



Sacrificial salts: Compensating the initial charge irreversibility in lithium batteries

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ABSTRACT

Lithium salts enlisting azide, oxocarbons, dicarboxylates and hydrazides have been identified as a practical mean to compensate the irreversible capacity loss of LIBs negative electrodes. During the first charge, the anion loses electrons and converts to gaseous N₂, CO or CO₂, within an acceptable potential range (3 to 4.5 V). We report an electrochemical study on these easily accessible “sacrificial salts”.

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1. Introduction

Lithium batteries, beyond their success in nomadic electronics, are considered for the transportation sector, whose share of CO₂ emissions is rising intolerably. For electronics, the quest is for ever increasing energy density, while for EVs, HEVs and Plug-in HEVs, a compromise is needed between safety and the availability of materials (Fe, Mn, organics...). Li-ion batteries (LIB) are built in the discharged state, the only reservoir of Li⁺ is contained in the positive electrode. With the most used negative electrode, graphite, 7–20% of the lithium emanating from the positive is consumed to build a passivation layer (SEI), meaning a corresponding deadweight of inactivated positive material. This is frustrating as its capacity, ≈ 120–160 mAh/g is much lower than graphite (360mAh/g). Shifting from carbon to silicon (≥2000 mAh/g) would not change this wasteful practice, as the SEI consumes >15% of capacity. Considering the shortcomings of intercalation (1 e[−]/T^M), a multi-electron reaction with phase nucleation (“conversion reaction”), e.g.: T^MO + 2 Li⁺ + 2e[−] ⇌ T^M° + Li₂O (T^M = Co, Ni, Mn...) is proposed [1–4]. With nano-sized phases, the reconstruction of T^MO from T^M° + Li₂O becomes partially reversible. Yet, the large specific capacities are to be brought together with a crippling penalty of 40% Li loss. Li_xMn₂O₄ was thought to offer an answer, as it operates in the 0 < x ≤ 1 range but accepts one extra Li to x = 2, which has been used for supplying extra lithium cells [5]. However, beyond x = 1, the phase change results in mechanical stress, shortening the lifecycle. A general solution to the initial capacity loss is proposed with the “stabilized lithium powder®”, a suspension in hydrocarbons [6,7]. This approach

has however severe handicaps: adding Li⁺ to either electrode poises the potential at 0 V, triggering several side reactions and abandoning the advantage of building LIBs in air.

Considering the stakes in terms of battery performance and proper material utilization, we suggest a novel approach in which a lithium salt with an oxidizable anion is admixed in the positive electrode. During the first charge, the anion loses electrons to be converted to gaseous species, chosen to be innocuous to further battery operation. A side benefit is the creation in the positive composite of controlled porosity. Electrolyte in the voids serves as ion reservoir, beneficial since the Li⁺ transference number is below unity. The gas(es) could be evacuated before sealing the battery, or through a valve. Already in practice, cells are charged without the lid (bag) sealed to avoid pressure (H₂C=CH₂) build-up.

For this purpose, we identified salt families able, in an acceptable potential range (3 to 4.5 V), to transform into N₂, CO or CO₂. We chose lithium: azide (LiN₃), squarate (Li₂C₄O₄), oxalate (Li₂C₂O₄), ketomalonate (Li₂C₃O₅) and di-ketosuccinate (Li₂C₄O₆) (Fig. 1) as easily accessible representatives of the three first families. In the systems containing N–N bonds, Li-poly(oxalyldiazide) was selected. We report here a feasibility study of the “sacrificial salts” concept in LIBs.

2. Experimental

LiN₃ was obtained by evaporation of the commercial aqueous solution and dried at 60 °C under vacuum. Lithium oxalate (Li₂C₂O₄), commercial, and di-lithium squarate (Li₂C₄O₄) synthesized using the corresponding acid 3,4-dihydroxy-3-cyclobutene-1,2-dione and Li₂CO₃ as starting materials were dried similarly

Di-lithium ketomalonate (Li₂C₃O₅) was synthesized from commercial sodium mesoxalate monohydrate treated in 50% ethanol with

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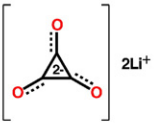
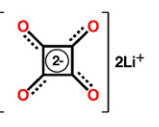

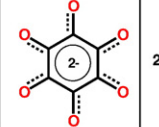
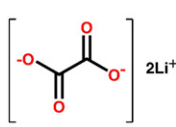
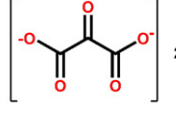
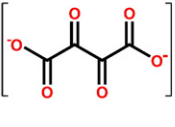
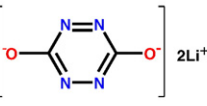
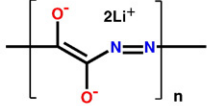
Family ↓	Representatives ↓			
Azides	$\left[\text{N} \equiv \text{N} \equiv \text{N} \right] \text{Li}^+$			
	(A) Specific capacity: 567 mAh/g			
Oxocarbons				
	570 mAh/g	(B) 440 mAh/g	360 mAh/g	305 mAh/g
Dicarboxylic acids				
	(F) 545 mAh/g	(C) 430 mAh/g	(D) 351.8 mAh/g	
Hydrazides				
	441 mAh/g		(E) 567 mAh/g	

Fig. 1. Structural formula and specific capacity of the compounds corresponding to the four “sacrificial salt” families.

stoichiometric H_2SO_4 then evaporated under reduced pressure. The acid $(\text{HO})_2\text{C}(\text{CO}_2\text{H})_2$ extracted with 100% ethanol and reacted with 5% excess of LiOH . The slurry was centrifuged and washed 3 times with ethanol to remove excess base. The final product ($\text{Li}_2\text{C}_3\text{O}_5$) was then obtained by dehydration at 165°C under vacuum.

Treating dihydroxyfumaric acid with of pyridinium hydrotribromide in 100% ethanol in the presence of lithium acetate (1:1:4) gave $\text{Li}_2[\text{CO}_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}_2]$ as a suspension which was centrifuged and washed $3\times$ with ethanol, followed by same dehydration procedure to form $\text{Li}_2\text{C}_4\text{O}_6$.

Oxalyldihydrazide $[\text{CONHNH}_2]_2$ in suspension in dry ACN was polycondensed with oxalyl chloride with pyridine as proton scavenger. The pale yellow polymer $[\text{COCONHNH}]_n$ was treated, inside the dry box with lithium methoxide in anhydrous DMF (1.1 equivalent / NH). The resulting bright yellow $[\text{COCON}(\text{Li})\text{N}(\text{Li})]_n$ was centrifuged and washed with anhydrous ethanol $2\times$ and dried. All commercial chemicals were from either Alfa, Aldrich, Fluka or Acros.

3. Characterisation

Fourier transform infrared (FTIR) spectra were recorded using a Nicolet Avatar 370DTGS spectrometer. Electrochemical analysis was carried out using a three electrode Swagelok® cell assembled in an argon-filled glove box and cycled using a VMP3 (Biologic) in galvanostatic mode. These cells comprise a Li foil as the negative and reference electrode, a Whatman GF/D borosilicate glass fiber sheet saturated with a 1 M LiPF_6 solution in ethylene carbonate (EC), dimethyl carbonate (DMC) (1:1 w/w) as the electrolyte, and unless otherwise specified, the positive electrode is made by mixing the sacrificial salts with 30 wt.% Ketjen black® (KJ-600). The cells were charged at a removal rate of $1 \text{ Li}^+ / 10 \text{ h}$. In order to detect the gas released, in-situ electrochemical mass spectrometric measurements were taken. The home-made experimental setup constituted a Swagelok® cell fitted with a capillary tube on top as gas outlet,

connected to a QMS 403C Aeolos mass spectrometer, and electrochemical measurements were recorded using a VSP (Biologic) at C/3. To avoid adventitious gas release from the lithium side, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ counter electrode was used for these measurements.

4. Results and discussion

Oxalate was the most obvious choice and known to oxidize to CO_2 in water, but it has no electrochemistry in aprotic solvents due to insolubility, though it has been proposed as an overcharge additive in batteries [8,9]. The choice of the higher homologues in this family, ketomalonic $[(\text{CO}_2)_2\text{CO}]^{2-}$ and diketosuccinic $[(\text{CO}_2\text{CO})_2]^{2-}$ anions was suggested by their higher HOMO states density, facilitating electron removal, leading to molecular breakdown. The lithium salts have seemingly not been prepared, nor their precursors $(\text{HO})_2\text{C}(\text{CO}_2\text{Li})_2$, H_2O and $[\text{LiO}_2\text{CC}(\text{OH})_2]_2$, $4\text{H}_2\text{O}$ when the electron-deficient central carbonyls hydrate to gem-diols under ordinary conditions. The oxocarbon $[\text{CO}]_n^{2-}$ have received due attention, being quasi-aromatic [10], especially for $n=4$. The azide anion has a very negative decomposition voltage ($\approx 0 \text{ V}$ vs. $\text{Li}^+/\text{Li}^\circ$). Handleable azides owes to their large metastability, N_3^- forming transient N_6 , rearranging to N_2 upon oxidation. While all dianions based on hard centers like oxygens have negligible solubility in aprotic solvents, that of the singly charged azide was measured at 32.6 mg/mL in NMP and 0.9 mg/mL in acetone (both PVF₂/HFP solvent in Bellcore technology). DSC/TG experiments revealed stability up to 250°C for all the salts.

4.1. FTIR spectroscopic measurements

The FTIR spectra are shown in Fig. 2 (A–E). In the case of LiN_3 (A) the asymmetric and symmetric stretching vibrations of the azido group $-\text{N}_3$ were observed at 2070 and 1630 cm^{-1} respectively [11]. $\text{Li}_2\text{C}_4\text{O}_4$ (B) shows an intense band at 1550 cm^{-1} , attributed to $\text{C}=\text{C}$ and $\text{C}=\text{O}$ bonds (stretching vibrations) and at 1100 cm^{-1} , corresponding to the $\text{C}-\text{C}$

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