 cm inner diameter). The active area of the cell was 10 cm<sup>2</sup>. A Masterflex L/S peristaltic pump (Cole-Parmer, Vernon Hills, IL) was used to press the Viton tubing to circulate the electrolytes through the electrodes at a flow rate of 60.0 mL·min<sup>-1</sup>. In each side of the battery,

12.0 – 13.0 mL of 1.00 M  $\text{NH}_4\text{Cl}$  electrolyte containing 0.50 M active material was employed. The flow cell was galvanostatically charged/discharged at room temperature within the voltage range of -0.30 – 0.30 V under 10 to 50  $\text{mA}\cdot\text{cm}^{-2}$  current density. Post-cell studies of the  $\text{C}_x\text{-FcNCl}$  electrolytes were conducted after full discharge.

**Full-cell Flow Battery Tests.** The setup of  $\text{C}_x\text{-FcNCl}/(\text{NPr})_2\text{VCl}_4$  AORFBs is the same as the half-cell batteries. In each battery, 12.0 – 13.0 mL 0.5 M  $\text{C}_x\text{-FcNCl}$  and 0.5 M  $(\text{NPr})_2\text{VCl}_4$  with 1.0 M  $\text{NH}_4\text{Cl}$  supporting electrolyte were used as a catholyte and an anolyte, respectively. The batteries were galvanostatically charged / discharged within the voltage range of 0.10 - 1.30 V for the  $\text{C}_1\text{-FcNCl}/(\text{NPr})_2\text{VCl}_4$  RFB, 0.10 - 1.20 V for the  $\text{C}_2\text{-FcNCl}/(\text{NPr})_2\text{VCl}_4$  RFB, and 0.10 - 1.05 V for the  $\text{C}_3\text{-FcNCl}/(\text{NPr})_2\text{VCl}_4$  AORFB at current densities of 10  $\text{mA}\cdot\text{cm}^{-2}$  to 50  $\text{mA}\cdot\text{cm}^{-2}$

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