CO$_2$/oxalate Cathodes as Safe and Efficient Alternatives in High Energy Density Metal-Air Type Rechargeable Batteries

Károly Németh$^{a,b}$ and George Srajer$^a$

DOI: 10.1039/b000000x

1 Introduction

High energy density batteries are expected to revolutionize transportation and allow for long-range all-electric vehicles. The fact that O$_2$ is available from air and does not have to be carried on the vehicle. It has been pointed out in recent years that high energy density rechargeable Li-O$_2$ batteries can be built when O$_2$ is converted to peroxide ions, O$_2^-$ during the discharge of the battery. In practice, such Li-O$_2$/peroxide batteries also produce Li-superoxide, LiO$_2$. Both of these discharge products are aggressive oxidants that are difficult to control and may lead to unwanted side reactions. They may oxidize the electrolyte and the porous carbon matrix often used as part of a gas-diffusion electrode in which the discharge product is deposited. A high concentration of peroxides deposited in a carbon or general combustible matrix may lead to thermal runaway reactions, even to explosive combustions, making such batteries a safety hazard. Other sources of hazards are posed e.g. by flammable electrolyte components and very reactive dendrites on the surface of bulk lithium electrodes. Many of these hazards can be avoided by appropriate materials and techniques, discussed e.g. in Ref. [1]. For example, all solid state Li-O$_2$ batteries$^{2,3}$ eliminate hazards related to dendrite formation and flammable electrolytes, however they continue to deposit peroxide in a mix of carbon and ceramic material still leaving potential for explosive combustion of carbon. Aqueous Li-O$_2$ batteries$^4$ produce lithium-hydroxide, LiOH, instead of Li$_2$O$_2$ in the cathode reaction O$_2$ + 2 H$_2$O + 4 e$^- \rightarrow 4$ OH$^-$. In these batteries the anode bulk lithium is immersed in an aprotic organic electrolyte separated by a solid Li-ion conducting ceramic membrane$^5$ from the aqueous solution of LiOH. The aqueous Li-O$_2$ battery has demonstrated only limited or energy inefficient rechargeability so far$^{6,7}$. Aqueous electrolytes are also disadvantageous as they allow for the development of explosive hydrogen gas when operated outside their safe voltages windows$^6$. For mechanical stability (e.g. avoiding punctation) the Li-ion conducting membranes tend to be thick and heavy, their ionic conductivity is low$^2$.

Rechargeable metal-air batteries also have to use high purity O$_2$ to avoid the formation of large amounts of carbonates due to the reaction of peroxides and hydroxides with CO$_2$ and that of nitrides in the case of non-aqueous metal-air batteries. Such reactions would lead to the elimination of practical rechargeability$^{12}$, though for a primary, non-rechargeable battery, the addition of large amounts of CO$_2$ ($\approx$ 20-80%) in the gas feed, as an assist to O$_2$, leads to 2-3 fold increase of the realizable energy density of such primary batteries$^{13,14}$. The carbonates produced from a mix of O$_2$ and CO$_2$ feed require very large overpotentials during the charging, at least as long as no catalyst will be found to reduce this overpotential to a practical value$^{10}$. The generation of pure O$_2$ from air, free of H$_2$O, N$_2$ and CO$_2$, needed for metal-O$_2$ batteries without an on-board O$_2$-tank, represents a great problem in itself. Unfortunately, large amounts of O$_2$ can only be stored in heavy tanks at high pressure, and the compression of O$_2$ requires such a large amount of energy that it renders batteries with on-board O$_2$-tanks impractical$^2$.

Additional problems arise from the storage of the discharge products. Solid discharge products deposited in the porous positive gas diffusion electrodes clog the pores of the electrode and increase its internal electrical resistivity, thereby decreasing its energy storage capacity$^2$. Ideally, discharge products
would be removed from the space between the electrodes and would be stored in a separate container, following the operating principle of flow batteries. The optimal solvents for the dissolution of peroxides should allow for sufficiently fast ion transport for fast discharge and charge, i.e., for high current densities. These solvents should also be safe, ideally non-flammable and non-reactive with peroxides and whiskers on anodes. The best solvents developed for metal-air battery electrolytes appear to be blends of ionic liquids (organic salts that are liquid at room temperature) and polar aprotic organic solvents. Even with such solvents, explosive combustion of the electrolytes cannot be ruled out when the concentration of peroxides becomes large.

2 Results and Discussion

2.1 Thermodynamics and Safety Considerations: Achieving High Energy Density and Improved Safety

The conversion of $\text{O}_2$ to peroxides, such as $\text{Li}_2\text{O}_2$, instead of oxides or hydroxides, is necessary to achieve practical rechargeability in metal-$\text{O}_2$ batteries. The above mentioned issues with metal-$\text{O}_2$/peroxide batteries motivated us to seek alternative electrochemistry utilizing air-available species other than $\text{O}_2$ allowing for safer and more practical high energy density batteries for long range all-electric vehicles. Besides $\text{O}_2$, only $\text{CO}_2$ is an air-available molecule with rich electrochemistry that has been studied extensively. The conversion of $\text{CO}_2$ to oxalate ions, according to the reaction $2\text{CO}_2 + 2e^- \rightarrow \text{C}_2\text{O}_4^{2-}$, can be carried out with $100\%$ selectivity and great efficiency using existing catalysts or properly chosen electrolytes/electrodes. All other major studied reduction products of $\text{CO}_2$ would either involve hydrogen and would thus be less robust, or would lead to the evolution of poisonous carbon monoxide. While the deposition of aggressive oxidant peroxides in combustible battery materials, such as carbon-based electrodes and electrolytes, may lead to explosive combustions when peroxides are in high concentrations, there are no such problems with oxalates, as they are non-oxidative, thermally stable and environmentally benign species. For example, $\text{Li}_2\text{C}_2\text{O}_4$ decomposes only at about 500 °C. Due to these features, oxalates are significantly safer discharge products than peroxides. Oxalates are also known to be easily and quantitatively oxidizable to $\text{CO}_2$, in both aqueous and organic electrolytes on various types of electrodes, including graphite. Thus, reversible electrochemistry can be based on $\text{CO}_2$/oxalate conversions.

Remarkably, with the application of the copper-complex catalyst from Ref. 16, the $\text{CO}_2$ reduction standard electrode potential becomes as high as $U_0(\text{CO}_2(g)/\text{C}_2\text{O}_4^{2-})=-0.03$ V and the back-oxidation happens at $U_0(\text{C}_2\text{O}_4^{2-}/\text{CO}_2(g))=+0.81$ V, leading to greatly reduced overpotentials and energy efficiency of the corresponding conversions. Coupled with a Li-anode ($U_0(\text{Li}/\text{Li}^+)=+3.04$ V), this Li-$\text{CO}_2$/oxalate battery would have an open circuit voltage of ≈ 3.0 V, which is practically identical with that of the Li-$\text{O}_2$/peroxide battery. The identical voltages also imply close reaction Gibbs free energies (≈ -575 kJ/mol), as both processes transfer two electrons per molecule of product.

Tables 1 and 2 present the respective formation and reaction

| Molecule / Crystal | $\Delta_f H^\circ$ (kJ/mol) | $\Delta_f G^\circ$ (kJ/mol) | Ref. |
|--------------------|--------------------------|--------------------------|------|
| $\text{C}_8\text{H}_8(g)$ | -208.70 | -347.95 | 18 |
| $\text{O}_2(g)$ | 0.00 | -61.17 | 19 |
| $\text{H}_2\text{O}(g)$ | -241.83 | -298.13 | 19 |
| $\text{CO}_2(g)$ | -393.52 | -457.26 | 19 |
| $\text{Li}(s)$ | 0.00 | -8.67 | 19 |
| $\text{Li}_2\text{O}(s)$ | -598.73 | -610.01 | 19 |
| $\text{Li}_2\text{O}_2(s)$ | -632.62 | -649.44 | 19 |
| $\text{Li}_2\text{C}_2\text{O}_4(s)$ | -1216.04 | -1242.96 | 19 |

With Tables 1 and 2.

| System | Reaction | $\Delta_f H^\circ$ (kJ/mol) | $\Delta_f G^\circ$ (kJ/mol) |
|--------|----------|--------------------------|--------------------------|
| n-octane | $\text{C}_8\text{H}_{18}(g) + 12.5 \text{O}_2(g) \rightarrow 8 \text{CO}_2(g) + 9 \text{H}_2\text{O}(g)$ | -5116 | -5259 |
| Li-ion($\text{LiCoO}_2$) | $\text{Li}_2\text{C}_6(s) + \text{Li}_1\text{CoO}_2(s) \rightarrow \text{C}_6(s) + \text{LiCoO}_2(s)$ | -213 | - |
| Li-0₂/oxide | $2 \text{Li}(s) + 1/2 \text{O}_2(g) \rightarrow \text{Li}_2\text{O}(s)$ | -599 | -562 |
| Li-O₂/peroxide | $2 \text{Li}(s) + \text{O}_2(g) \rightarrow \text{Li}_2\text{O}_2(s)$ | -633 | -571 |
| Li-[O₂+CO₂]/carbonate | $2 \text{Li}(s) + \text{CO}_2(g) + 1/2 \text{O}_2(g) \rightarrow \text{Li}_2\text{CO}_3(s)$ | -823 | -738 |
| Li-O₂/oxalate | $2 \text{Li}(s) + 2 \text{CO}_2(g) \rightarrow \text{Li}_2\text{C}_2\text{O}_4(s)$ | -590 | -579 |
energies, while Table 3 lists energy densities and capacities of several Li-air type batteries in comparison with gasoline (n-octane) and a typical Li-ion battery. These data indicate that Li-CO$_2$/oxalate batteries may compete with Li-O$_2$/peroxide ones for applicability in long-range all-electric vehicles. Indeed, the gravimetric energy density of the Li$_2$C$_2$O$_4$ formation is 11.5 kWh/kg, slightly greater than that of Li$_2$O$_2$ (11.3 kWh/kg), within 11% to n-octane (12.8 kWh/kg), in reference to the weight of Li, assuming air based O$_2$ or CO$_2$ intake. When O$_2$ or CO$_2$ is carried on the vehicle, or in reference to the weight of the discharge products, the gravimetric energy density of Li$_2$C$_2$O$_4$ is 1.6 kWh/kg, about 2.2 times smaller than that of Li$_2$O$_2$, due to the larger weight of Li$_2$C$_2$O$_4$, still about 3 times larger than that of a LiCoO$_2$-based Li-ion battery. The practical energy densities of the oxalate and peroxide based batteries would differ significantly less, as they would also involve the mass of other battery components, such as electrolytes, membranes, current collectors, cases, etc. Furthermore, in case of the corresponding Na batteries (instead of Li ones), the weight-factor would be reduced to 1.7 from 2.2. The gravimetric and volumetric capacities (Li-densities) of Li$_2$C$_2$O$_4$ are lower than those of Li$_2$O$_2$ by a factor of about 2.2. While the gravimetric capacity of Li$_2$C$_2$O$_4$ is about twice as much as that of LiCoO$_2$, the volumetric one is only about 80% of it.

The energy and capacity density values of Li$_2$C$_2$O$_4$ are quite practical to allow for long range electric vehicles. A car that takes up 13 US (liquid) gallons (about 49 L) of n-octane, stores about 88.6 kWh energy for useful work, assuming 20% engine efficiency. The equivalent of this energy would be released by the production of 7.7 gallons of Li$_2$C$_2$O$_4$ at a rather poor electric motor efficiency of 90%. The amount of oxalates needed may further be reduced with greater motor efficiency (96% as of Ref. 27), electrically storing energy from braking or due to reduced idle time. Solvents for (partial) dissolution of the oxalates (or peroxides) may require additional space though. The weight of 7.7 gallons of Li$_2$C$_2$O$_4$ is 62 kg, only about 27 kg more than that of 13 gallons of gasoline (35 kg). The increase in the weight of the vehicle by the battery may be reduced by lighter, carbon-composite based cars, and by electric motors lighter than internal combustion engines, to maintain the same driving distance and approximately the same volume for energy storage as known for present day gasoline driven cars.

The energy storage efficiency of the Li-CO$_2$/oxalate battery can be estimated from the voltage ratio of the discharge and charge processes at constant current. Using the voltages of 3.0 and 3.8 V for discharge and charge, respectively, associated with the copper-complex catalyst of Ref. 16, the energy storage efficiency of the Li-CO$_2$/oxalate battery is estimated to be 79%. In practice, this value would be significantly lower but likely higher than that of Li-O$_2$/peroxide batteries, 65%, due to considerable overpotentials on charge in the latter ones.

In principle, a 1:1 molar mix of O$_2$ and CO$_2$ could lead to a further increased energy density in Li-[O$_2$+CO$_2$]/carbonate batteries, however, in practice either the O$_2$ or the CO$_2$ gets reduced, leaving electrically utilizable energy densities (per mol of product) at the level of Li-O$_2$/peroxide or Li-CO$_2$/oxalate batteries. When O$_2$ gets reduced, the presence of CO$_2$ leads to carbonate formation, producing a lot of additional heat, formally through the reaction of Li$_2$O with CO$_2$. The voltage of such a Li-[O$_2$+CO$_2$]/carbonate battery was found identical

| System          | OCV (V) | Density of product (kg/L) | Energy Density gravimetric (Wh/kg) (air) | Energy Density volumetric (Wh/L) (tank) | Charge Capacity gravimetric (mAh/g) | Charge Capacity volumetric (mAh/cm$^3$) | Rechargeability |
|----------------|--------|---------------------------|----------------------------------------|---------------------------------------|-----------------------------------|---------------------------------------|-----------------|
| n-octane       | -      | -                         | 12814                                  | 9008                                  | -                                 | -                                    | N               |
| Li-ion (LiCoO$_2$) | 3.6   | 5.05                      | -                                      | -                                     | -                                 | 273                                   | N               |
| Li$_2$O$_2$/peroxide | 2.9   | 2.02                      | 11151                                  | 5955                                  | 10512                             | 1787                                  | 3610            |
| Li$_2$O$_2$/peroxide | 3.0   | 2.25                      | 11329                                  | 6050                                  | 7758                              | 1165                                  | 2621            |
| Li-[O$_2$+CO$_2$]/carbonate | 3.0   | 2.10                      | 11329                                  | 6049                                  | 4500                              | 724                                   | 1520            |
| Li-CO$_2$/oxalate | 3.0   | 2.14                      | 11488                                  | 6134                                  | 3375                              | 525                                   | 1125            |

2 RESULTS AND DISCUSSION

2.1 Thermodynamics and Safety Considerations: Achieving High Energy Density and Improved Safety

Table 3 Theoretical gravimetric and volumetric energy ($\Delta G^\circ$) densities and capacities of energy storage reactions, as well as open circuit voltages (OCV), densities of products and rechargeabilities, $\Delta G^\circ$ values have been taken from Table 2. Note that the OCV for the Li-CO$_2$/oxalate cell is based on the standard electrode potential of $U_0$(CO$_2$(g)/C$_2$O$_2^-$(aq)) = -0.03 V from Ref. 14 and on $U_0$(Li(s)/Li$^+$) = -3.04 V from Ref. 17. OCV-s of the other cells are based on Refs. 21, 22, 6 and 23. The OCV of the Li-(O$_2$+CO$_2$)/carbonate cell is identical to that of the Li-O$_2$/peroxide one, as of Ref. 13, i.e. the addition of CO$_2$ to a Li-O$_2$/peroxide cell produces extra heat instead of electrical energy, while its rechargeability is debated. O$_2$ or CO$_2$ may be supplied from air or from a gas tank carried on the vehicle leading to different energy densities. Discharge capacities are referenced to bulk lithium and are identical for all Li-air type systems (3830 mAh/kg and 2045 mAh/cm$^3$), while charge capacities are referenced to solid discharge products. Densities of solids are based on crystal structures at standard state.
2.1 Thermodynamics and Safety Considerations: Achieving High Energy Density and Improved Safety

RESULTS AND DISCUSSION

The current best rechargeable Li/ambient-air batteries produce mostly Li$_2$CO$_3$ during discharge.

Interestingly, in some electrolytes based on ionic liquids, it is the CO$_2$ that gets reduced to oxalate and O$_2$ does not formally participate in reactions. Selective reduction of CO$_2$ to oxalate from ambient air through a catalyst and simultaneous reduction of O$_2$ to peroxide is also possible, potentially allowing for a rechargeable Li-air battery by eliminating the presence of carbonates.

Pure O$_2$ or CO$_2$ could also be supplied from a tank stored on board of the vehicle. At a relatively safe and practical 120 bar pressure and 30 °C temperature, the density of CO$_2$ is 0.802 kg/L, while that of O$_2$ is only 0.160 kg/L. With good thermal insulation, potentially even solid CO$_2$, ‘dry ice’, could be stored on board, with a high density of 1.6 kg/L. For the above mentioned 88.6 kWh useful energy, the space required for CO$_2$ storage would be between 8.8 and 18 gallons, while that of O$_2$ would be at 32 gallons. The compression of O$_2$ requires far more work though than that of CO$_2$. This is obvious also from the economical availability of ‘dry ice’, or the use of CO$_2$ as working fluid in air conditioning in both vehicles and buildings.

Even though the work invested in the compression of these gases may be returned to some extent when a higher pressure gas is applied on the respective electrodes, CO$_2$ appears far more advantageous for on-board storage than O$_2$, for its far better compressibility. CO$_2$ can be collected efficiently from air as well, via CO$_2$-sponge materials, based on economically available ion-exchange resins allowing for CO$_2$ intake from air at rates of 0.25-0.83 g CO$_2$/m$^2$/s (up to 3.0 kg CO$_2$/m$^2$/h) despite the low, ≈ 0.04 mol % concentration of CO$_2$ in air.

On charge, oxalate salts from metal-CO$_2$/oxalate batteries will be converted to CO$_2$ that will not react with other battery components, such as the electrolyte or the porous carbon electrode, at the charging electrode potential. Peroxide salts from metal-O$_2$/peroxide batteries will, however, be converted to highly reactive oxygen species such as singlet oxygen that may react with the electrolyte and the porous carbon or other combustible battery components.

Figure 1 shows one possible implementation of a simple Li-CO$_2$/oxalate battery. The porous positive gas-diffusion electrode contains catalysts, such as the copper-complex mentioned above, for the reversible conversion of CO$_2$ to oxalate ions. During discharge, CO$_2$ is converted to oxalate ions that migrate through an anion-exchange membrane into the central compartment of the cell where they mix with Li$^+$ ions released from a bulk Li-anode, while electrons move from the anode to the cathode. In this implementation, the aprotic electrolyte in the central compartment may be composed of a blend of an ionic liquid and a polar organic solvent, sim-
In order to maximize the power density, i.e. the rate of charging/discharging the battery, the kinetic processes involved in the electron transfers and ion transports have to be made quick. The rate of oxalate ion transport in the cathode, through the membrane and in the central compartment determines the current density of the battery (rate of charge/discharge capacity) and should be subject of optimization. On charge, oxalate ions migrate to the positive electrode where they get oxidized back to CO$_2$, while Li$^+$ ions get reduced and deposited on the negative electrode and electrons move from the positive electrode to the negative one through the outer circuit. Many variants of the above described simple implementation of a Li-CO$_2$/oxalate battery are possible and some are discussed to a larger extent in Ref. $^{32}$.

### 2.2 Kinetics Considerations: Optimization of the Power Density

In order to maximize the power density, i.e. the rate of charging/discharging the battery, the kinetic processes involved in the electron transfers and ion transports have to be made quick. The application of CO$_2$ instead of O$_2$ offers several specific advantages in this respect as well.

In case CO$_2$ is taken from a tank and is supplied as a moderately high pressure (10-140 bar) gas or supercritical fluid into the battery, it can serve both as a solvent and a source of electroactive species in the same time. Fundamental aspects of electrochemistry in supercritical CO$_2$ have been investigated by Abbott et al. $^{36,37}$. The use of high pressure or supercritical CO$_2$ appears attractive for achieving very fast ion transport and thus high charge/discharge rates, as diffusion may be very fast in such high-pressure or supercritical medium when the concentration of voids is large enough. $^{38}$ As liquid or fluid CO$_2$ has low solubility for salts, a polar modifier needs to be added, such as 1,1,1,2-tetrafluoroethane (HFC 134a),$^{37}$ propylene carbonate,$^{39,40}$ or glymes.$^{41}$ Both propylene carbonate and glymes are excellent solvents (or solutes) for (or in) pressurized CO$_2$ and mix well with supercritical CO$_2$ fluid. Propylene carbonate at room temperature and 10 to 55 bar pressure can dissolve 10 to 60 mol% CO$_2$, respectively.$^{39}$ while diglyme at $40\degree$C and 10 to 71 bar pressure dissolves 20 to 85 mol% CO$_2$, respectively.$^{42}$ Note that the critical point of pure CO$_2$ is at $T_c=31\degree$C and $p_c=74$ bar. The compression of the pressurized/supercritical electrolyte com-

---

**Fig. 2** Schematic view of a rechargeable Li-CO$_2$/oxalate flow battery. The purple stripe refers to a Li-ion selective membrane, the orange one to the catalytic CO$_2$/oxalate electrode. The arrows indicate the flow of the electrolyte during charge and discharge. For maximum charge/discharge rates a pressurized solution or supercritical fluid electrolyte is applied consisting of high pressure (10-140 bar) mixture of CO$_2$, polar modifier (propylene carbonate, glyme, etc) and supporting electrolyte (organic salt, ionic liquid). As the electrolyte passes between the protected Li anode and the catalytic CO$_2$/oxalate cathode, it dissolves the discharge product Li$_2$C$_2$O$_4$ and deposits it in the product container either through locally expanding volume and reduced pressure, or through a filter. The flow of the electrolytic fluid is recompressed after the deposition of Li$_2$C$_2$O$_4$ and circulated back toward the electrodes. On charge, the flow of the electrolyte is reversed, Li$_2$C$_2$O$_4$ is dissolved in the electrolyte in the product container and is converted back to Li and CO$_2$ on the electrodes. The increased pressure causes CO$_2$ to migrate back to the CO$_2$ container through a CO$_2$ selective membrane and valve. A similar flow battery may be realized at atmospheric pressure applications) or an atmospheric CO$_2$ absorbing unit (for normal pressure applications).
sumes a fraction of the energy stored in the battery, however, this fraction can be kept small (<3%) for isothermal compression and even smaller when electrochemical compression is used, as discussed by Christensen et al. in Ref. 2 for Li-O2 batteries.

In addition to the polar modifier, supporting electrolyte is also needed to increase the ionic conductivity of the electrolyte, at least until it is saturated with discharge products. The supporting electrolyte is typically composed of organic salts (ionic liquids), such as tetrabutylammonium tetrafluoroborate 27, or imidazolium salts 42 and may be composed of the oxalate ion containing organic salts mentioned above, as well. Additionally, many organic salts show anomalous melting point depression in pressurized CO2 which in principle allows such pressurized room temperature ionic liquids to be used as electrolytes in themselves, i.e. without the glymes or organic carbonates or other polar modifiers while also maintaining increased concentration of voids for faster ion transport.

A flow battery based on pressurized-supercritical CO2 is depicted in Fig. 2. It is composed of a negative electrode with protected metal (Li, Na, Mg, Al, etc) source, a positive electrode current collector with a catalyst for CO2 reduction and oxalate oxidation covering its surface, and a flow of CO2-rich solution or supercritical fluid between the electrodes. As the flow passes between the electrodes it becomes enriched in oxalate salts during discharge. The oxalate salts will be deposited in a container where the pressure may decrease due to increased volume and the CO2 and the polar modifier or solvents will be recompressed and circulated back to between the electrodes. In case a non-compressible solvent is used, it may be pumped through a filter leaving the excess discharge products in the product container. On charge, the flow of the supercritical fluid or that of the pressurized solution will be reversed, oxalate ions will be oxidized back to CO2, metal ions reduced and the regenerated CO2 will be stored back in the CO2 tank. The charge/discharge rates of such a battery are expected to primarily depend on the catalytic density on the surface of the positive electrode, as the concentration of the CO2 is very high and transport of electroactive species to and from the catalyst is expected to be very fast due to the directed flow of the voids-rich fluid or liquid. The rates also depend on the ionic conductivity of the protective skin (or cation selective membrane) on the negative electrode. Highest discharge rates are expected for supercritical fluid electrolytes for the greatest concentration of voids supporting ion transport.

In case CO2 is not supplied from a tank but taken up from the air through a CO2 absorbing material mentioned above, a similar flow battery scheme can be utilized, with a circulated electrolyte at atmospheric pressure. In order to maximize the speed of transport of oxalate ions, the use of deep eutectic solutions is suggested as primary component of the electrolyte, as it opens the way to hopping based fast oxalate ion transport as opposed to slow simple diffusion. It is expected that the mix of oxalate ions containing solid organic salts (such as those mentioned above with pyrrolidinium, imidazolium or tetrabutylammonium cations) and the discharge product metal-oxalates forms room temperature liquids based on principles of deep eutectic mixtures. Examples of such deep eutectic liquids with oxalate salts exist, and provide alternatives to ionic liquids as solvents. For example, the mixture of choline chloride and oxalic acid forms a room temperature liquid electrolyte, even though the individual components are solids themselves. Electrochemistry in such deep eutectic solvents with carboxylic acids has been studied by Abbott et al. and by LeSuer et al. 38,44. The ionic conductivity of such deep eutectic liquids was found to be similar to that of ionic liquids. In the proposed mix of organic oxalates and metallic oxalates it is expected that the oxalate ions would chelate the metal cations and oxalate transport would happen through hopping of oxalate ions between neighboring chelating sites, instead of diffusion. Since the concentration of the chelating sites is very high in the proposed deep eutectic liquids, a fast oxalate ion transport is expected. Note, that only the transport of oxalate ions is expected to be fast in such liquids, other anions would be transported much slower. Also note that the previously studied choline chloride and oxalic acid mixture does not allow for hopping based oxalate transport as it does not contain metal cations as chelating sites, thus the proposed hopping based oxalate ion transport is yet to be investigated experimentally. The deep eutectic solvent may be diluted by the addition of polar aprotic solvents, such as propylene carbonate and dimethoxyethane, to decrease its viscosity, especially for the fully charged state where the metal oxalate component may be missing as is yet to be produced during the discharge. When the deep eutectic liquid becomes saturated with the dissolved metal oxalates, the precipitating excess oxalates would be deposited in the discharge product container. On charge, the oxalates in the product container would be dissolved in the deep eutectic electrolyte and brought to the electrodes where metal and CO2 would be generated as the battery is being charged. Also note that the cell in Fig. 1 can also be used in a flow battery design, in this case the CO2 is supplied through a gas diffusion electrode separated by an oxalate ion conducting membrane from the electrolyte. The above described flow battery designs also have the advantage of minimizing the amount of the electrolyte and other additional components reactive to the reactants and the products. Many variants of the CO2/oxalate battery are possible utilizing the principles described here.

A primary battery with Na anode and CO2/oxalate cathode has recently been realized by Das et al. as an unexpected by-product of Na+(O2+CO2) battery experiments, observing that oxygen admixture to CO2 can act as a catalyst for the produc-
tion of oxalate salts during discharge in appropriately chosen ionic liquid electrolytes while no oxide or carbonate discharge products are formed. The voltage of this battery (≈2.25 V, OCV) is about 18% smaller than that of an analogous Na-(O$_2$+CO$_2$)/(peroxide+carbonate+oxalate) battery presented in the same work (≈2.75 V, OCV, see Fig. 1 of Ref. 14 or that of a Na-O$_2$/(peroxide) battery (2.6 V, theoretical OCV). This experimental result indicates the feasibility of metal-air type batteries with CO$_2$/oxalate cathodes, and also indicates that oxalate formation may be similarly energetic as peroxide formation when proper catalysts and electrolytes are used. This observation is in agreement with what we described above about the thermodynamics of CO$_2$/oxalate conversion using experimental data with the copper complex catalyst by Angamuthu et al.16 and the measured enthalpies and Gibbs free energies of formation of Li$_2$C$_2$O$_4$.

3 Conclusions
We have proposed to use CO$_2$/oxalate electrodes instead of O$_2$/peroxide or O$_2$/hydroxide ones in high energy density rechargeable metal-air type batteries. The advantages of CO$_2$/oxalate electrodes may be realized in terms of significantly improved safety and environmental friendliness, high energy and power density, robust and more efficient rechargeability and efficient on-board storage or air-based intake of CO$_2$.

4 Acknowledgements
K. N. gratefully acknowledges helpful discussions with Drs. M. Balasubramanian, G. Crabtree, N. Markovic, L. Trahey, and M. van Veenendaal at Argonne National Laboratory and A. K. Unni, C. U. Segre and L. Shaw at IIT. This research was supported by the U.S. DOE Office of Science, under contract No. DE-AC02-06CH11357.

References
1 M. Armand and J.-M. Tarascon, Nature, 2008, 451, 652–657.
2 J. Christensen, P. Albertus, R. S. Sanchez-Carrera, T. Lohmann, B. Kozinsky, R. Liedtke, J. Ahmed and A. Kojic, Journal of The Electrochemical Society, 2012, 159, R1–R30.
3 G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson and W. Willeke, Phys. Chem. Lett., 2010, 1, 2193–2203.
4 A. Kraytsberg and Y. Ein-Eli, Journal of Power Sources, 2011, 196, 886–893.
5 F. Li, T. Zhang and H. Zhou, Energy & Environmental Science, 2013, 6, 1125.
6 T. Ogawara, A. Débart, M. Holzapfel, P. Novák and P. G. Bruce, J. Am. Chem. Soc., 2006, 128, 1390.
7 B. Kumar, J. Kumar, R. Leese, J. P. Fellner, S. J. Rodrigues and K. M. Abraham, Journal of The Electrochemical Society, 2010, 157, A50–A54.
8 S. J. Visco and Y. S. Nimon, Active Metal/Aqueous Electrochemical Cells and Systems, Patent, US7666232, 2010.
9 J. Fu, Solid State Ionics, 1997, 96, 195–200.
10 T. Zhang and H. Zhou, Nature Comm., 2013, 4, 1817.
11 C. Wessells, R. Ruffo, R. A. Huggins and Y. Cui, Electrochem. and Solid-State Lett., 2010, 13, A59–A61.
12 S. R. Gowda, A. Brunet, G. M. Walhraff and B. D. McCloskey, J. Phys. Chem. Lett., 2013, 4, 276–279.
13 K. Takechi, T. Shiga and T. Asaoka, Chem. Commun., 2011, 47, 3463.
14 S. K. Das, S. Xu and L. A. Archer, Electrochemistry Communications, 2013, 27, 59–62.
15 B. G. Kim, J.-N. Lee, D. J. Lee, J.-K. Park and J. W. Choi, ChemSusChem, 2013, 6, 443–448.
16 R. Angamuthu, P. Byers, M. Lutz, A. L. Spek and E. Bouwman, Science, 2010, 327, 313–315.
17 W. M. Haynes, CRC Handbook of Chemistry and Physics 2011-2012, Taylor & Francis, 2011.
18 W. D. Good, J. Chem. Thermodyn., 1972, 4, 709–714.
19 NIST-JANAF Thermochemical Tables, ed. M. W. Jr. Chase, American Chemical Society and the American Institute of Physics, Washington DC, 4th edn, 1998, pp. 1–1951.
20 B. B. Letson and A. R. Taylor, Heats of formation of lithium chloride and lithium oxalate, including details on the construction and operation of a solution calorimeter, U.S. Dept. of the Interior, Bureau of Mines, 1965, vol. 6583.
21 K. Mizushima, P. Jones, P. Wiseman and J. Goodenough, Materials Res. Bull., 1980, 15, 783.
22 R. Yazami and P. Touzain, A reversible graphite-lithium negative electrode for electrochemical generators, 1983, 9, 365.
23 M. M. Thackeray and et al., Lithium-Oxygen (Air) Electrochemical Cells and Batteries, Patent, US8337121, 2012.
24 L. Skarlos, Preparation of Oxalic Acid, Patent, US3720591, 1973.
25 D. Dollimore and D. Tinsley, J. Chem. Soc., 1971, (A), 3043–3047.
26 Š. Slukić, R. Baron and R. G. Compton, Electroanalysis, 2007, 19, 918–922.
27 T. Oikawa, T. Tajima, K. Masumoto, H. Akita and H. Kawaguchi, International Compressor Engineering Conference, 2002, C12–4.
28 Bernd Dienhart et al., Optimized CO$_2$ Operated Air Conditioning System, Patent, US6588223, 2003.
29 B. R. Lackner, The European Physical Journal, Special Topics, 2009, 176, 93–106.
30 K. S. Lackner and A. Wright, Laminar Scrubber Apparatus For Capturing Carbon Dioxide From Air And Methods Of Use, Patent, US7833328, 2010.
31 J. Hassoun, F. Croce, M. Armand and B. Scrosati, Angew. Chem., 2011, 50, 2999–3002.
32 K. Neneth, M. van Veenendaal and G. Srajer, Electrochemical energy storage device based on carbon dioxide as electroactive species, Patent, US8391978, 2013.
33 Bernatowicz et al., Methods and apparatus for the formation of heterogeneous ion exchange membranes, Patent, US7671688, 2004.
34 A. Rachocki, K. Pogorzalek-Glaser, A. Piteraszk and J. Tritt-Goc, J. Phys.: Condens. Matter, 2008, 20, 505101.
35 A. G. Pinkus and R. Harizan, Poly(methylene-oxalate) and precursors thereto, Patent, US7250291, 1993.
36 A. P. Abbott and J. C. Harper, J. Chem. Soc., Faraday Trans., 1996, 92, 3895–3898.
37 A. P. Abbott and C. A. Eardley, Journal of Physical Chemistry B, 2000,
REFERENCES

38 A. P. Abbott, D. Boothby, G. Capper, D. L. Davies and R. K. Rasheed, *J. Am. Chem. Soc.*, 2004, **126**, 9142–9147.

39 P. D. Mantor, O. Abib, Jr., K. Y. Song and R. Kobayashi, *Journal of Chemical Engineering Data*, 1982, **27**, 243–245.

40 H. Kawanami, A. Sasaki, K. Matsuiia and Y. Ikushima, *Chem. Comm.*, 2003, **7**, 896–897.

41 D. Kodama, M. Kanakubob, M. Kokuboa, S. Hashimotoa, H. Nanjob and M. Katoa, *Fluid Phase Equilibria*, 2011, **302**, 103–108.

42 A. M. Scurto and W. Leitner, *Chem. Comm.*, 2006, **35**, 36813683.

43 A. M. Scurto, E. Newton, R. R. Weikel, L. Draucker, J. Hallett, C. L. Liotta, W. Leitner and C. A. Eckert, *Ind. Eng. Chem. Res.*, 2008, **47**, 493–501.

44 C. A. Nkuku and R. J. LeSuer, *J. Phys. Chem. B*, 2007, **111**, 13271–13277.