LAYERED OXIDES FOR Na-ION BATTERIES

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Na-ion batteries are attracting much more interests as lithium-free high-voltage batteries because lithium resource is not abundant in the Earth's crust. Indeed, we found many papers on Na batteries reported even in the last IMLB. When we look back on the history of Na-ion batteries in Figure 1, there have appeared to be a few pioneering reports to demonstrate Na-ion full cells by Shacklette, Doeff, Alcántala, and Barker's groups in 1988, 1993, 2001, and 2003, respectively [1]. We note that the battery sodium-ion of Pbpolyphenylene//P2-Na_xCoO₂ developed by Japanese and U.S. companies demonstrates good cycle-life according to their patents



Figure 1 Yearly number of papers on sodium batteries. Data are based on Web of Knowledge in Oct. 2015 and summarized by our MS students, Mr. Hashimoto, Asari, Hashimoto and Hironaka. Conferences on Na are also inserted.

submitted in 1987-1988. In 2009, we succeeded in high performance Na-ion batteries by the development of sodium insertion shuttle-cock battery with adequate electrolyte [2]. Our present motivation is to achieve highly energetic Na-ion made from abundant materials free from toxicity.

Layered transition metal oxides are promising candidates as positive electrode materials for Na-ion batteries because of the relatively high capacity, good cycle stability, and acceptable voltage range. Considering a difference in the standard potential between Li and Na, high operating voltage is required for positive electrodes to realize high energy Na-ion batteries. By studying on composition and structure of layered oxides, P2-

Na_{2/3}Ni_{11/36}Mn_{23/36}Al_{1/18}O₂ shows ca. 150 mAh/g of reversible capacity with relatively high operating voltage of more than 3.5 V vs. Na as shown in Figure 2. Furthermore, calculated energy density (Wh/kg) of the Na-ion hard-carbon//P2batteries of Na_{2/3}Ni_{11/36}Mn_{23/36}Al_{1/18}O₂ is approaching about 90% the of conventional Li-ion graphite//LiCoO2. We will present and discuss our recent progress and perspective in the layered oxides for positive electrodes of Na-ion batteries.



Figure 2 from Compare voltage (V_{ave}^{014}) and energy density (Wh/kg) versus gravimetric capacity (mAh/g) for selected positive electrode materials for Na-ion batteries. Energy density was calculated with the hard carbon (reversible capacity of 300 mAh/g with $V_{ave} = 0.3$ V vs Na metal) as negative electrode materials.

References

- [1] N. Yabuuchi, S. Komaba, et al., Chem. Rev., 114 (2014), 11636.[2] S. Komaba et al, ECS Meeting, Abst. #684, Vienna, Austria (2009).