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Supporitng Information: The role of hydrogen bond donor and water content on the electrochemical reduction of Ni^{2+} from Deep Eutectic Solvents - an experimental and modelling study

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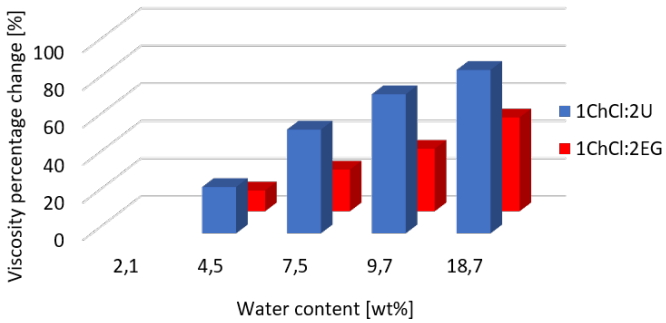
1 Physico-chemical properties of Dep Eutectic Solvents

Table S1 Water content measured before and after electrochemical experiments at 60 °C in 1ChCl:2U and 1ChCl:2EG containig 0.2 M $NiCl_2$ and different water concentrations

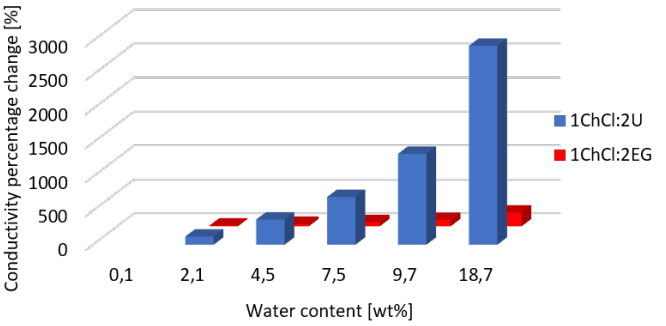
[*wt%*]		[*vol%*]		[*mol%*]		[*mol/l*]	
1ChCl:2U + 0.2M $NiCl_2$ + x *wt%* H_2O							
0.1(GB)	±0.1	0.1	±0.1	0.4	±0.2	0.1	±0.1
1.2(blank)	±0.2	1.4	±0.2	5.2	±0.9	0.7	±0.1
2.1	±0.1	2.5	±0.1	9.1	±0.3	1.3	±0.2
4.5	±0.1	5.3	±0.1	19.4	±0.5	2.9	±0.1
7.5	±0.1	8.8	±0.1	26.3	±0.4	4.8	±0.1
9.7	±0.2	11.7	±0.2	33.8	±0.8	6.5	±0.2
18.7	±0.3	22.5	±0.3	55.3	±0.7	11.3	±0.2
1ChCl:2EG + 0.2M $NiCl_2$ + x *wt%* H_2O							
0.1(GB)	±0.1	0.1	±0.1	0.6	±0.5	0.1	±0.1
0.8(blank)	±0.1	0.9	±0.1	3.8	±0.3	0.5	±0.1
2.8	±0.5	3.1	±0.6	13.3	±1.9	1.7	±0.3
5.3	±0.2	5.7	±0.2	22.1	±0.6	3.4	±0.1
7.3	±0.3	7.8	±0.3	26.5	±0.9	4.6	±0.2
10.2	±0.3	10.8	±0.3	38.4	±1.0	6.0	±0.2
20.2	±0.4	21.4	±0.5	59.2	±1.3	11.9	±0.3

Table S2 Viscosity and conductivity at 60°C of 1ChCl:2U and 1ChCl:2EG containing 0.2 M $NiCl_2$ and different water contents

H_2O [*wt%*]	η [Pa·s]		σ [mS/cm]	
1ChCl:2U + 0.2 M $NiCl_2$ + x *wt%* H_2O				
0.1(GB)	±0.1	-	-	2.42	±0.17
2.1	±0.1	0.085	±0.001	5.32	±0.12
4.5	±0.1	0.064	±0.001	11.39	±0.28
7.5	±0.1	0.038	±0.001	19.40	±0.33
9.7	±0.2	0.022	±0.001	34.80	±0.52
18.7	±0.3	0.011	±0.001	73.28	±0.35
1ChCl:2EG + 0.2 M $NiCl_2$ + x *wt%* H_2O				
0.1(GB)	±0.1	-	-	21.91	±0.23
2.8	±0.5	0.018	±0.001	24.48	±0.37
5.3	±0.2	0.016	±0.001	29.76	±0.52
7.3	±0.3	0.014	±0.001	35.28	±0.34
10.2	±0.3	0.012	±0.001	42.63	±0.67
20.2	±0.4	0.009	±0.001	66.11	±0.29



(a)



(b)

Fig. S1 The relative percentual change (to the dry DES) of the (a) viscosity and (b) conductivity for 1ChCl:2U and 1ChCl:2EG containing 0.2 M $NiCl_2$ and different water contents at 60 °C.

2 Molecular Dynamics modelling

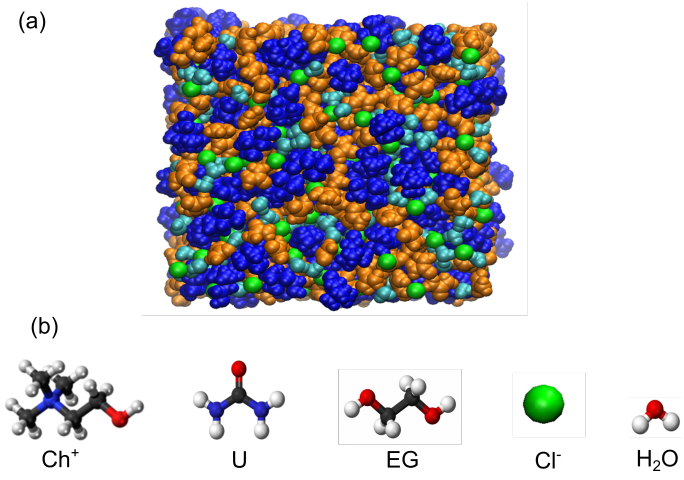


Fig. S2 Optimized structures of (a) modelled box containing DES and (b) DES constituents at 60 °C.

Table S3 Modelled coordination numbers of Ni^{2+} lingands at 60 °C in 1ChCl:2U and 1ChCl:2EG containing 0.2 M of $NiCl_2$ and different H_2O content.

1ChCl:2U + 0.2 M $NiCl_2$ + x *wt*% H_2O								
x	0.0	0.1	2.1	4.5	7.5	10	20	100
Cl^-	2.8	2.8	2.4	2.5	2.6	2.5	2.2	0.4
Ch^+	0.5	-	-	-	-	-	-	-
U	2.5	2.7	1.3	0.6	0.4	-	-	-
H_2O	-	0.2	1.8	3.1	3.4	4.3	5.0	5.6
Σ CN	5.8	5.7	5.4	6.2	6.4	6.8	7.2	6.0
1ChCl:2EG + 0.2 M $NiCl_2$ + x *wt*% H_2O								
x	0.0	0.1	2.1	5.3	7.3	10	20	100
Cl^-	3.3	3.2	3.0	2.9	2.8	2.7	2.2	0.4
Ch^+	-	-	-	-	-	-	-	-
EG	1.4	1.4	0.1	-	-	-	-	-
H_2O	-	0.4	2.8	3.2	3.7	3.8	5.8	5.6
Σ CN	4.7	5.0	5.9	6.1	6.5	6.5	8.0	6.0

Table S4 Interaction energy between HBD, H_2O and Ni^{2+} obtained for 1ChCl:2U and 1ChCl:2EG containing 0.1 *wt*% and 2.1 *wt*% at 60 °C

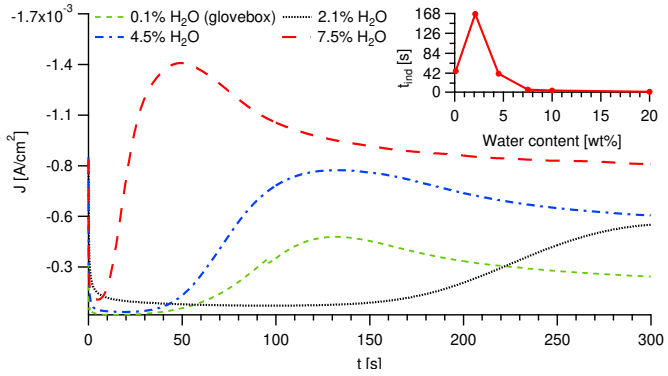
x	$E_{int 0.1 wt\% H_2O}$ [kJ/mol]	$E_{int 2.1 wt\% H_2O}$ [kJ/mol]
1ChCl:2U + 0.2 M $NiCl_2$ + x *wt*% H_2O		
Ni^{2+}-U	-3077.7	-3618.8
Ni^{2+}-H_2O	-271.8	-1961.5
1ChCl:2EG + 0.2 M $NiCl_2$ + x *wt*% H_2O		
Ni^{2+}-EG	-1562.3	-606.6
Ni^{2+}-H_2O	-291.1	-1861.6

3 Ni^{2+} electroreduction in DESs

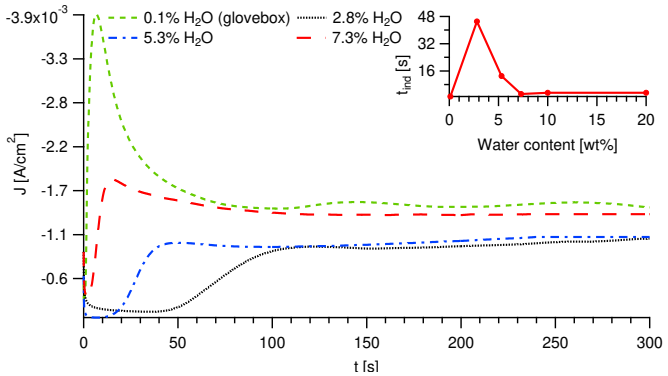
Due to a difference in the Ni^{2+} reduction potentials in both 1ChCl:2U and 1ChCl:2EG ($\sim 100mV$), and in order to avoid incorporation of DES decomposition by-products, potentials of $E = -0.70V$ for 1ChCl:2U and $E = -0.60V$ for 1ChCl:2EG were selected to guarantee a similar potential difference in respect to the onset potential of the mixtures.

Figure S3 shows CAs for different water contents in 1ChCl:2U (a) and 1ChCl:2EG (b). All CAs can be divided into three characteristic regions [1]. Right upon application of potential, the absolute current density initially decreases and remains low (but not zero) for a certain t_{ind}, which spans from less than 1 s to more than 100 s for the slowest depositions. During this time, metal atoms are adsorbed on the surface and may aggregate in form of nanoclusters, but do not contribute to increase the active surface area. Only after a certain t_{ind}, the negative current increases due to 3-dimensional (3D) growth by direct attachment of the stable clusters [2,3]. Finally, the current reaches a maximum which is related to diffusional coupling.

As it can be seen from Figure 3(a), for 1ChCl:2U, when the H_2O concentration decreases to 2.1 *wt*%, t_{ind} increases (red, blue and black curves). However, when the water content drops to the minimum (0.1 *wt*%) under glovebox conditions (green curve), t_{ind} decreases, reflecting that Ni^{2+} reduction is facilitated in the driest DES, and that a small amount of H_2O inhibits the formation of growing Ni nuclei. In the case of 1ChCl:2EG, the variation of t_{ind} with water content is much smaller than for 1ChCl:2U. Surprisingly, Figure 3(b) shows that t_{ind} of the driest DES (0.1 *wt*%



(a)



(b)

Fig. S3 CA measurements in (a) 1ChCl:2U and (b) 1ChCl:2EG containing 0.2 M $NiCl_2$ and x *wt%* H_2O at 60 °C for 300 s on steel. Inset: t_{ind} in function of water content.

of H_2O) is not only shorter than this of 2.8 *wt%* H_2O, but is the shortest of all the 1ChCl:2EG DESs with up to 7.3 *wt%* of H_2O.

Notes and references

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