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A Perspective on Liquid Salts for Energy and Materials

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Liquid salts comprising molten salts and ionic liquids offer important media to address both energy and materials challenges. Here we review topics presented in the current Faraday Discussion volume related to improved electrowinning of metals, optimisation of processes, new electrochemical device concepts, chemistry in ionic liquids, conversion of biomass, carbon chemistry and nuclear applications. The underlying phenomenology is then reviewed and commentary given. Some future applications are then discussed, further exemplifying the high potential rewards achievable from these chemistries.

Introduction

Molten salt chemistry is an area of considerable technical importance; however, it has somewhat slipped from the mainstream of chemical focus over the decades. With the advent of ionic liquid chemistry and rediscovery of the power of molten salt chemical processes, attention is increasingly turning back to molten salt chemistry, especially in areas such as Energy Materials.

Molten salts consist entirely of ions and are characterised by high melting points (e.g. >200°C) due to strong bonding between anions and cations. In the solid state they exhibit very low ionic conductivity and negligible electronic conductivity. Typically there is a very large volume change on melting (~25%) creating significant free volume in the molten state. They exhibit high ionic conductivity and negligible electronic conductivity with modest viscosity. Application of a voltage above decomposition of melt (~2-3 V) results in decomposition, eg for LiCl this causes the production of lithium on the cathode and evolution of chlorine on the anode.

Ionic liquids are closely related to molten salts, although they tend to be liquid at or near to ambient temperature. They offer good solvation characteristics but are not necessarily highly polar.

Molten salts are widely utilised in many important applications. Examples include the production of aluminium through cryolite electrolysis in the Hall-Heroult process, the production of lithium through the electrolysis of lithium chloride[1] and the production and purification of titanium as in the FFC Cambridge process[2].

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Molten salt chemistry research can contribute to a reduction in energy costs and use in a number of ways. Firstly by Improving efficacy of existing processes for producing high energy metals (e.g. Al, Li, Si and Ti), secondly by developing new metallurgical processes, thirdly by bringing forward new energy concepts that offer improved storage and conversion of energy and fourthly though creating new energy materials that can enable this. Here we consider various possible approaches to achieve these objectives,

Improved Electro-winning

Whilst the activity available in molten salt chemistry greatly enables the technology, this also creates major issues in achieving stable operation, especially relating to corrosion. For example, providing an inert anode for electro-winning a metal from an oxide is a fairly stringent test. To achieve this, the following material properties are required[3]:
1. Insolubility in a molten salt electrolyte up to 1000°C
2. Thermal stability up to 1000°C with adequate resistance to thermal shocks
3. Resistance to the oxygen produced at the anode
4. Low electrical resistivity
5. Low oxygen over-potential
6. Resistance toward fluoridation/chlorination
7. Does not contaminate the electro-won metal
8. Adequate mechanical strength and stable electrical connections
9. Low cost and easy fabrication into large shapes

This often involves formation of a stable, corrosion layer at the surface that blocks further degradation. There is also interest in novel compositions such as Nb doped TiO_2[3] to improve electrode stability.

Efficient electro-reduction of Ta_2O_5 to Ta has been achieved at a graphite electrode in a $MgCl_2$-NaCl-KCl melt at 700°C via a

TaO$_2$ intermediate. This new composition has been tuned to utilise the MgCl$_2$ to support the metal production and increase the longevity of the anode, with MgO and Cl$_2$ being the anodic products, avoiding decomposition of the carbon anode.[4] Similarly Mg produced via Mg reduction/deoxidation in electrolysis of MgCl$_2$ has been utilised to remove residual oxygen from a Ti cathode yielding less than 100 ppm(O) Ti.[5]

Optimisation of Processes

The production of aluminium from its ore is energy intensive and has a large carbon footprint. One approach to reduce CO$_2$ output is to utilise natural gas instead of carbon at the anode in the electro-winning of aluminium from alumina in molten fluorides. This produces water as well as carbon dioxide and effectively reduces the CO$_2$ output by a factor of 2.[6]

A solid oxide ion conducting membrane has been applied to a number of metal carbide syntheses in CaCl$_2$ at 900°C.[7] The membrane separates the anodic and cathodic processes and affords more precise control of the carbon stoichiometry. The process can also yield intricate nanostructured carbides as shown schematically in Figure 1.
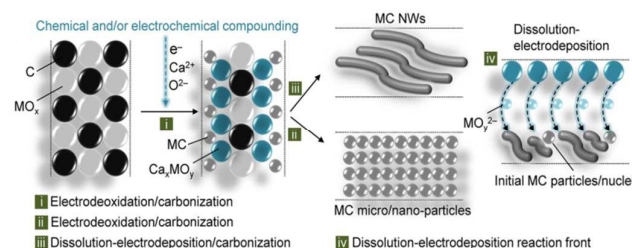

Figure 1 Schematic representation of the route from metal oxide to metal carbide via electro-reduction of MO$_x$/C MCs in molten CaCl$_2$, reproduced by permission from [7]

In another approach, electrochemical reduction of SiO$_2$ in the presence of NiO has been shown to yield Si nanowires with diameters 60-150nm.[8] Here, silica was reduced to silicon at the Ni-Si alloy droplet/SiO$_2$/CaCl$_2$ three-phase interphase and dissolved into the alloy droplets, in a tip growth process of Si nanowires, figure 2.
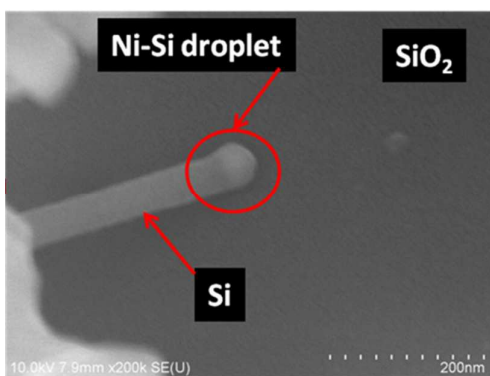

Figure 2 Tip growth of Si nanowires on SiO$_2$ electroreduction in molten CaCl$_2$ facilitated by presence of NiO, reproduced by permission from [8].

Devices

Molten salt chemistry is proving particularly powerful for developing nanomaterials for energy materials. This is highly important in energy storage devices such as batteries and supercapacitors. Supercapacitors act to store charge at high surface area interfaces and tend to operate over a potential range. Their best mode of operation is in storing large amounts of energy to be delivered in a short timescale, ie in power driven application. Batteries tend to store energy within the materials and, at least for traditional insertion/intercalation chemistry, operate over well-defined potential ranges. Batteries are best suited to storing energy over longer timescales than supercapacitors. With the development of conversion chemistries[9], this distinction has become blurred with materials offering characteristics intermediate between batteries and supercapacitors. Chen has formalised this concept in terms of a supercapattery[10] and has reported this concept using an ionic liquid solution of LiClO$_4$[11]. An interesting example of such behaviour with considerable charge storage spread over 3V is in AlFe nanowires.[12] Here, the electrode was based on very fine nanowires prepared by electrodeposition on copper in an AlCl$_3$ based ionic liquid.

Pringle *et al* reported an exciting new concept, thermoelectrochemical cells wherein the changes in redox couple potentials of a redox ionic liquid electrolyte with temperature, were exploited to generate an effective device.[13]

Chemistry in Ionic Liquids

Ionic liquids offer near ambient temperature systems with excellent solvating ability to perform chemistry in the absence of water. A highly efficient and stable system for hydro-formylation has been developed[14], this involves a biphasic system with a rhodium catalyst dissolved in one ionic liquid phase and a diphosphine functionalised ionic liquid in the other. This chemistry is now being applied to a range of processes including processing of biomass.

Biomass

Lignin is the most abundant biopolymer after cellulose and is particularly difficult to convert into useful chemicals in an economically sustainable manner. Finding alternative technologies to process this would have great benefit to concepts such as biorefineries. In an innovative approach the Nottingham team the mediator 2,2'-azino-bis(3-ethylbenthiazoline-6-sulfonic acid) diammonium salt (ABTS) has been evaluated by means of cyclic voltammetry (CV) for enhancing the oxidation of the three types of lignin (organosolv, Kraft and lignosulfonate) in the ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate, [C$_2$mim][C$_2$SO$_4$])[15], Figure 3.

In a different approach, carbon nano-sheets were obtained from a typical waste biomass, used coffee beans, through heating in

carbonate and chloride molten salts.[16] These carbons showed high capacitance and demonstrated good oxygen reduction kinetics when tested in symmetric full cell capacitor and alkaline cell modes, respectively. Carbonate derived carbons had smaller surface area, they exhibited less surface functional groups and increased order in structure and performance was improved in both mode.
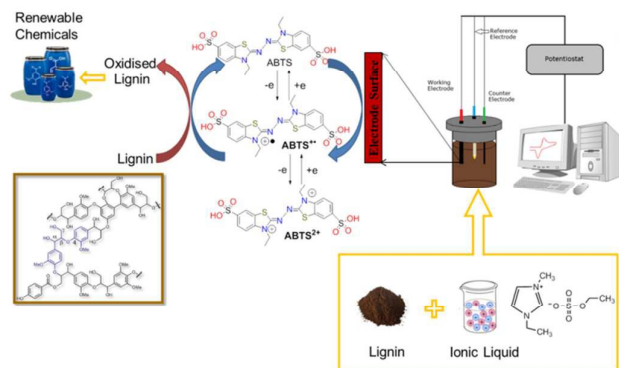

Figure 3 Scheme showing electro-oxidation of lignins in ionic liquid, reproduced by permission from Liquid Salts for Energy and Materials Faraday Discussion presentation [17]

Carbons

An alternative approach to CO_2 capture via gas sequestration is to convert CO_2 to carbon. This can be achieved via the electroreduction of CO_2 in a molten lithium carbonate/chloride mixture.[18] Morphologies can be controlled by modifying electrochemical conditions, including substrate and a range of quasi spherical and nanofibrous particles have been achieved in short term electrolysis studies.

In a similar approach, nanoflakes were produced on electrolysis of CO_2 over much longer timescales in LiCl/KCl molten electrolytes that also contained carbonates.[19]

An interesting route to high quality graphene sheets has been found to involve electrochemical exfoliation of graphite in molten LiCl. This process was found to be greatly enhanced by the presence of a little water in the molten chloride.[20].

An important process that operates in reverse is the Direct Carbon Fuel Cell (DCFC), this concept attempts to convert carbon sources directly to CO_2 electrochemically and so to obtain maximal conversion efficiency.[21] This process can in one configuration utilise a molten carbonate mediator at a solid oxide electrode to achieve high performance. Commonly, CO is a major product, via Boudouard processes, reducing potential efficiency. This contrasts with the reverse systems mentioned in preceding paragraphs that convert CO_2 to C with minimal CO. It is important to note, however, that the carbon capture experiments tend to be at lower temperature which would reduce the influence of the CO producing reactions.

A remarkable observation is the spontaneous combustion of a carbonate/xerogel spent mixture after DCFC testing under ambient conditions.[22] This is a strong indication of the presence of exotic, highly reactive species such as peroxide in molten salt chemistry.

Nuclear Applications

Pyrochemical reprocessing of nuclear fuels is an important application involving molten salts. In a typical process LiCl-KCl molten salt is used as the medium for electrorefining of spent fuels. Liquid metal cathodes, such as Cd, Bi, Al, are utilised to extract and separate actinides and lanthanides and this can be suitably monitored utilising cyclic voltammetry identifying a series of intermetallic compositions in model Ce and La systems.[23] Molten salt stable microelectrodes have been developed via microfabrication techniques to perform in situ electroanalysis and utilised to characterise intermetallic formation in model molten Bi systems.[24] The thermal diffusivity of various molten carbonate electrolytes has also been determined as a function of temperature using a novel laser flash system.[25]

High temperature [35]Cl NMR has been utilised to probe changes in local structure on dissolving the model compound $CeCl_3$ in LiCl. [26] Coordination can also be probed by techniques such as EXAFS and molecular dynamic simulations provide highly complementary information to such experimental measurements, on coordination chemistry of dissolved lanthanides or actinides. [27]

Underlying phenomena/chemistry

[35]Cl NMR has also been utilised to investigate the changes in liquid dynamics through probing spin lattice relaxation time across the molten LiCl-KCl system. Surprisingly the variation in T1 activation energy was not linear with composition and instead a maximum was observed near the eutectic composition.[26] As motion might be expected to be easier in the lower melting eutectic region, this suggests that location of the maximum E_a at the eutectic is coincidental. Perhaps this may relate to the mixed alkali effect[28], supposed to be related to entropic effects, which shows a hindrance to ionic motion in liquids or glasses on introduction of secondary ions, i.e. K in molten LiCl.

In the chloride melts used for electro-refining of titanium, titanium is usually present in 2+ or 3+ states. Addition of fluoride has been shown to facilitate Ti formation through facilitating disproportionation reactions such as $3Ti^{2+} \rightarrow 2Ti^{3} + Ti$.[29]

Comments

There is a rich and diverse chemistry that can occur in molten salt electrolytes, that gives rise to their many important potential applications. Species that are almost unthinkable in more familiar systems such as conventional aqueous and non-aqueous electrolytes, or indeed in state solid state reactions, are encountered in the molten state. This can include small

amounts of dissolved metals in melts, as well as peroxide and superoxide species. The Lux–Flood definition of acid–base theory is helpful in understanding some of these chemistries.[30] This definition describes an acid as an oxide ion (O^{2-}) acceptor and a base as an oxide ion donor.

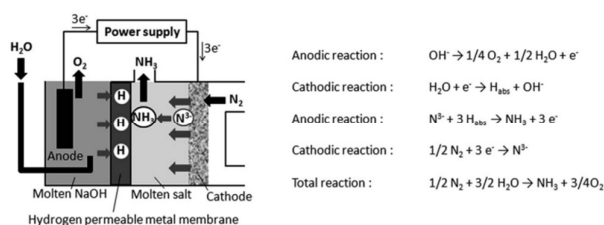MgO (base) + CO_2 (acid) → $MgCO_3$
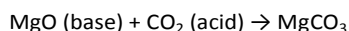
This can help to explain the suitability of molten carbonates and hydroxides to grow high oxidation state crystals *e.g.* peroxide, Cu^{3+}, Bi^{5+}.[31] Another example is the attack of zirconia electrolytes by peroxidic species in molten carbonate assisted direct carbon fuel cells. In fact, this seems only to be a problem in oxidising conditions and is not a problem under the reducing conditions encountered under operating conditions.[21] In molten hydroxides and carbonates we can anticipate the presence of species such as superoxide, O_2^-; peroxide, O_2^{2-}; and percarbonate, CO_4^{2-} especially on the anodic side.[32] The presence of small concentrations of dissolved alkali metals is also possible in cathodic environments, giving further opportunities for "exotic" chemistry.

A useful concept to further explore the nature of such processes in molten salts is optical basicity. This concept was first developed by John Duffy for solid oxides and glasses parametrising the basicity through spectroscopic probe ions.[33] This has recently been transferred to low melting salts such as ionic liquids (ILs).[34] These were doped with $Mn(NTf_2)_2$ (NTf_2 = bis(trifluoromethanesulfonyl)imide) as a probe of the IL anion basicity by means of UV-Vis spectroscopy. The $^6A_1 \rightarrow {}^4A, {}^4E(G)$ transition band of Mn^{2+} is influenced by the electron donor properties, *i.e.*, Lewis basicity, of the coordinating ligands but remains—to the first order—independent from the ligand field. IL anions showed an order of $BF_4^- < ClO_4^- < NTf_2^- \sim MeSO_3^- < NO_3^- < DCA^- < TFA^- < EtSO_4^- \sim OTos^- < Cl^- < Br^-$ with respect to rising optical basicity.

Immediate Applications

There are many applications of ionic liquids and molten salts that may come to fruition in the near future. For ionic liquids, examples include use in paints to reduce volatile organic compounds[35] and as a solvent in 3-d ink jet printing.[36] Molten salt electrochemistry also finds many important applications such as electrorefinining of Neodymium, which is so important in wind turbine magnets, in molten LiF electrolyte.[37] A particularly exciting application is the production of ammonia from nitrogen using renewable electricity. A new approach involving reduction of nitrogen in a cathode compartment with water oxidation in the anode compartment, with H-transfer through a separating membrane, has recently been described, figure 4.[38]

Figure 4 Schematic of ammonia production in separated cells using molten hydroxide and chloride electrolytes, reproduced by permission from [38]

Conclusions

Molten salts offer a very exciting environment for developing new chemical and electrochemical approaches. Environments are often aggressive and hard to manage; however, this offers new routes and functionalities to find solutions that may not otherwise be accessible. In short this is an important area that is re-emerging with great potential for new advances.

Acknowledgements

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