The challenge of negative electrode materials for advanced Li-ion batteries

Doron Aurbach, Ella Zinigrad, Daniel Hirshberg, Ortal Yariv
Department of Chemistry
Bar-Ilan University
Ramat-Gan 52900 Israel

Meng Jiang and Bob Powell
GM R&D center
Chemical and Materials Systems Lab, 30500 Mound Rd.
Warren MI 48090 USA
Doron.Aurbach@biu.ac.il

Li-ion batteries have conquered the market as power sources for portable electronic equipment. But there are additional challenges for advanced rechargeable Li-ion batteries as power sources for electrical propulsion (EV). They must demonstrate high energy density, prolonged cycle life, very good low/high temperature performance and excellent safety feature. The limiting factor in terms of energy density for Li batteries is the positive electrode. The positive materials determine both the capacity and the voltage of Li-ion batteries. While the energy density of Li-ion batteries is determined by the positive electrode, the performance in terms of cycle life and stability seems to be determined by the negative electrode. Graphite has been widely used in current commercial Li-ion batteries. Si-based (such as Si alloy or Si-C composite) compounds have also drawn many attentions as alternative negative electrode for advanced Li-ion batteries. However, both graphite and Si-based electrodes are thermodynamically unstable in ALL relevant Li salt solutions that can be used in Li-ion batteries. Both types of negative electrodes can function in Li-ion batteries only due to highly complicated passivation phenomena, based on surface film formation due to reduction of solution species at low potentials. Neither Li-carbon compounds nor Li-Si alloys are stable in any relevant polar-aprotic solution that can be used in Li-ion batteries. Li insertion into these hosts are accompanied by structural changes (volume expansion), strains, stresses, exfoliation, cracks formation and possible continuous reduction of solution species despite the above mentioned passivation phenomena. It should be noted that if it will be possible to demonstrated really suitable air and sulfur cathodes for rechargeable Li batteries, the Li metal anodes will have to be replaced by carbonaceous or Si anodes. For advanced Li-ion batteries, it is highly important to develop new electrolyte solutions with high anodic stability and unique surface chemistry at low potentials that will promote development of effective passivation of graphite and Si-based electrodes. We and others found recently that electrolyte solutions which include fluorinated alkyl carbonates as co-solvents may be excellent for full cells comprising Li-Si anodes and the above mentioned advanced high potential or high capacity cathodes[3]. For Li-S or Li-O_2 systems[1,2], alkyl carbonate solvents are not suitable due to their reactivity with Li-sulfides and Li-oxides formed therein. Ether based solutions may be suitable for both Li-S and Li-oxygen systems[4,5]. In this work we examined a several types of carbon and Si electrodes as anodes for advanced rechargeable Li-ion batteries. These included several graphite materials, soft and hard disordered carbons. We examined several solutions with an emphasis on wide temperature performance (from -30 ^{0}C to 60 ^{0}C).

Alkyl carbonates and fluoro-alkyl carbonates based solutions with $LiPF_6$ electrolyte were investigated. This Li salt was chosen because in its solutions, the Al foils used as current collectors for the cathodes reach their best passivation. We also examined an ethereal solution based on glyme solvents. The main components included dimethyl carbonate (DMC) with these four cyclic carbonates: ethylene carbonate (EC), fluoroethylene carbonate (FEC), difluoroethylene carbonate (2FEC), and vinylene carbonate (VC) and di-glyme. The following electrolyte solutions were examined:

1. The reference system DMC:EC 1:1 1M $LiPF_6$, (κ_{-30^oC} = 0.1 mS/cm).
2. DMC:EC 1:1 1M $LiPF_6$ with addition of 2% VC, (κ_{-30^oC} = 4.8 mS/cm).
3. DMC:FEC 4:1 1M $LiPF_6$, (κ_{-30^oC} = 2.1 mS/cm).
4. DMC:2FEC 4:1 1M $LiPF_6$, (κ_{-30^oC} = 3.2 mS/cm).
5. Diglyme CH_3O-$(CH_2CH_2O)_2CH_3$/LiTFSI, (κ_{-30^oC} = 4.7 mS/cm).

Solutions 2-4 may be highly suitable for high energy density Li-ion batteries comprising high voltage positives and both carbon or silicon anodes, while solution 5 may be relevant for Li-oxygen batteries. The dependence of the specific conductivity of the above alkyl carbonate solutions on the temperature obeys: $\ln \kappa = a + bT^{-1} + cT^{-2}$ (a-c are constants).

The stability limits of the above systems (solutions, electrodes' materials) were studied. The surface chemistry developed on electrodes (negative and positive) was investigated as well. We intend to exhibit a systematic study leading to optimization of electrodes/solutions for advanced Li batteries. The safety features of selected combination were studies by thermal analysis (ARC and DSC measurements).

References:

1. Marom, R.; Amalraj, S. F.; Leifer, N.; Jacob, D.; **Aurbach D.;***J of Materials Chemistry* ,**21**, 9938-9954, **(2011).**
2. Etacheri V.; Marom R.; Elazari R.; Salitra G.; **Aurbach D**.; *Energy Environ. Sci*.,4, 3243-3262 **(2011)**.
3. Etacheri, V; Haik, O.; Goffer, Y.; Roberts, G. A.; Stefan, I. C.; Fasching, R.; **Aurbach, D.**.; *Langmuir*, **28**, 965-976 **(2012)**.
4. Elazari R.; Salitra G.; Garsuch A.; Panchenco A.; **Aurbach D.**; *Adv. Mater*. ,**23**, 5641-5644 **(2011)**.
5. Sharon, D. ;Etacheti, V.;Afri, M.; Arnd, G.; Frimer, A.; **Aurbach, D**.;*J. Phys. Chem. Lett*.,**4**, 127 (2013)