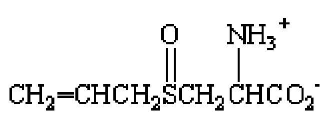
Electrochemical characterization of allium sativum as a cathode for lithium batteries

Pier Paolo Prosini and Isabella Chiarotto*

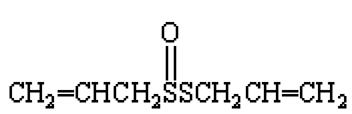
ENEA, C.R. Casaccia, via Anguillarese 301, Rome 00060, Italy
* Universita' degli Studi di Roma "La Sapienza", via del Castro Laurenziano 7, Rome 00161, Italy

The active cathode material of a secondary lithium battery is a host compound into/from which lithium can be reversibly inserted/extracted over a large composition range [1]. Transition metal oxides, such as $LiCoO_2$, layered $LiNiO_2$ [2,3] and $LiMn_2O_4$ [4] have found application as positive electrode materials for high power applications. These materials provide high potentials (about 4 V vs. Li) and good reversible capacities (about 120 mAh g^{-1}). The use of $LiMn_2O_4$ solves problems related to cost and Co and Ni toxicity, but the disproportionation of Mn^{3+} remains a severe problem [5]. In recent years, much effort has been made to identify new materials suitable for use as positive electrodes in rechargeable lithium batteries. De Jonghe and others [6] have discovered a class of cathode based on organo-sulfur compounds. Electrical energy is produced when electrons released from lithium oxidation cleave the sulfur-sulfur bonds. To recharge the cell, the process is reversed and the molecules are rejoined. While unique in a battery, a related reaction is commonplace in many life forms. For more than 100 years, chemists have known that the principal component of the oil that distills from garlic is allyl disulfide [7]. Only recently, however, it was explained how this and other organo-sulphur compounds are produced when garlic is crushed [8]. Before garlic is crushed, the intact cell contains *S*-2-propenyl-L-cysteine *S*-oxide, or alliin, which can be found in the cell cytoplasm.



alliin

Within the cell there are vacuoles that contain an enzyme known as alliinase. When the cell is crushed, the enzyme is released. The enzyme transforms the natural product alliin into an intermediate that reacts with itself to form a compound known as allicin.



allicin

When garlic is crushed, the amount of allicin increases with time as the alliin is converted into allicin, releasing pyruvic acid and ammonia. In ethanol extraction of crushed aged garlic, allicin yields diallyl trisulfide (73%), diallyl disulfide (8%), and ajoene (8%) [9].

The sulphur compounds extracted from garlic could find application as depolarizing agents to realize electrodes for lithium battery. In this work the electrochemical performance of dry garlic powder as well as the methanol extract are presented.

To prepare the electrodes for the electrochemical characterization, dry garlic powder or alternatively the methanol extract were mixed with 20% carbon black, to increase the electronic conductivity, and bound with poly-tetra fluoro ethylene (Aldrich). The mixture was rolled into a thin sheet of uniform thickness from which 1.0 cm diameter pellets were cut. Battery cells were assembled in a T-shaped hydraulic connector, lithium metal was used both as counter and reference electrode. Glass fiber disks were used as separators, and stainless-steel cylinders as current-collectors. The cells were filled with a 1 M solution of $LiPF_6$ (Merck, battery grade) in ethylene carbonate:dimethyl carbonate (EC/DMC) 1:1. The cells showed to reversibly cycle lithium-ions. The first cycle specific capacity was about 40 mAh g^{-1}. The average capacity fading evaluated during 500 cycles was 0.1% per cycle. The electrode specific capacity increased replacing the garlic powder with the methanol extract. Figure 1 shows selected voltage profiles for an electrode prepared with the dry extract. During the first discharge step the specific capacity was as high as 170 mAh g^{-1}. In following cycles a capacity fading affected the electrode but the fading rapidly declined and after 30 cycles the electrode delivered a stable specific capacity of 80 mAh g^{-1}. The identification of the electroactive compounds in the garlic extract could bring to develop a new class of organic compounds characterized by high capacity and good reversibility. Research is in progress to verify this very interesting possibility that would open the lithium batteries to cheaper and safer cathode materials.

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REFERENCES

1. J. B. Goodenough, Solid State Ionics, **69**, 184, 1994.
2. K. Mizushima, P. C. Jones, P.J. Wiseman and J. B. Goodenough, Mater. Res. Bull., **15,** 783, 1980.
3. M.G.S.R. Thomas, W.I.F. David and J. B. Goodenough, Mater. Res. Bull., **20,** 1137, 1985.
4. M.M. Thackeray, P.J. Johnson, L.A. De Picciotto, P.G. Bruce and J. B. Goodenough, Mater. Res. Bull., **19** 179, 1984.
5. J. Hunter, J. Solid State Chem., **39,** 142, 1981.
6. M. Liu, S. J. Visco, and L. C. De Jonghe, J. Electrochem. Soc., **138**, 1896, 1991.
7. F.W. Semmler, Archiv der Pharmazie, **230**, 434-448, 1892.
8. E. Block, Angewandte Chemie, International Edition in English, **31**, 1101-1264., 1992.
9. H.D. Reuter,H.P. Koch, L.D. Lawson, in: *Garlic: the Science and Therapeutic Application of Allium sativum L. and Related Species*; H.P. Koch and L.D. Lawson, Eds. Williams & Wilkins, Baltimore, 1996.

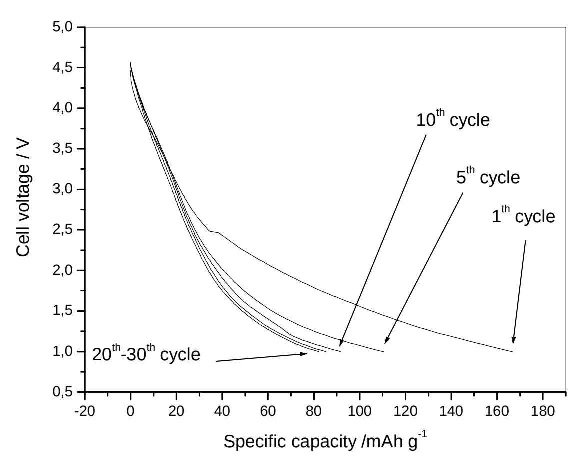

Figure 5. Selected voltage profiles for an electrode prepared with the methanol extract. Charge current density was 32 mAh g^{-1}. Cathode load was 6.0 mg cm^{-2}.