

A possible way of utilizing a polyvalent metal as a negative electrode of storage battery

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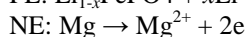
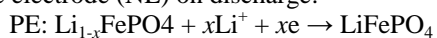
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Graphite is widely utilized as a negative electrode of lithium ion batteries (LIBs). Lithium metal as a negative electrode has high energy density, but it cannot be used because its dendritic growth on charge process causes a short circuit or isolated lithium metal. In order to enhance the energy density, in late years, non-noble metals (such as Ca, Mg, Al etc) yielding polyvalent cations are highly expected to be used as a negative electrode for future polyvalent-metal storage batteries (PSBs). Here we propose a concept of a novel battery system consisting of a non-noble polyvalent metal (such as Ca, Mg, Al etc) in combination with a well-established positive electrode for LIBs. Especially, magnesium metal has been attracting significant attention, not only from the viewpoints of its low standard electrode potential (-2.36 V vs SHE) and large theoretical capacity (2234 mAhg⁻¹), but also from the viewpoints of safer handling, abundance, and inexpensiveness.

Figure 1 illustrates our concept of "septum-free" PSB. In the proposed polyvalent battery systems in Fig. 1(a), a positive material for LIBs (e.g., LiFePO₄ or LiCoO₂, etc) is employed and a non-noble metal (other than Li) is used as a negative electrode, and both kinds of cations are contained in the same solvent. In terms of the negative electrode, since Li ions are the most non-noble in the supposed battery system, the other non-noble metals such as Ca, Mg, Al can be used as a negative material because Li metal cannot be plated on those electrodes. On the other hand, in terms of the positive electrode, during discharge process, polyvalent cations are quite difficult to be intercalated into the host material of the LIB positive electrode, whereas only Li ions are preferentially intercalated easily into the host. On charge, the Li ions can be deintercalated from the host at the positive electrode, and the polyvalent cations (Ca²⁺, Mg²⁺, Al³⁺ etc) are electrodeposited preferentially by preempting Li ions. Thus, the Li compound structure plays a role of the Li pass filter on discharge, and the electrodeposition of Li can be controlled electrochemically. In principle, there are many combinations of the positive and negative electrode materials to compose a PSB, and, PSBs can deliver various EMF values, according as the combination.

The positive electrode was prepared by coating on a platinum plate with a mixture of 80 wt% commercial LiFePO₄, 10 wt% carbon black and 10 wt% PVdF. Magnesium ribbon was utilized as a negative electrode and a reference electrode. The electrolyte was used 1 M phenylmagnesium-chloride; 0.2 M LiBF₄ and 0.2 M AlCl₃ in THF.^{1,2} Beaker cells were prepared in a dry Ar atmosphere. In this system, the following redox reactions would occur at the positive electrode (PE) and the negative electrode (NE) on discharge:



Battery tests were carried out in constant current mode, the result of which is shown in Fig. 2. It is found that the

present PSB can be charged and discharged reversibly, and deliver a high voltage of about 2.4 V vs Mg. However, the discharged capacity was less than the charged capacity due to oxidative decomposition of the electrolyte with a narrow electrochemical window. X-ray diffraction profiles have shown that LiFePO₄ is changed to FePO₄ after charge and FePO₄ is turned into LiFePO₄ after discharge.

For future practical application, we have to overcome two problems. (1) It is necessary to establish electrolytes with a wide electrochemical window for the non-noble metals (Ca, Mg, Al etc). (2) In principle, the present PSB system needs a relatively large amount of electrolyte to accommodate the active ions of positive and negative electrodes, but it may be settled by using an electrolyte containing supersaturated salts.

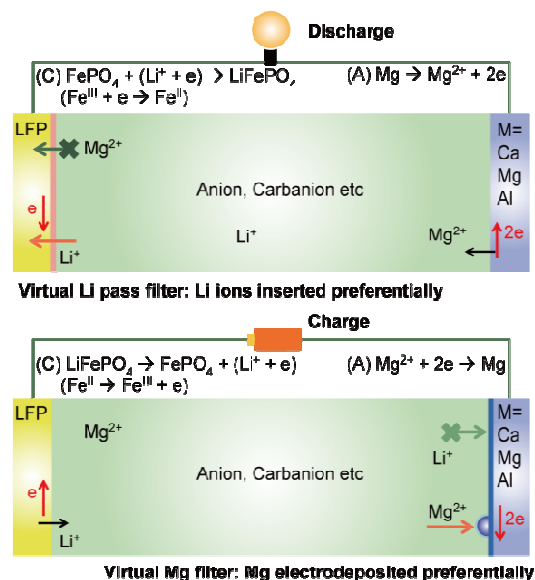


Figure 1. A concept of the dual-salt polyvalent storage battery. The battery consists of a non-noble metal (M = Ca, Mg, Al etc) negative electrode and a positive electrode for LIBs and the electrolyte containing two kinds of cations, i.e., Li ions and polyvalent M ions.

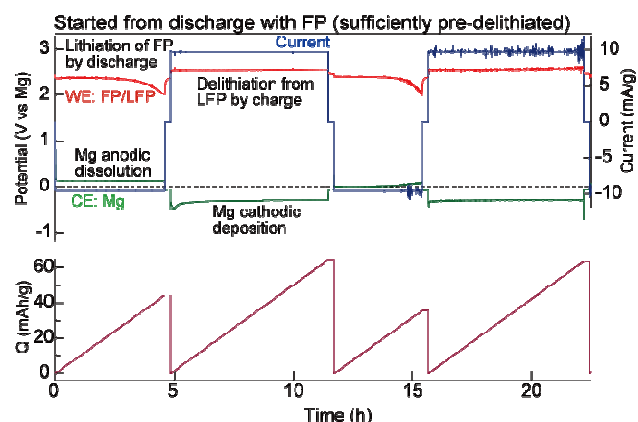


Figure 2. Charge/discharge behavior in constant current conditions. (cut off voltage: 2.0 V for discharge, 2.8 V for charge or constant capacity $Q = 60 \text{ mAh g}^{-1}$).

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2. S. Yagi, A. Tanaka, Y. Ichikawa, T. Ichitsubo and E. Matsubara, *J. Electrochem. Soc.* **160**(3), C83-C88 (2013).