

Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

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Effects of Gamma Radiation on Electrochemical Properties of Ionic Liquids

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Ionic liquids/electrochemical window/irradiation

Summary.

The electrochemical properties of ionic liquids (ILs) make them attractive for possible replacement of inorganic salts in high temperature molten salt electrochemical processing of nuclear fuel. To be a feasible replacement solvent, ILs need to be stable in moderate and high doses of radiation without adverse chemical and physical effects. Here, we exposed seven different ILs to a 1.2 MGy dose of gamma radiation to investigate their physical and chemical properties as they related to radiological stability. The

azolium-based ILs experienced the greatest change in appearance, but these ILs were chemically more stable to gamma radiation than some of the other classes of ILs tested, due to the presence of aromatic electrons in the azolium ring. All the ILs exhibited a decrease in their conductivity and electrochemical window (at least 1.1 V), both of which could affect the utility of ILs in electrochemical processing. The concentration of the irradiation decomposition products was less than 3 mole %, with no impurities detectable using NMR techniques.

Introduction

The field of ionic liquids (ILs) originally received notice as a low temperature replacement for high temperature molten inorganic salt electrochemistry [1,2]. ILs have unique solvent properties that have been further studied and exploited as replacement solvents in a wide range of applications such as solar power [3], batteries [4], and gas adsorption [5]. One of the most promising physical properties of ILs is their negligible vapor pressure [6] and, paired with the synthesis of stable hydrophobic ILs [7], their replacement for organics became possible as solvents in liquid/liquid separations [8], gas/liquid separations [9], and organic syntheses [10]. The practical use of ILs in aqueous/IL separation for metal species was soon ended due to their complex mechanisms of extraction, which in most cases lead to loss of the IL [11].

The depressed melting points of ILs make them a prime candidate for electrochemical processes, as ILs can act as both a bulk solvent and the electrolyte at or near ambient

temperatures. One of the current methods to reprocess nuclear fuels is through electrochemical processing using an inorganic eutectic for the solvent and electrolyte at temperature greater than 600 °C [12]. Previous reports have investigated the electrochemical properties (i.e., reduction/oxidation potentials) of several actinides (U, Np, and Pu) in select ILs [13,14], and in some cases ILs were found to stabilize traditionally unstable actinide species [15].

For ILs to be feasible replacements for inorganic eutectic melts currently used in electrochemical refining of nuclear fuel, the ILs need to exhibit minimal radiological degradation. A few ILs were previously subjected to variable intensities of gamma irradiation [16]. One IL was subjected to alpha, beta, and gamma irradiation (alpha dose= 1 kGy, beta and gamma dose= 400 kGy) [17]. In all previous works, the results showed minimal changes to the physical properties, (i.e., calculated G-values, NMR shifts, spectroscopic shifts, etc.) but the effects of irradiation on the IL electrochemical window were not reported. Another paper investigated the effect of ionized radicals on the chemical stability of different ILs in attempts to understand the mechanisms of decomposition in radiological fields [18].

In the present work, we investigated several different classes of ILs and explore the effects of high gamma irradiation equivalent to an expected annual dose in processing of commercial fuel (~1.2 MGy) on their physical properties and electrochemical windows.

We selected two subsets of ILs, azolium-based and bis(trifluoromethylsulfonyl)imide ([NTf₂]⁻)-based, as these are the most commonly used ILs in radiological applications. After irradiation, all ILs showed a significant increase in color and a large decrease in conductivity (by at least one order of magnitude), but degradation products are below the NMR detection limit (< 3 mole %). The gamma irradiation decreased the electrochemical window between 19% and 61%, relating to at least a 1.1 V decrease.

Experimental

Chemicals

All ILs were used as received from the vendors. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₂mim][NTf₂]) (99 % purity) was purchased from Covalent Associates. 1-Methyl-3-octylimidazolium hexafluorophosphate ([C₈mim][PF₆]) (99 %), 1-hexyl-3-methylimidazolium chloride ([C₆mim][Cl]) (98 %), 1-ethyl-3-methylimidazolium tetrafluoroborate ([C₂mim][BF₄]) (98 %), triethylsulfonium bis(trifluoromethylsulfonyl)imide ([S₂₂₂][NTf₂]) (98 %), 1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide ([C₄C₁pyr][NTf₂]) (98 %), and 1-butyl-3-methylimidazolium 2-(2-methoxyethoxy)ethylsulfate (EcoEng41M) (98 %) were all purchased from Solvent Innovation. Butyltrimethylammonium bis(trifluoromethylsulfonyl)imide ([N₄₁₁₁][NTf₂]) (99 %) was purchased from IoLiTec. No special handling

techniques (e.g., inert atmosphere) or preparation (e.g., heating with reduced pressure) were used during experimental preparation or storage of the ILs. Ferrocene, acetonitrile, and methanol were purchased from Aldrich and used as received.

⁶⁰Co Irradiation

Aliquots of each IL were placed into 30-mL glass vials, without caps, and all the vials were put into a glass secondary container (also without a cap) before being lowered into the chamber of the irradiator. (The system was not sealed during irradiation as unknown volumes of gaseous compounds could be released, pressurizing the containers. This allowed for absorption of atmospheric gases during irradiation, such as oxygen and water, both compounds can effect the radiolysis pathways.) The samples were irradiated to 1.2 MGy gamma dose over 273 hours of exposure, from a 438.5 Gy/h ⁶⁰Co source, before being removed and capped. The 1.2 MGy dose is approximately equivalent to one year of continuous processing of uranium-based fuels in a commercial processing facility.

UV-Vis

An Ocean Optics USB2000+ Miniature Fiber Optic UV-Vis spectrometer was used to collect spectra. Four spectra were collected of each sample and averaged using Ocean Optics SpectraSuite operating software. Prior to collecting ultraviolet visible spectra, background spectra of cuvetts

were collected and automatically subtracted from subsequent spectra.

Each IL was diluted volumetrically 200 fold with methanol before analysis. A 1 cm quartz cuvet was used which was cleaned between analyses. The cleaning procedure, after discarding the IL from the cuvet, was to rinse cuvet with methanol and water, then submerged in a solution of Alconox and cleaned with a test tube brush. The cuvet was finally rinsed with DI water, dried, and put in the UV-Vis to ensure no contaminant absorbance.

Conductivity

Conductivity measurements were taken using a Markson Model 1052 conductivity meter. Approximately 10 mL of each IL was transferred into a clean container and measured at ambient temperature.

NMR

NMR spectra were collected on an Avance 300 MHz (7 Tesla) Bruker magnet. Samples for NMR analysis were dissolved in deuterated dimethylsulfoxide.

Electrochemical

Electrochemical measurements were conducted using a Gamry Reference 600 potentiostat with Bioanalytical RDE-2 electrode stand equipped with a glassy carbon (GC) working electrode (3 mm diameter) and a Pt wire auxiliary and quasi-reference. Samples (1 mL) of IL (pre- and post-irradiated) were purged with N₂ for 1 h prior to measuring the electrochemical windows. The electrochemical

windows potentials are reported when the current reached 30 μA . Stock solution of 0.06 M ferrocene (FeCp_2) in acetonitrile was used as an internal standard. After each cyclic voltammogram (CV) was collected, 200 μL of the FeCp_2 solution (yielding a 10 mM FeCp_2 in the IL) was added to the IL followed by a five minute purge with N_2 . Following the five minute purge, the $\text{FeCp}_2/\text{FeCp}_2^+$ was measured at all measured scan rates. All electrochemical scans were set so $\text{FeCp}_2/\text{FeCp}_2^+$ was at +0.0 V.

Results and Discussion

Physical Properties

There was significant change in the color of the azolium-based ILs after gamma irradiation, Figure 1. The bathochromic shift in the azolium-based ILs was confirmed in the UV-vis spectra, supplemental data. The molar absorptivity of the $\pi - \pi^*$ transition is known to be large for azolium-based ILs, which contributes to the significant coloration of the ILs [19]. The bathochromic shift exhibited by all irradiated ILs is presumably due to a shift in the energy levels of the excited states. The excited π^* state is more affected by dipole-dipole interactions and/or changes in the hydrogen-bonding environment than the π state. If the polarity of the irradiated ILs increased, the π^* energy levels are decreased and the absorbance shifts to a longer wavelength [20]. Less dramatic color changes were observed in the $[\text{N}_{4111}]^+$ and the $[\text{C}_4\text{C}_1\text{pyr}]^+$ -based ILs. The cause of the significant color change seen in the $[\text{S}_{222}]^+$

based IL is unknown. The changes in the IL structure were minimal and the concentration of chromophoric specie(s) were below detection limits with ^1H and ^{13}C -NMR, supporting a very large molar absorptivity of the colored species.

A large decrease in the conductivity was observed after radiological exposure, as shown in Table 1. All samples showed a significant decrease in the conductivity after irradiation. Although the water contents were not measured pre- and post-irradiation, it is believed that a higher water content was present in the pre-irradiated ILs as no special handling of the ILs was taken, the hygroscopic nature of these ILs would allow them to absorb atmospheric H_2O . The absorbed H_2O would be expected to affect the physical properties of the IL by decreasing the viscosity through solvation of the ions. Solvation of the ions should increase the conductivity as the solvated ions have increased mobility because of the lower viscosity. The presence of H_2O in the ILs during exposure to the radiation could introduce different pathways for degradation through the formation of $\text{H}\cdot$ and/or $\cdot\text{OH}$ radicals. The radiologically degraded H_2O will decrease the water content, thus increasing the viscosity of the ILs and lowering the conductivity. The radiological degraded products could also increase the viscosity, via recombination of radiological intermediates with bulk ILs, thus could decrease the conductivity of the IL. More rigorous studies are needed to better understand the effect of solvated water in ILs exposed to a radiological field. A better method for

excluding H₂O from the ILs during irradiation, could help to clarify changes in conductivity.

Electrochemical

Gamma irradiation decreased the electrochemical window of all ILs by at least 1.1 V, Table 2. The decrease in the windows is not specific to the cation (anode potential) or the anion (cathode potential), as both potentials decreased after irradiation (see Figure 2). The most radiologically stable cations were the aromatic, imidazolium, and cyclic non-aromatic, pyridinium, but our measurements show these cations are not the most electrochemically stable (i.e., the highest anodic potential). The azolium-based ILs yield a more radiological stable cation as the π electrons have the ability to dissipate the energy associated with radiolysis [21]. The relatively greater radiation resistance of the pyrrolidinium-based IL is not understood, as cyclic non-aromatics do not traditionally exhibit increased radiological stability and merits further investigation. Post irradiation, a trend in the cathode potentials is not clear (i.e., the range of decrease for the [NTf₂]-based ILs was 0.5 to 1.4 V).

Conclusions

For ILs to become a viable replacement solvent in nuclear processing, the affects of gamma irradiation need to be better understood. In the ILs tested here, there was a significant color change after irradiation, but the concentrations of contaminant(s) was below detection

limits (< 3 mole %). The color change was greatest in the aromatic azolium systems, but at this level of irradiation, the color change was independent of anion identity. The presence of water and oxygen during irradiation not only increased the complexity of the systems, via other molecules that could react to yield highly reactive intermediates, but also could affect the physical properties that were investigated here. In all cases, both the cathode and anode potentials decreased after irradiation. The aromatic contributions of the azolium-based ILs provided stability not seen in the other ILs tested here, while the cyclic characteristics of the pyridinium-based IL had some increased stability compared to the onium-based IL. At this time, no conclusions can be made relating to stability of the anions and further work is needed to understand the anion stability. Due to the lack of controlling the water content of the ILs, the effects of water on these systems during irradiation are not known and could be a reason for the large variation of results and further studies investigating the effect of water should be implemented.

References

1. Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L.:
Dialkylimidazolium chloroaluminate melts: a new class of
room-temperature ionic liquids for electrochemistry,
spectroscopy and synthesis. *Inorg. Chem.* **21**, 1263 (1982).
2. Hussey, C. L.: Room-temperature molten salt systems. *Adv.
Molten Salt Chem.* **5**, 185 (1983).
3. Van Valkenburg, M. E.; Vaughn, R. L.; Williams, M.; Wilkes,
J. S.: Thermochemistry of ionic liquid heat-transfer fluids.
Thermochimica Acta **425**, 181 (2005).
4. Seki, S.; Ohno, Y.; Kobayashi, Y.; Miyashiro, H.; Usami, A.;
Mita, Y.; Tokuda, H.; Watanabe, M.; Hayamizu, K.; Tsuzuki,
S.; Hattori, M.; Terada, N.: Imidazolium-based room-
temperature ionic liquid for lithium secondary batteries. *J.
Electrochem. Soc.* **154**, A173 (2007).
5. Blanchard, L. A.; Hancu, D.; Beckmann, E. J.; Brennecke, J.
F.: Green processing using ionic liquids and CO₂. *Nature*,
399, 28 (1999).
6. Earle, M. J.; Esperanca, J. M. S. S.; Gilea, M. A.; Canongia L.,
Jose N.; Rebelo, Luis P. N.; Magee, Joseph W.; Seddon, K.
R.; Widegren, J. A.: The distillation and volatility of ionic
liquids. *Nature* **439**, 831 (2006).
7. Wilkes, J. S.; Zaworotko, M. J.: Air and water stable 1-ethyl-
3-methylimidazolium based ionic liquids. *Chem. Commun.*
965 (1992).
8. Dai, S.; Ju, Y. H.; Barnes, C. E.: Solvent extraction of
strontium nitrate by a crown ether using room-temperature
ionic liquids. *Dalton Trans.* 1201 (1999).

9. Anthony, J. L.; Anderson, J. L.; Maginn, E. J.; Brennecke, J. F.: Anion effects on gas solubility in ionic liquids. *J. Phys. Chem. B.* **109**, 6366 (2005).
10. Chiappe, C.: Organic synthesis : ionic liquids in organic synthesis : effects on rate and selectivity. *Ionic Liquids in Synthesis* (2nd Edition) Wiley-VCH GmbH & Co. Weinheim, p. 265-292, 2008.
11. Li, Z.; Chang, J.; Shan, H.; Pan, J.: Advance of room temperature ionic liquid as solvent for extraction and separation. *Rev. Anal. Chem.* **26**, 109 (2007).
12. Ackerman, J. P.: Chemical basis for pyrochemical reprocessing of nuclear fuel. *Ind. Eng. Chem. Res.* **30**, 141 (1991).
13. Nikitenko, S. I.; Moisy, P.: Formation of higher chloride complexes of Np(IV) and Pu(IV) in water-stable room-temperature ionic liquid [BuMeIm][Tf₂N]. *Inorg. Chem.* **45**, 1235 (2006).
14. Oldham, W. J., Jr.; Costa, D. A.; Smith, W. H.: Development of room-temperature ionic liquids for applications in actinide chemistry. ACS Symposium Series 818(Ionic Liquids), American Chemical Society Washington D.C. 188-98, 2002.
15. Costa, D. A.; Smith, W. H.; Dewey, H. J.: Actinide chemistry in the EMIC/AlCl₃ room temperature ionic liquid. *Electrochem. Soc. Proc.* **99-41**, 80 (2000).
16. Berthon, L.; Nikitenko, S. I.; Bisel, I.; Berthon, C.; Faucon, M.; Saucerotte, B.; Zorz, N.; Moisy, P.: Influence of gamma irradiation on hydrophobic room-temperature ionic liquids [BuMeIm][PF₆] and [BuMeIm][(CF₃SO₂)₂N]. *Dalton Trans.* 2526 (2006).
17. Allen, D.; Baston, G.; Bradley, A. E.; Gorman, T.; Haile, A.; Hamblett, I.; Hatter, J. E.; Healey, M. J. F.; Hodgson, B.; Lewin, R.; Lovell, K. V.; Newton, B.; Pitner, W. R.; Rooney, D. W.; Sanders, D.; Seddon, K. R.; Sims, H. E.; Thied, R. C.:

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- An investigation of the radiochemical stability of ionic liquids. *Green Chem.*, **4**, 152 (2002).
18. Behar, D.; Gonzalez, C.; Neta, P.: Reaction kinetics in ionic liquids: pulse radiolysis studies of 1-butyl-3-methylimidazolium salts. *J. Phys. Chem. A* **105**, 7607 (2001).
19. Katoh, R.: Absorption spectra of imidazolium ionic liquids. *Chem. Lett.* **36**, 1256 (2007).
20. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C.; Eds.; in *Spectrometric Identification of Organic Compounds*, J. W. Wiley: New York, p. 91-96, 1991.
21. Spinks, J. W. T. and Woods, R. J. in *An Introduction to Radiation Chemistry* Second Edition, John Wiley & Sons, New York, p. 387-391, 1976.

Table 1. Changes in conductivity after gamma irradiation of various ILs

Ionic Liquid	Before Irradiation Conductivity (mS/cm)	After Irradiation Conductivity (mS/cm)
EcoEng41M	0.970	0.014
[C ₈ mim][PF ₆]	0.314	0.018
[C ₆ mim][Cl]	0.320	0.012
[C ₂ mim][BF ₄]	0.521	0.007
[C ₂ mim][NTf ₂]	8.97	0.016
[N ₄₁₁₁][NTf ₂]	0.051	0.010
[S ₂₂₂][NTf ₂]	6.64	1.06

Table 2. Comparison of electrochemical windows before and after 1.2MGy gamma irradiation

Ionic Liquid	Unirradiated			Irradiated			Window Width
	Cathode	Anode	Window	Cathode	Anode	Window	
EcoEng41M	-1.8	+1.8	3.6	-0.9	+1.4	2.3	-1.3
[C ₈ mim][PF ₆]	-2.9	+2.2	5.1	-1.4	+1.6	3.0	-2.1
[C ₆ mim][Cl]	-2.6	+1.0	3.6	-2.0	+0.5	2.5	-1.1
[C ₂ mim][BF ₄]	-2.2	+1.6	3.8	-1.3	+1.3	2.6	-1.2
[C ₂ mim][NTf ₂]	-2.4	+2.2	4.6	-1.0	+1.1	2.1	-2.5
[N ₄₁₁₁][NTf ₂]	-2.6	+2.0	4.6	-2.1	+1.0	3.1	-1.5
[S ₂₂₂][NTf ₂]	-1.8	+2.0	3.8	-1.0	+0.5	1.5	-2.3
[C ₄ C ₁ pyr][NTf ₂]	-2.4	+1.6	4.0	-1.2	+1.2	2.4	-1.6

GC/Pt/Pt; 100 mV/s scan rate; reference to FeCp₂/FeCp₂⁺ at +0.0 V

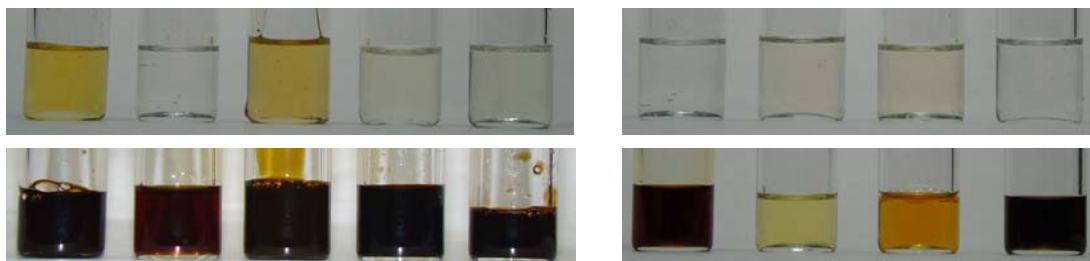


Fig. 1. (*Top left*) Pre-irradiated samples of azolium-based ILs (*Bottom left*) Post-irradiated (from left to right in both photos on left; EcoEng41M, [C₂mim][NTf₂], [C₆mim][Cl], [C₂mim][BF₄], and [C₈mim][PF₆]). (*Top right*) Pre-irradiated samples of [NTf₂]-based ILs (*Bottom right*) Post-irradiated (from left to right in both photos on right: [C₂mim][NTf₂], [N₄₁₁₁][NTf₂], [C₄C₁pyr][NTf₂], and [S₂₂₂][NTf₂]).

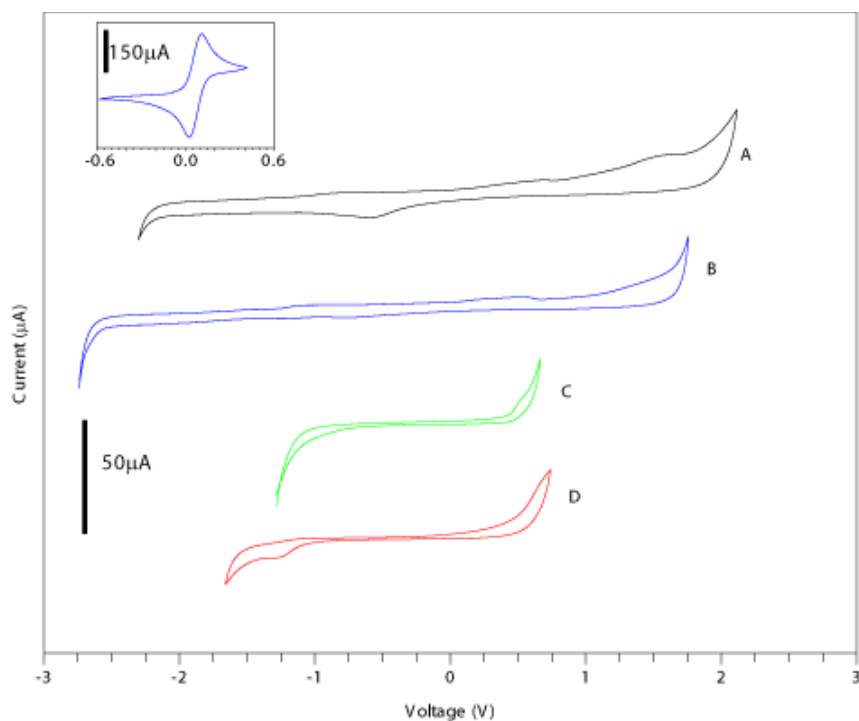
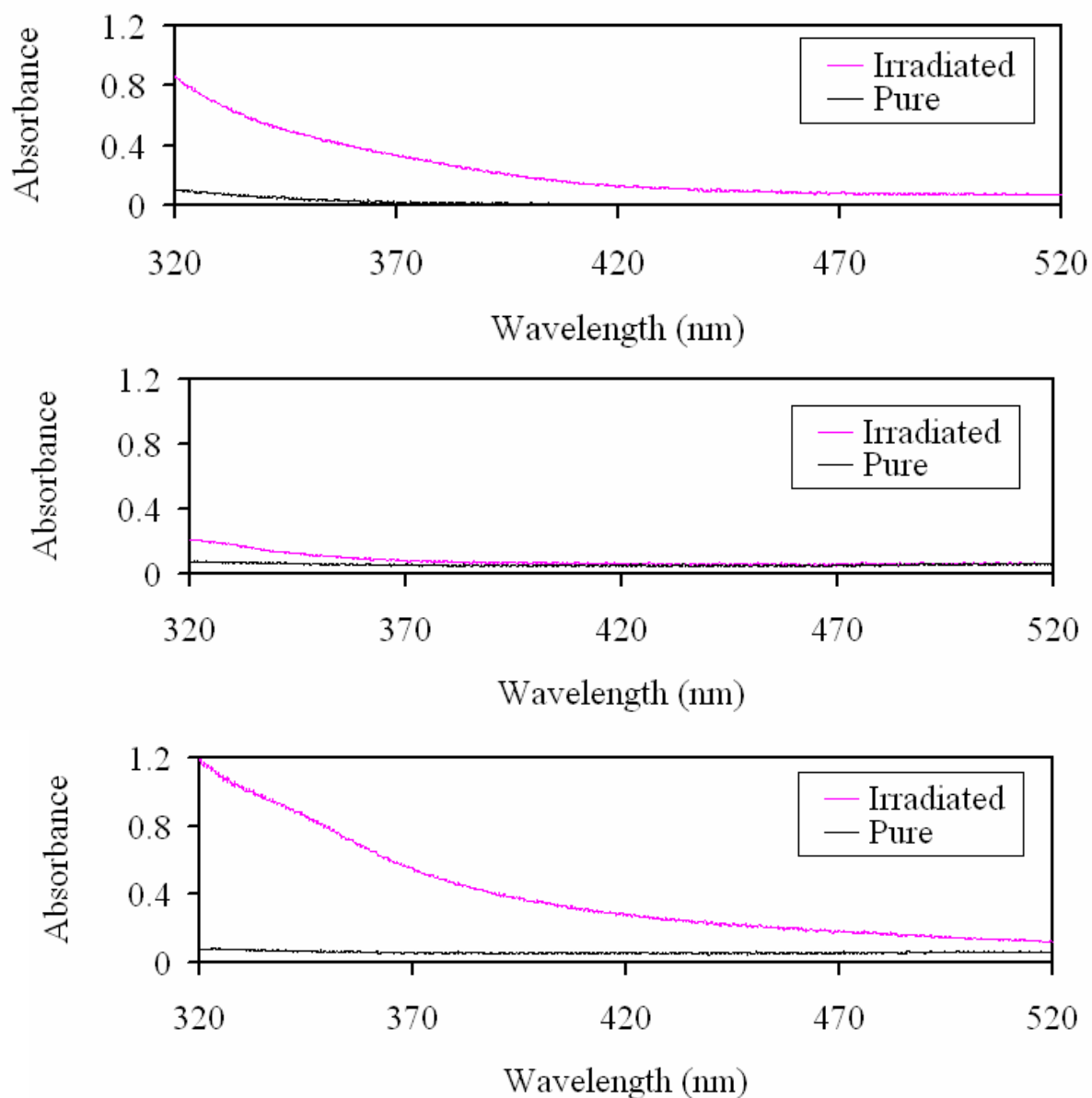


Fig. 2. Comparative electrochemical windows for pre- and post-irradiation ILs. A) pre-irradiated [C₂mim][NTf₂], B) pre-irradiated [S₂₂₂][NTf₂], C) post-irradiated [C₂mim][NTf₂], D) post-irradiated [S₂₂₂][NTf₂], *Insert*) 10mM FeCp₂/FeCp₂⁺ in [C₂mim][NTf₂]. GC/Pt/Pt; 100mV/s scan rate; references to FeCp₂/FeCp₂⁺ at +0.0V.



Supporting Information: comparison of pre- and post-irradiation UV-vis spectra. (*Top*) [C₂mim][NTf₂], (*middle*) [N₄₁₁₁][NTf₂], and (*bottom*) [C₈mim][PF₆].