Disodium Rhodizonate and the Derivatives as Organic Electrode Active Materials for Sodium-ion Battery

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Abstract As a new type electrode active material group for Na-ion battery, oxocarbonic acid-type organic compounds with planar molecules such as disodium rhodizonate ($Na_2C_6O_6$) and the derivatives were investigated. Instead of transition metal, the functional groups with double bond against carbon such as C=O and/or C=N can work as the redox center in these organic electrodes. It should be new guiding principle for metal free electrode active materials.

1. Introduction

Although Li-ion batteries became the most popular power sources for personal digital assistants (PDA) due to the highest energy density, the Li-ion battery is relatively costly in comparison with the other rechargeable batteries. On the other hand, ecofriendly Na-ion batteries are attracting much attention for large-scale battery. However, the host compounds for Na insertion have been mainly restricted to 2D layered or 3D corner sharing structures, because the ionic volume of Na is 2 times larger than that of Li. Besides these inorganic compounds with open matrix, low density organic compounds with planar molecule are also promising as a new type electrode active materials for Na-ion battery. Especially, we expected that oxocarbonic acid-type organic compounds can be used as a metal free electrode for Na-ion battery, because the C=O carbonyl groups can function as the redox center, instead of transition metal.

In this presentation, the charge/discharge performances of disodium rhodizonate ($Na_2C_6O_6$) and the derivatives are introduced as the typical organic electrode active material candidates with C=O and/or C=N functional groups.

2. Experimental

$Na_2C_6O_6$ was purchased and used without further purification. $Na_2C_4O_4$ and $Na_2C_5O_5$ were synthesized by following substitution reaction; $H_2C_xO_x$ + 2NaOH -> $Na_2C_xO_x$ + H_2O [x = 4 and 5]. To fabricate cathode electrode, $Na_2C_xO_x$ [x = 4, 5, and 6] were mixed with acetylene black (DENKA) and PVdF binder (KUREHA Corporation) with a weight ratio of 70 : 25 : 5. The electrochemical performances were evaluated by using a 2032 coin-type cell with non-aqueous electrolyte (1 M $NaClO_4$/PC or EC+DMC, Tomiyama Pure Chemicals Co.) against a sodium metal anode (SIGMA-Aldrich).

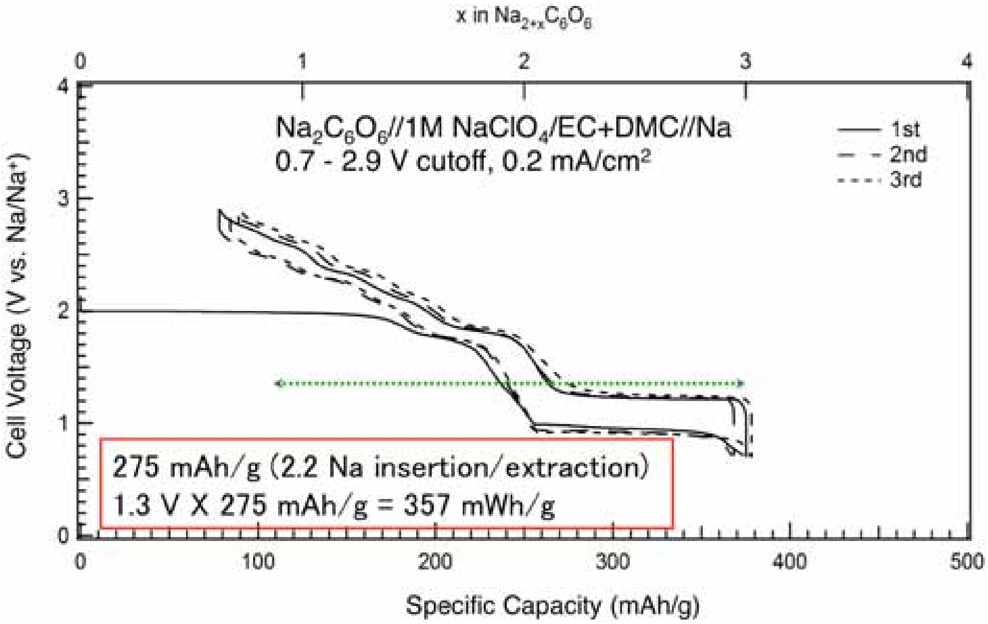
3. Results and Discussion

According to the theoretical capacity estimation of oxocarbonic acid type cathodes based on the number of carbonyl group per molecular, disodium heptagonate ($Na_2C_7O_7$) must have the largest value (554 mAh/g). Unfortunately, we have not yet succeeded in the synthesis, because of the instability. As the second best in the oxocarbonic acid type cathodes, disodium rhodizonate is also promising cathode against Na as shown in Table 1. Contrary to our expectation, most of 2Na in $Na_2C_6O_6$ were hardly able to be extracted by initial charge. However, stable reversibility could be obtained successfully below 2.9 V against Na. In the case of the charge/discharge test between 0.7 and 2.9 V, it showed reversible capacity of 275 mAh/g, corresponding to 2.2 Na insertion at a rate of 0.2 mA/cm^2 (Fig. 1). It is noteworthy that $Na_2C_6O_6$ is a very rare organic cathode active material with practical reversible capacity for sodium [1].

In the presentation, new polyaza-acenedione derivatives will be also introduced as the other organic electrode candidates with C=N functional group.

Table 1　Expectations and results for disodium rhodizonate cathode against Na.

Characteristics	Expectations
Metal free	Low cost
	Low environmental impact
Hydrogen free	Less side reaction with electrolyte
Molecular crystal	Flexible for deep cycling
4 C=O active sites per molecule	High theoretical capacity (497 mAh/g)
π-electron system	High electronic conductivity
Layer matrix	High Na diffusivity
Strong C=O bond	Less oxygen release
Na salt	Na source in Na-ion battery



275 mAh/g (2.2 Na insertion/extraction)
1.3 V X 275 mAh/g = 357 mWh/g

Fig. 1　Charge/discharge profiles of $Na_{2+x}C_6O_6$ in 0.7 – 2.9 V vs. Na/Na^+.

4. References

[1] K. Chihara, N. Chujo, A. Kitajou, and S. Okada, *Electrochim. Acta*, **110** (2013) 240-246.

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