Electronic Supplementary Material (ESI) for Energy Advances.

Oxidative Dissolution of Lithium and Manganese from Lithium Manganospinel ($LiMn_2O_4$): Towards Climate-Smart Processes for Critical Metal Recycling

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Electronic Supporting Information

ESI1: Experimental

Chemical reagents used: $LiMn_2O_4$ (~325 mesh powder, 99.5% metal basis, Alfa Aesar) and alkaline NaClO (8% Cl, Fisher Scientific) were used as supplied. Experiments were undertaken using a specified mass of $LiMn_2O_4$ and 80 mL (100 g) of NaClO solution in a round-bottomed flask equipped with a Liebig condenser, thermostatted at a specified temperature, for 1 h, in a fume cupboard. Aliquots of the resulting pink solution were withdrawn from the flask, and after the settling of any solids in the samples, the pink solution was placed in a high precision synthetic quartz cuvette (Hëlima Analytics, 1 cm path-length) and analysed using a Jenway 7315 spectrophotometer at ambient temperature (20 ± 2 ^{o}C).

ESI2: Oxidative Dissolution Chemistry

We consider the oxidative dissolution reaction of lithium manganospinel in alkaline hypochloride as comprising the following steps, based on the Mn^{III} to Mn^{VII} oxidative sequence previously proposed by us.[S1]

Heterogeneous oxidation of Mn^{III} to Mn^{IV}:

$$LiMn_2O_4(s) \rightarrow xLi^{+}(aq) + xe^{-} + Li_{1-x}Mn_2O_4(s) \qquad \text{(SAi)}$$

$$xClO^{-}(aq) + 2xe^{-} + xH_2O(l) \rightarrow xCl^{-}(aq) + 2xOH^{-}(aq) \qquad \text{(SAii)}$$

$$\mathbf{2LiMn_2O_4(s) + xClO^{-}(aq) + xH_2O(l) \rightarrow 2Li_{1-x}Mn_2O_4(s) + 2xLi^{+}(aq) + xCl^{-} + 2xOH^{-}(aq)} \qquad \textbf{(SA)}$$

Heterogeneous oxidation of Mn^{IV} and residual Mn^{III} to Mn^{VI}:

$$Li_{1-x}Mn_2O_4(s) + \tfrac{1}{2}(1-x)ClO^{-}(aq) + \tfrac{1}{2}(1-x)H_2O(l) \rightarrow$$
$$(1-x)Li^{+}(aq) + Mn_2O_4(s) + \tfrac{1}{2}(1-x)Cl^{-}(aq) + (1-x)OH^{-}(aq) \qquad \text{(SBi)}$$

$$Mn_2O_4(s) + 2ClO^{-}(aq) + 4OH^{-}(aq) \rightarrow 2MnO_4^{2-}(aq) + 2Cl^{-}(aq) + 2H_2O(l) \qquad \text{(SBii)}$$

$$\mathbf{Li_{1-x}Mn_2O_4(s) + \tfrac{1}{2}(5-x)ClO^{-}(aq) + (3+x)OH^{-}(aq) \rightarrow}$$
$$\mathbf{(1-x)Li^{+}(aq) + 2MnO_4^{2-}(aq) + \tfrac{1}{2}(5-x)Cl^{-}(aq) + \tfrac{1}{2}(3+x)H_2O(l)} \qquad \textbf{(SB)}$$

Homogeneous oxidation of Mn^{VI} to Mn^{VII}:

$$\mathbf{2MnO_4^{2-}(aq) + ClO^{-}(aq) + H_2O(l) \rightarrow 2MnO_4^{-}(aq) + Cl^{-}(aq) + 2OH^{-}(aq)} \qquad \textbf{(SC)}$$

In reaction (SA), the lithium manganospinel, which comprises a stoichiometrically equivalent amount of Mn^{III} and Mn^{IV} speices, is partially oxidised by hypochlorite, releasing lithium ions, to afford the solid $Li_{1-x}Mn_2O_4$, which contains $(1+x)Mn^{VI}$ and $(1-x)Mn^{III}$ species. The relevant half-reaction (SAi) has been studied electrochemically,[S2-S7] where two voltammetric oxidation peaks are observed at[S4,S5] 0.89 and 1.01 V *vs.* $Ag/AgCl/Cl^{-}$(1 M LiCl), which correspond to partial lithium ion extraction from the tetrahedral sites in the presence and absence of lithium-lithium interactions, respectively,[S4,S5] with reverse peaks at 0.69 and 0.89 V *vs.* $Ag/AgCl/Cl^{-}$ (1 M LiCl) corresponding to the two different lithium ion re-insertion events. The cyclic voltammograms at single particles[S5] corresponding to reaction (SAi) reveal chemically reversible but electrochemically quasi-reversible characteristics:[S4,S5] the *onset* potential for the oxidation varies with particle shape and size,[S7] and is *ca.* 0.7 V *vs.* Ag/AgCl/Cl$^-$(1 M LiCl), with the mid-point potentials ($E_{mid} = ½(E_p^{Ox} + E_p^{Red})$) being 0.79 and 0.95 V *vs.* Ag/AgCl/Cl$^-$ (1 M LiCl). These indicate that reaction (SA) will only be fast provided there is sufficient driving force for the reaction.

The experiments by Unwin *et al.*[S5] were undertaken at ambient temperature, using a Ag/AgCl/Cl$^-$(1 M LiCl) reference electrode. At 25 °C, the mean ionic activity coefficient is[S8] 0.774, which, assuming it does not vary by very much when considering ambient temperatures, and that no silver chloride complex ion is involved in the potential-determining reactions, affords a reference potential of 0.216 V *vs.* SHE, so that the minimum oxidant strength is *ca.* 1.0 V *vs.* SHE. This is close to the oxidising strength of alkaline hypochlorite (*ca.* 0.8 – 0.9 V *vs.* SHE),[S8,S9] so that *it is likely that reaction (SA) is slow*. The use of sodium hydroxide as the alkaline stabiliser to hypochlorite will give an additional energy barrier, since reaction (SAi) requires higher potentials in sodium hydroxide electrolytes.[S6]

Considering the further oxidation reactions, we start with reaction (SB). This has been split into two steps: in the first, reaction (SBi), any residual Mn^{III} is oxidatively de-lithiated to afford a spinel-related manganese dioxide.[S2,S3] Since MnO_2 oxidation to the manganate ion has an oxidation potential of *ca.* 0.6 V *vs.* SHE,[S9] reaction (SBii) is expected to be rapid.[S10] Thus, overall, reaction (SB) is expected to be rapid.

Reaction (SC), which is insensitive to pH, is, likewise, anticipated to be rapid: under standard conditions, the half-equation $MnO_4^{2-} - 2e^- \rightarrow MnO_4^-$ has an oxidation potential of
-0.56 V *vs.* SHE.[S9]

Thus, for the overall reaction,

$$\mathbf{2LiMn_2O_4(s) + 7ClO^-(aq) + 2OH^-(aq) \rightarrow 2Li^+(aq) + 4MnO_4^-(aq) + 7Cl^-(aq) + H_2O(l)} \qquad \textbf{(SD)}$$

it is likely that the rate-limiting step in the oxidative dissolution of both lithium and manganese from $LiMn_2O_4$ under alkaline conditions is the initial reaction, equation (SA).

ESI3: Interplay between Mass Transport and Surface Kinetics in Reactive Dissolution

Reaction (SD) is a heterogeneous reaction between aqueous hypochlorite and the $LiMn_2O_4$ particle surface. It will require hypochlorite ions and water molecules to be transported from bulk solution to the solid/liquid interface, where the reaction occurs, with lithium, chloride and hydroxide ions as the reaction products being transported back to the bulk solution, together with any unreacted hypochlorite (the reaction is stirred).

Accordingly, since the concentration of $LiMn_2O_4$ at the particle surface (concentration = density/molar mass = 4.29 g cm^{-3}/181 g mol^{-1} = 23.7 M) is *ca.* ten times greater than the concentration of hypochlorite in bulk solution (2.8 M), the reaction can be considered as pseudo-first order in ClO^-, so that reaction (SA) can be modelled as:

$$A^{bulk} \xrightarrow{k_1} A^{surf} \underset{k_b}{\overset{k_f}{\rightleftarrows}} B^{surf} \xrightarrow{k_3} B^{bulk} \qquad \textbf{(SE)}$$

where A and B represent the solution-based reactant (ClO^-) and product (Cl^-, Li^+, *etc.*), respectively, and bulk and surf superscripts indicate their location in the main solution, or at the interface, respectively. The mass transfer coefficients are k_1 and k_3, with k_f and k_b being the rate constants for the forward and reverse heterogeneous electron transfer reactions, respectively, with the equilibrium constant, K_2 being their ratio: $K_2 = k_f/k_b$. Note that in reaction (SE) we consider the transport properties of all of the reactants to be the same, and those for all of the products to be identical (but different to the reactants).

Since mass transfer flux must match the reaction kinetics, the rate of the surface reaction (in moles per unit area per unit time) is given by:[S11]

$$Rate\ of\ surface\ reaction = k_f c_A^{surf} - k_b c_B^{surf} = k_1\left(c_A^{bulk} - c_A^{surf}\right) = k_3\left(c_B^{surf} - c_B^{bulk}\right) \qquad \textbf{(S1)}$$

in which c_i^j is the concentration of species i in location j. Algebraic manipulation of the terms in equation (S1) to eliminate surface concentrations affords the expression:

$$Rate\ of\ surface\ reaction = K\left(c_A^{bulk} - \frac{c_B^{bulk}}{K_2}\right) \qquad \textbf{(S2)}$$

where,

$$\frac{1}{K} = \frac{1}{k_1} + \frac{1}{k_f} + \frac{1}{K_2 k_3} \qquad \textbf{(S3)}$$

The variable K in equation (S2) has three important general limits:

(i) if the particle suspension is stirred rapidly, k_1 and k_3 may tend to infinity, so that $K \rightarrow k_f$ and the rate of reaction is controlled by the rate of the forward surface kinetics: $Rate\ of\ surface\ reaction = k_f\left(c_A^{bulk} - \frac{c_B^{bulk}}{K_2}\right)$;

(ii) for an irreversible chemical reaction, $K_2 \rightarrow \infty$, and thus, the rate of reaction is controlled by the hybrid of both reactant mass transfer and reactant surface kinetics: $K \rightarrow \frac{k_1 k_f}{k_1 + k_f}$ and $Rate\ of\ surface\ reaction = \frac{k_1 k_f}{k_1 + k_f} c_A^{bulk}$; and

(iii) if the reaction is undertaken at high temperature, since mass transfer activation is less sensitive than chemical reaction activation,[S12] k_f and k_b are both much greater than k_1 and k_3, and, therefore $\frac{1}{K} \to \frac{1}{k_1} + \frac{1}{K_2 k_3}$ leading to

$$Rate\ of\ surface\ reaction = \frac{k_1 k_3 K_2}{k_1 + K_2 k_3}\left(c_A^{bulk} - \frac{c_B^{bulk}}{K_2} \right).$$

ESI4: Estimation of the Mass Transport Coefficient and its Temperature-Dependence

The interplay between transport and kinetics for the assumed rate-limiting step, reaction (SA), complicate the temperature-dependence of the observed permanganate formation: for example, in a diffusion-controlled process, the rate may not scale directly with diffusion coefficient.

Given that the stirred particle suspension has an additional transport contribution induced through heating the suspension, we can estimate the value of the mass transfer coefficient (k_{mt}) using the correlation suggested by Harriott,[S13] employing the protocol detailed by Sherwood, Pigford and Wilke[S14] to ascertain the minimum value for k_{mt} as the terminal velocity of a spherical particle falling under gravity, at each temperature.

Thus, we may first estimate the terminal velocity (u_{ts}) of a spherical $LiMn_2O_4$ particle from Stokes's law:

$$u_{ts} = \frac{d_p^2 \left| \rho_{LiMn_2O_4} - \rho_{H_2O} \right| g}{18\eta} \qquad \textbf{(S4)}$$

In equation (S4), d_p is the diameter of the spherical particle (44 μm), ρ_i is the density of species i, η is the viscosity of the aqueous phase, and g is the gravitational acceleration. The continuous aqueous phase was assumed to have the physical properties of pure water, as data pertaining to their temperature-dependence are readily available (see Table S1).[S8] For the specific temperatures used, it was necessary to employ linear interpolation from those data.

Table S1: *Temperature-dependence of the viscosity and density of pure water, taken from reference S8*

Temperature /°C	**Density /g mL^{-1}**	**Viscosity / μPa s**
100	0.95840	281.8
90	0.96535	314.5
80	0.97182	354.4
70	0.99778	404.0
60	0.98320	466.5
50	0.98803	547.0
20	0.99821	1002

Second, we may infer the Reynolds number at this terminal velocity (Re_{ts}) for each specified temperature, using equation (S5):

$$\mathrm{Re}_{ts} = \frac{d_p u_{ts} \rho_{H_2O}}{\eta} \qquad \textbf{(S5)}$$

Third, we estimate the terminal velocity in free fall (u_t) through interpolation of the data provided by Sherwood, Pigford and Wilke,[S14] which we found fit the curve given in equation (S6) in the range $0 \leq \lg(\mathrm{Re}_{ts}) \leq 5$, with a correlation coefficient $R^2 = 0.9965$. Note that this analysis assumed the curve was valid for $\mathrm{Re}_{ts} < 1$.

$$\lg\left(\frac{u_t}{u_{ts}}\right) = 0.031\left\{\lg\left(\mathrm{Re}_{ts}\right)\right\}^2 - 0.3356\lg\left(\mathrm{Re}_{ts}\right) + 0.9189 \qquad \textbf{(S6)}$$

Fourth, using the free-fall terminal velocity rather than the Stokes' law terminal velocity, the Reynolds number (Re) can be determined using equation (S5). This enables the mass transfer coefficient, k_{mt}, to be determined at each temperature through the correlation for forced convection around a sphere:

$$Sh = 2.0 + 0.6\,\mathrm{Re}^{1/2}\,Sc^{1/3} \qquad \textbf{(S7)}$$

in which Sh is the Sherwood number ($Sh = \frac{k_{mt} d_p}{D}$),Sc is the Schmidt number (kinematic viscosity normalised by the diffusion coefficient of hypochlorite, D). Diffusion coefficients at different temperatures were estimated through an Arrhenius relationship, using $D_0 = 2.032 \times 10^{-5}$ cm^2 s^{-1} as that for chloride in water[S8] at 25 °C, employing an activation energy of 15 kJ mol^{-1}, based on that determined for aqueous electrolytes using radio-frequency heating.[S12] This generates temperature-dependent mass transfer coefficients on the order of 10^{-4} m s^{-1} (see Table S2), which exhibit an Arrhenius activation energy of *ca.* 16 kJ mol^{-1}.

Table S2: *Temperature variation of mass transfer coefficients.*

Temperature /°C	**k_{mt} /μm s^{-1}**
95	671.5
83	564.4
73	483.0
72	475.4
54	348.6

ESI5: References

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