Short communication

# An azamacrocyclic electrolyte additive to suppress metal deposition in lithium-ion batteries

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## ABSTRACT

An azamacrocyclic compound (1,4,8,11-tetraazacyclotetradecane, cyclam), which forms strong chelate complexes with metal ions such as Mn(II) and Fe(II), is tested as an electrolyte additive to suppress metal deposition. The tetradentate cyclic ligand is electrochemically stable within the working voltage of lithium-ion batteries (0.0–4.5 V *vs.* Li/Li$^+$), hence it is practicable as an electrolyte additive. Deposition of Mn on a graphite electrode, which is severe when a Li/graphite cell is cycled in a Mn(II)-containing electrolyte solution, is greatly suppressed by adding cyclam. Our elemental analysis reveals negligible Mn deposits on a graphite electrode indicating the beneficial role of cyclam. The suppression of metal deposition is further indicated by the absence of an internal short between Li metal and lithium cobalt oxide positive electrode.

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## 1. Introduction

Metal dissolution from the positive electrode and redeposition on the negative electrode is one of the well-known failure processes in lithium-ion batteries (LIBs) [1–4]. A typical example is Mn dissolution from spinel-structured lithium manganese oxide (LiMn$_2$O$_4$, LMO hereafter). The detrimental effect of Mn dissolution on LMO positive electrode is minor as the reversible capacity of LMO only decreases by a marginal amount [5]. However, the harmful effect on negative electrodes is more critical [6–8], particularly on graphite electrodes on which the dissolved Mn ions are readily electroplated [1,3]. In such cases, several undesirable features ensue. First, a local galvanic cell is formed via a coupled redox reaction, in which Mn ions are deposited (reduction) and the charged (lithiated) graphite is discharged (oxidation) [3,4]. The net result is self-discharge of graphite electrodes. Second, the passivating solid electrolyte interphase (SEI) layer on the graphite surface is broken due to the deposition of electrically conductive Mn metal [1]. The net result is reductive electrolyte decomposition and concomitant film deposition on the as-deposited metal surface, which leads to an increase in film resistance and electrode polarization. Third, the dendritically grown metal deposits can penetrate the separator

to reach the positive electrode surface, eventually resulting in an internal short. Metal dissolution from impurity metals (such as Fe and Ni) in the conductive carbons (for example, Super P) that are loaded in positive electrodes has a similar harmful effect on LIBs [9].

In this study, an azamacrocyclic compound (1,4,8,11-tetraazacyclotetradecane, cyclam) is tested as an electrolyte additive to suppress the metal deposition. Note that this cyclic ligand cannot prevent metal dissolution, but it can suppress metal deposition by forming a strong 1:1 chelate complex with metal ions (M(II) + cyclam = M(II)(cyclam), where M = Mn, Fe and Ni) [10]. Also, note that metal deposition becomes thermodynamically unfavorable once the metal ions form strong complexes because the standard electrode potential becomes increasingly negative. Also, metal deposition becomes kinetically slower due to the formation of chelate complexes [11]. To examine such additive effects, the electrochemical stability of cyclam within the working voltage of LIBs (0.0–4.5 V *vs.* Li/Li$^+$) is assessed. Subsequently, two different control experiments are performed. In one experiment, a small amount of Mn(II) ions is intentionally added to the background electrolyte to simulate dissolved Mn(II) ions, and the deposition of Mn metal on graphite electrode in additive-free and additive-added electrolyte solutions is compared. In the second experiment, to assess internal shorts, a small amount of Fe powder is intentionally added to the positive electrode layer to simulate a metal impurity in the conductive carbon. The

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dissolution of Fe powder, the deposition on the Li metal negative electrode, and the presence of an internal short between the Li metal and the positive electrode are examined in additive-free and additive-added electrolyte solutions.

## 2. Experimental

### 2.1. Electrochemical stability of cyclam

Electrochemical stability of cyclam ($C_{10}H_{24}N_4$, Aldrich, 98%) against oxidation and reduction was examined by tracing linear sweep voltammograms on aluminum foil (anodic stability) and copper foil (cathodic stability) working electrodes in the voltage range of 0.0–6.0 V (vs. Li/Li$^+$). For this experiment, 50 m$M$ cyclam (the maximum solubility was 0.3 $M$) was dissolved in the background electrolyte (1.0 $M$ LiPF$_6$ dissolved in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 = $v/v$)). Since the redox currents that evolve from the background electrolyte are superimposed with those of cyclam, the redox current coming from cyclam is obtained by subtracting the redox current of the cyclam-free electrolyte from that of the cyclam-added electrolyte.

### 2.2. Mn deposition on graphite electrode

To prepare the graphite electrode, a mixture of graphite powder (DAG 87, Sodiff), Super P, and poly(vinylidenefluoride) (PVdF, KF-1100) (85:5:10 in wt. ratio) is dispersed in $N$-methylpyrrolidone (NMP), and the resulting slurry is coated on copper foil. A beaker-type three-electrode cell is fabricated with the as-prepared graphite electrode, a Li metal counter electrode, and a Li metal reference electrode. A porous polypropylene–polyethylene–polypropylene (PP–PE–PP) film is used as the separator. Along with the background electrolyte, a Mn(ClO$_4$)$_2$ solution in EC/DEC is added to the beaker cell to perform galvanostatic cycling; a Mn(II) concentration of 10 m$M$ is used. To examine the additive effect of cyclam, 20 mL of cyclam-containing solution (1 wt.% in EC/DEC) is added.

AC impedance data are obtained after 30 cycles to assess film resistance. To analyze the residual Mn(II) ion concentration in the electrolytes and the Mn deposits on the graphite electrodes, inductively coupled plasma/atomic emission spectroscopy (ICP-AES; OPTIMA 4300DV, PerkinElmer) is employed. To that end, after 30 cycles the cells are disassembled in an argon-filled globe box and the electrolyte solutions are collected. To analyze the Mn deposits, the graphite electrodes are collected, and the Mn deposits are leached by using a mixture of nitric, hydrofluoric, and hydrochloric acids.

### 2.3. Internal short by the deposited Fe

For this experiment, iron powder (Alfa Aesar, 6–10 μm) is intentionally added (0.6 mg cm$^{-2}$) to the composite lithium cobalt oxide (LiCoO$_2$, LCO) electrode, which is prepared by coating a slurry of LCO (KD10, Umicore), Super P, and PVdF (KF-1100) (94:3:3 wt. ratio) in NMP onto aluminum foil. Two-electrode 2032 coin-cells are fabricated by using this composite LCO electrode along with a Li foil counter electrode and a PP–PE–PP separator. To examine the additive effect of cyclam, 200 μL of cyclam-containing solution (1 wt.% in EC/DEC) is added to the background electrolyte. To induce Fe dissolution from the LCO electrode and deposition on the Li foil, the coin cells are galvanostatically cycled.

## 3. Results and discussion

### 3.1. Electrochemical stability of cyclam

In order for the azamacrocyclic compound to serve as an additive, it should be electrochemically stable within the working potential of LIBs [12]. Fig. 1a shows the linear sweep voltammograms that are traced in
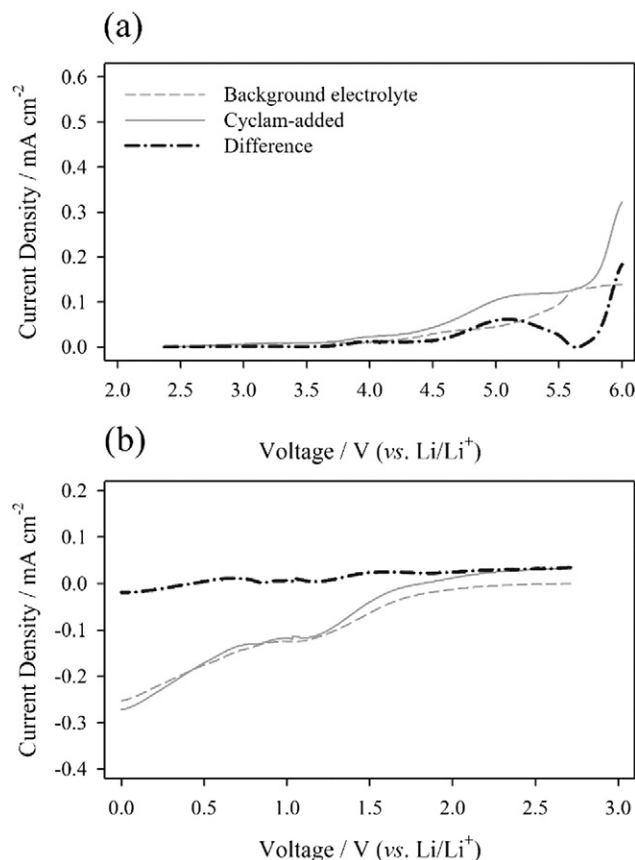


**Fig. 1.** Linear sweep voltammograms: (a) positive direction and (b) negative direction. Counter and reference electrodes = Li foil. Voltage range = 0.0–6.0 V (vs. Li/Li$^+$). Scan rate = 10 mV s$^{-1}$.

the background electrolyte and the cyclam-added electrolyte. The cyclam-added electrolyte is oxidatively decomposed at >4.5 V, in which range the background electrolyte also produces an oxidation current [13]. In order to determine the oxidation current associated with cyclam, a difference profile is obtained. As is seen in Fig. 1a, the oxidation of cyclam starts at ca. 4.5 V (vs. Li/Li$^+$). On the negative scan (Fig. 1b), the two electrolyte solutions show a comparable reduction current up to 0.0 V, and thus their difference profile is featureless. These linear sweep voltammogram results show that cyclam is electrochemically stable over the 0.0–4.5 V range, which is the normal working range of LIBs.

### 3.2. Suppression of Mn deposition on graphite electrode

Fig. 2a presents the 1st charge (de-lithiation)/discharge (lithiation) voltage profiles of the Li/graphite cells, which are obtained in three different electrolytes. The profile obtained from the background electrolyte shows the typical charge/discharge voltage profile for graphite electrodes, in which the lithiation and de-lithiation capacities are 383 mA h g$^{-1}$ and 332 mA h g$^{-1}$, respectively. The Mn(II)-added electrolyte gives a markedly different voltage profile with an abnormally high discharge (reduction) capacity (up to 1400 mA h g$^{-1}$) and a charge (oxidation) capacity limited to 200 mA h g$^{-1}$. The unusually high reduction capacity is attributed to the occurrence of severe parasitic reactions, which are likely the reduction of Mn(II) ions on the graphite surface and the reductive electrolyte decomposition on the as-generated metallic Mn surface [1]. The unusually small charging capacity is attributed to poor lithiation in the preceding discharge period, which is caused