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Non-aqueous Mg electrochemistry for rechargeable batteries

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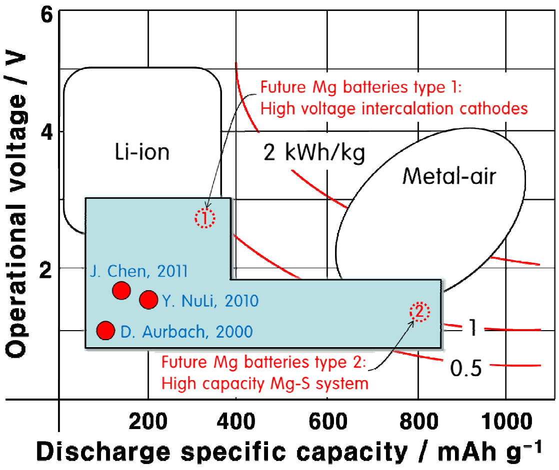
Today's non-aqueous Mg electrochemistry enables development rechargeable Mg battery technology which operational potential is 1–2 V and the specific capacity of possible reversible cathodes is 100–200 mAh g^{-1}. Considering the abundant Mg resources on earth, the low red-ox potential and the high specific capacity as an electron donor (anode), magnesium metal is an attractive material for negative electrodes in post lithium-ion (or non-lithium) batteries. Also the volumetric capacity of Mg (3833 mAh cc^{-1}) is higher than that of Li (2046 mAh cc^{-1}). Nowadays, several research groups are developing new concepts and materials for high energy density Mg rechargeable batteries. There are two representative future directions to realize the high energy density: 1) high voltage insertion cathode and 2) high capacity conversion cathode. The first approach is to increase the operational voltage up to 3 V by developing high voltage insertion cathodes (3 V *vs*. Mg is the highest relevant potential due to the anodic limitation of the relevant electrolyte solutions) with a specific capacity up to ~300 mAh g^{-1} (the maximal capacity of insertion compounds of the Mg_xMO_2 type). The second approach is to increase the specific capacity up to 800 mAh g^{-1} by developing conversion cathodes based on sulfur (Mg_xS) which operational voltage is 1~2 V.

During the last decade, R&D efforts related to rechargeable Mg batteries have been conducted by several research groups and companies. A few promising Mg ion insertion cathode materials have been demonstrated. However, composing them in full cells *vs*. Mg anodes was stumbled mainly due to compatibility issues between most of relevant cathode's materials and electrolyte solutions in which Mg anodes are reversible. Electrolyte solutions in which Mg is deposited and dissolved fully reversibly have to be based on ether solvents (THF, glymes) and complex electrolyte solutions formed by reacting R_2Mg or RMgCl Lewis base with $XR_{3-n}Cl_n$ Lewis acid (n=0–3, X=Al, B).

Observation of reversible Mg deposition and dissolution in Grignard solutions dates back to the 1920s. But the anodic stability window was too narrow (~1 V *vs*. Mg/Mg^{2+}) to be used as an electrolyte in batteries. A first breakthrough was the invention of non-Grignard Mg complex electrolyte solutions with reasonable anodic stability window (~2 V *vs*. Mg/Mg^{2+}) by Gregory *et al.* (Dow Chemical, co.) in 1990.[1] That paper deals with whole systems: cathodes, electrolytes, and their compatibility and it contains numerous concepts and working ideas, by which further research work was motivated. They demonstrated a full cell comprising Co_3O_4 cathode| 0.25 M $Mg(BBu_2Ph_2)_2$ in THF/DME | Mg anode. The performance of this cell was poor but it was a first attempt in the field. The incompatibility between relevant positive electrodes and electrolyte solutions for Mg batteries was solved by developing organo-halo-aluminate ($Mg(AlCl_2EtBu)_2$/ THF solutions and Chevrel-phase-Mo_6S_8 cathodes.[2] By introducing electron-withdrawing Al^{3+} as the core of the anions, and Cl^- as an inorganic ligand, the organo-halo-aluminate electrolyte solutions provided much higher anodic stability (~2.2 V *vs*. Mg/Mg^{2+}) and the Chevrel phase Mo_6S_8 cathodes provided high rate diffusion of divalent Mg^{2+} ions, without any chemical stability problem with the electrolyte solution. Recent development of next generations of rechargeable Mg batteries included interesting work of NuLi *et al.* who demonstrated a Mg insertion cathode based on mesoporous manganese silicate, which exhibited ~200 mAh g^{-1} at 1.6 V *vs*. Mg/Mg^{2+}.[3] Chen *et al.* showed that exfoliated MoS_2 cathode can be used with complex electrolyte solutions: ~170 mAh g^{-1} at 1.8 V *vs*. Mg/Mg^{2+}.[4]

Since the demonstration of 3 V class electrolyte solutions,[5] there have been continuous efforts to develop high voltage cathodes in these solutions. Strategies for reducing the nucleophilicity, volatility, and air-sensitivity of the Mg electrolytes were also developed. Alternatively, reversible Mg alloying with Bi, $Bi_{1-x}Sb_x$, or Sn anodes for "Mg-ion" battery in conventional electrolyte solutions was also reported. As a result, a prototype of 3 V class Mg battery has been demonstrated recently.[6] But the cycleability and stability was not enough to call it a breakthrough. This presentation will discuss fundamental issues on the way to the next breakthrough in this field: concepts, materials, and new electrolyte systems for 3 V class Mg batteries. Figure 1 is a scheme of a road map: past, present, future for R&D of rechargeable Mg batteries.



D.Aurbach (2000) – Mo_6S_8 | 0.25 M $Mg(AlCl_2EtBu)_2$ in THF | Mg
Y. NuLi (2010) – mesoporous $Mg_{1.03}Mn_{0.97}SiO_4$ | 0.25 M $Mg(AlCl_2EtBu)_2$ in THF | Mg
J. Chen (2011) – exfoliated MoS_2 | $Mg(AlCl_3Bu)_2$ in THF | nano-sized Mg

Fig. 1 Operational voltage and specific capacity of Mg batteries compared with other electrochemical power sources.

References

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