Supporting Information

Fluorine-Free Ionic Liquid Electrolytes for Sustainable Neodymium Recovery Using an Electrochemical Approach

Kalani Periyapperuma,[a] Jennifer M. Pringle,[a] Laura Sanchez-Cupido,[b] Maria Forsyth,[a] and Cristina Pozo-Gonzalo[a,*]

[a] Institute for Frontier Materials, Deakin University, Melbourne, Victoria 3125, Australia.

[b] TECNALIA, Basque Research and Technology Alliance (BRTA), Paseo Mikeletegi 2, 20009 San Sebastián, Spain

**Corresponding author*: cpg@deakin.edu.au

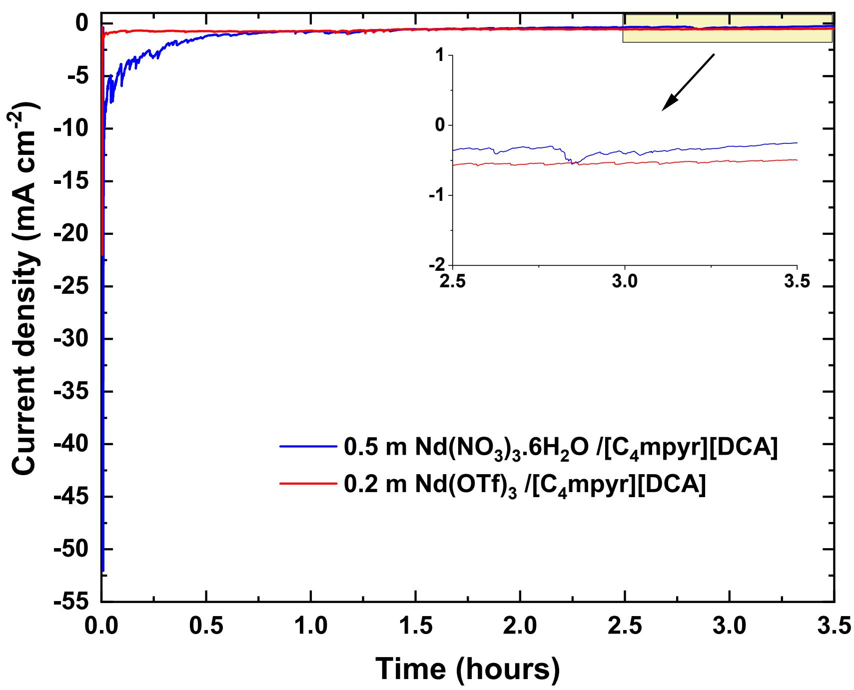

Figure S1. Chronoamperometric profiles for Nd electrodeposition in 0.2 m $Nd(OTf)_3$ (-2.94 V vs $Fc^{+/0}$) and 0.5 m $Nd(NO_3)_3.6H_2O$ (-2.24 V vs $Fc^{+/0}$) in [C_4mpyr][DCA] electrolytes on Ni metal at 50 °C.

Table S1: Summary of the theoretical yield and Nd recovery efficiencies (current efficiency) from 0.2 m $Nd(OTf)_3$ and 0.5 m $Nd(NO_3)_3.6H_2O$ in $[C_4mpyr][DCA]$ electrolytes at 50 °C (Nd^{3+} reduction time duration = 3.5 hours).

Electrolyte	**Charge passed (mAh)**	**Nd^0 Theoretical (mg)**	**Nd^{3+} in 1 ml of electrolyte (mg)**	**Theoretically recovered Nd from 1 ml of electrolyte (%)**	**Current efficiency (%)**
0.2 m $Nd(OTf)_3$	0.153	0.27	28.8	0.9%	35
0.5 m $Nd(NO_3)_3.6H_2O$	0.225	0.40	72.1	0.6%	60

[Theoretically recovered Nd from 1 ml of electrolyte= Theoretically deposited Nd^0 / Nd^{3+} in 1 ml of electrolyte]

Table S2: Summary of the operating parameters and electrochemical outcomes of selected Nd literature. (m - mol kg^{-1}, M - mol l^{-1})

Electrolyte	**Substrate**	**Temp. (°C)**	**Scan rate (mV s^{-1})**	**Onset E_{red} (V)**	**$j_{peak\ reduction}$ (mA cm^{-2})**	**Ref.**
0.03 M $Nd(TFSI)_3$ in $[C_4mpyr][DCA]$	Pt	25	100	No defined peak	-0.1 (coupled with IL reduction)	1
0.1 m $Nd(OTf)_3$ $[P_{66614}][DCA]$	GC	75	10	-3 vs $Fc^{+/0}$	-0.07	2
	Pt			No peak	--	
	Cu			-3 vs $Fc^{+/0}$	-0.25	
0.06 M $Nd(NO_3)_3$ in $[C_4mpyr][TFSI]$	Pt	25	20	-2.2 V vs Ag/Ag^+	-4	3
0.5 M $Nd(TFSI)_3$ in $[P_{2225}][TFSI]$	Pt	50	100	-2.1 V vs $Fc^{+/0}$	-0.25 x 10^{-4}	4
		75			-0.35 x 10^{-4}	
		90			-0.4 x 10^{-4}	
		105			-0.4 x 10^{-4}	
0.05 M $Nd(TFSI)_3$ in $[P_{2225}][TFSI]$	quartz	90	2	-2.79 V vs $Fc^{+/0}$	-0.12	5
		100			-0.15	
0.1 M $NdCl_3$ in DMSO	Pt	R.T.	20	-2.45 V vs $Fc^{+/0}$	-2	6
0.5 M $Nd(TFSI)_3$ in [DEME][TFSI]	Pt	80	10	-3.3 V vs Ag/Ag^+	-0.8	7
$Nd(TBP)_3]^{3+}$ in TBP/$[P_{2225}][TFSI]$	Pt	100	10	-2.4 V vs $Fc^{+/0}$	-7.5	8
0.1 m $Nd(TFSI)_3$ in $[P_{66614}][TFSI]$ + 0.4 wt% H_2O	Glassy carbon	75	100	-2.5 V vs $Fc^{+/0}$	-5	9
0.2 m $Nd(OTf)_3$ in $[C_4mpyr][DCA]$	Ni	50	100	-2.5 V vs $Fc^{+/0}$	-12	Present study
0.2 m $Nd(NO_3)_3.6H_2O$ in $[C_4mpyr][DCA]$	Ni	50	100	-1.75 V vs $Fc^{+/0}$	-38	

$[C_4mpyr][DCA]$ = *N*-Butyl-*N*-methylpyrrolidinium dicyanamide, $[P_{66614}][DCA]$ = Trihexyl(tetradecyl)phosphonium dicyanamide, $[C_4mpyr][TFSI]$ = *N*-Butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, $[P_{2225}][TFSI]$ = Triethylpentylphosphonium bis(trifluoromethylsulfonyl)imide, DMSO = Dimethyl sulfoxide, [DEME][TFSI] = *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide, TBP = Tri-*N*-butylphosphate, $[P_{66614}][TFSI]$ = Trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imid]

References

1 M. Razo-Negrete, R. Ortega-Borges, V. Zinovyeva, C. Cannes, C. Le Naour, G. Trejo-Córdova and Y. Meas, *Int. J. Electrochem. Sci.*, 2019, **14**, 10431–10447.

2 L. Sanchez-Cupido, J. M. Pringle, A. Siriwardana, C. Pozo-Gonzalo and M. Forsyth, *Aust. J. Chem.*, 2020, **73**, 1080–1087.

3 E. Bourbos, I. Giannopoulou, A. Karantonis, I. Paspaliaris and D. Panias, *J. Sustain. Metall.*, 2018, **4**, 395–406.

4 H. Kondo, M. Matsumiya, K. Tsunashima and S. Kodama, *Electrochim. Acta*, 2012, **66**, 313–319.

5 H. Ota, M. Matsumiya, N. Sasaya, K. Nishihata and K. Tsunashima, *Electrochim. Acta*, 2016, **222**, 20–26.

6 E. Bourbos, A. Karantonis, L. Sygellou, I. Paspaliaris and D. Panias, *Metals (Basel).*, 2018, **8**, 803.

7 M. Matsumiya, M. Ishii, R. Kazama and S. Kawakami, *Electrochim. Acta*, 2014, **146**, 371–377.

8 M. Matsumiya, Y. Kikuchi, T. Yamada and S. Kawakami, *Sep. Purif. Technol.*, 2014, **130**, 91–101.

9 L. Sanchez-Cupido, J. M. Pringle, A. L. Siriwardana, A. Unzurrunzaga, M. Hilder, M. Forsyth and C. Pozo-Gonzalo, *J. Phys. Chem. Lett.*, 2019, **10**, 289–294.