Electronic Supplementary Material (ESI) for Green Chemistry.

Electrochemical oxidation as alternative for dissolution of metal oxides in deep eutectic solvents

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Supplementary information:

Chronocoulometry and open circuit potential measurements

Chronocoulometry measures the charge passed through an electrode as a function of time at a fixed potential and gives a measure of process kinetics. This process has been tested for iron sulfide and arsenide minerals in DES media, where it was shown that charge passed was correlated to the band gap of the minerals, with a smaller band gap resulting in faster dissolution rates, but only within the anion groupings.[1, 2] Applying this to a selection of d-block metal oxides and PbO results in the same general trend applying, i.e. the more conducting oxides are more easily oxidised than the more insulating oxides. From this limited selection of metal oxides there does not appear to be any trend for oxidation state or periodic group.

Open circuit potential (OCP) measurements were carried out on MO paste in EG:ChCl to examine the stability of the MOs and their tendency to chemically dissolve (**Table 1** & **Figure 2**). The MOs investigated can be divided into two groups: those that remain stable even after one hour (Fe_3O_4, Co_3O_4 and NiO), and those that show a decrease in potential with time (CuO, Cu_2O, ZnO and PbO). When the OCP value of the electrode is stable with respect to time, the equilibrium established between the MO and the electrolyte is relatively stable, i.e. resistant to corrosion reactions from the surrounding electrolyte. On the other hand, when the OCP changes over time it shows that the MO is prone to chemical dissolution in the electrolyte, as the changing metal ion concentration in solution affects the potential. However, OCP values do not correlate to chronocoulometry or band gap values.

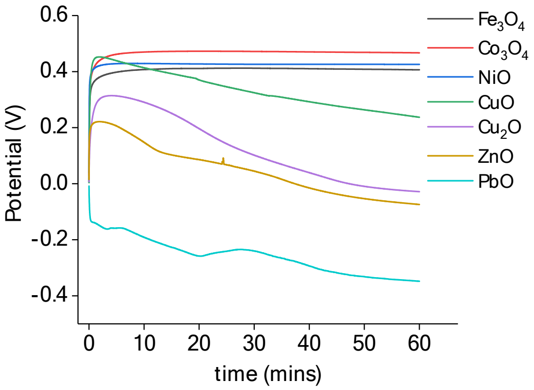

Figure S1: Open circuit potential of metal oxides paint casted in EG:ChCl, with a 0.32 cm^2 Pt flag WE, a Pt flag CE and an Ag/AgCl (0.1 M in EG:ChCl) reference electrode.

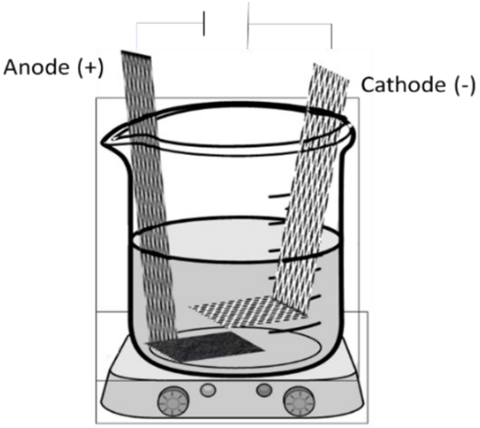

Figure S2: Schematic representation of the cell used for bulk electrochemical dissolution of metal oxides in DES media. A slurry of the metal oxide is pasted onto the anode.

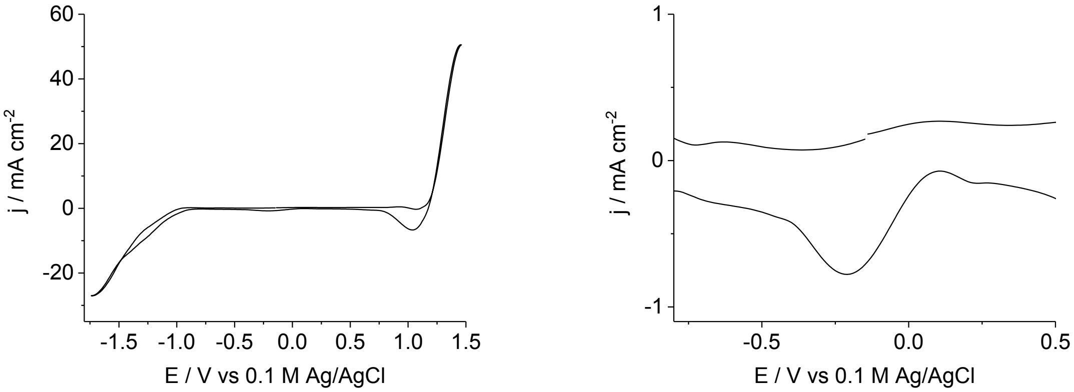

Figure S3: Cyclic voltammogram of pure EG:ChCl with a Pt disc WE, a Pt flag CE and an Ag/AgCl (0.1 M in EG:ChCl) RE. Scan rate: 5 mV s^{-1} (right: zoomed-in "superoxide" region). The cathodic decomposition reaction is likely evolution of H_2 gas, whereas the anodic decomposition reaction is likely evolution of O_2 and/or Cl_2 gas. A reductive process can be seen in the suspected "superoxide" region, of perhaps dissolved O_2 to either superoxide O_2^{-} or oxide O^{2-} species; however, no corresponding oxidation process is present, indicating that no superoxide is generated during the oxidative sweep, i.e. species is too short-lived or diffuses into the bulk during the timescale of the experiment.

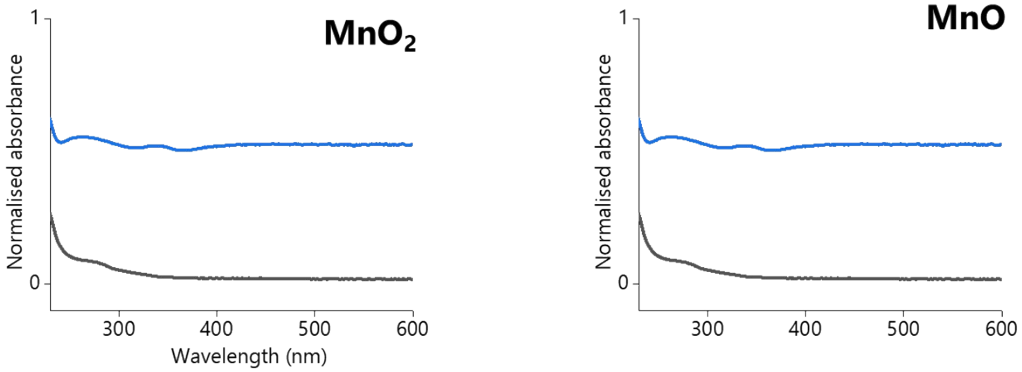

Figure S4: UV-Vis spectra of manganese oxides in EG:ChCl after chemical (black) and electrochemical (blue) dissolution.

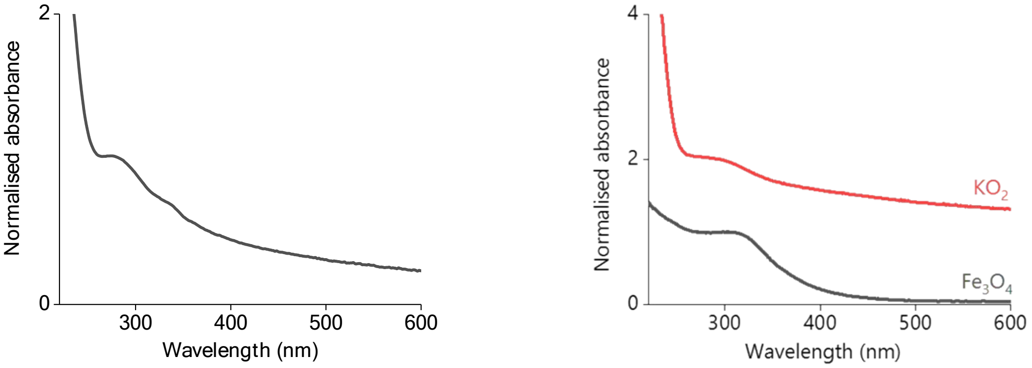

Figure S5: UV-Vis spectra of solution of KO_2 after chemical dissolution in EG:ChCl (left), and compared to the solution obtained from anodic dissolution of Fe_3O_4 (right).

Table 1: Band gap, dissolution rate, and OCP values for selected metal oxides in EG:ChCl.

Metal Oxide	**Band Gap (eV)**	**Q (C)**	**OCP (V)**
Fe_3O_4	0.2 [3]	6.5	0.406
MnO_2	1.33 [4]	7	-
CuO	1.6 [5]	5.2	0.237
Cu_2O	2.2 [5]	6.5	-0.028
Fe_2O_3	2.2 [6]	2.2	-
Co_3O_4	2.4 [5]	4.8	0.467
PbO	3.21 [7]	4.5	-0.348
CoO	3.3 [5]	6.0	-
ZnO	3.37 [8]	5.7	-0.074
NiO	3.5 [5]	4.5	0.426
MnO	3.5 [5]	6.14	-

References

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