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Effects of organic acids as reducing agents in the synthesis of $LiFePO_4$

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ABSTRACT

In this work, several organic acids are evaluated as reductants in the synthesis of $LiFePO_4$, where $FePO_4$ is one of the starting materials. The investigated acids include formic, glycolic, oxalic, maleic, and malonic acids, which have minimal carbon content. Mono-carboxylic acids have favorable decomposition mechanisms as reductants compared to bi-carboxylic acids. On the other hand, bi-carboxylic acids follow a more complicated path to produce H_2 and H_2O. Only one of the two carbonyl groups in bi-carboxylic acids is involved in producing CO, although there are slight variations among bi-carboxylic acids. When a reductant is not sufficiently strong to reduce all of the Fe(III)PO_4, Fe_2O_3 and Li_3PO_4 are formed through ion exchange reactions between un-reacted Fe(III)PO_4 and LiOH. It is believed that the volatility of organic acids and the ion exchange reactivity of LiOH produce impurities. The replacement of organic acids and LiOH with less volatile mono-carboxylic acids and LiR (R = alkyl) may improve the purity of the $LiFePO_4$ obtained.

1. Introduction

Since the introduction of $LiFePO_4$ as a cathode material [1] for Li-ion batteries, there have been numerous research efforts to commercialize this safe cathode material. Carbon coating [2–4] and ion doping [5–9] have improved both electronic and ionic conductivity. Additionally, nanoparticle synthesis [10–12] shortens the ion diffusion path of the material, enabling it to respond at high currents. Fine structure control [13,14] of the synthesis improves performance reliability. As a result, some $LiFePO_4$ products can already be found on the market. $LiFePO_4$ is an attractive material for large batteries rather than for portable electronic devices because of its relatively low density. Many researchers have used Fe(III) raw materials [15–17] for $LiFePO_4$ synthesis due to their low cost relative to Fe(II) materials, even though it is more difficult to produce $LiFePO_4$ with Fe(III) materials. In order to use Fe(III) materials, a reducing agent is needed in the reaction. In our work, new organic acids are introduced as reducing agents, and comparative studies are conducted on the synthesis of $LiFePO_4$. Using organic acids is advantageous for several reasons. First, the addition of acid can be precisely controlled before the reaction. Second, both the synthesis and carbon coating processes can be performed at the same time in a one-step reaction. There is a wide range of acids to choose from, which can be advantageous in controlling the quality of the carbon coating. Third, a well-mixed reductant in the reaction makes close contact with the solid reactants, which may not be easy when a gaseous reductant is used. Organic acids can not only improve the method of $LiFePO_4$ production, but can also be adopted to study the synthesis of high-voltage olivine cathode materials, such as $LiMnPO_4$ [18], $LiCoPO_4$ [19], and $LiNiPO_4$ [20,21].

This comparative synthetic work was performed with small organic acids that had a relatively small carbon coating role. Because of this, we could assess the reducing activity of each acid alone because carbon acts as a reductant at high temperatures. Ascorbic acid [22,23] is a very effective reductant. However, it has many carbon atoms. When ascorbic acid is required for a reaction, it can be difficult to control carbon formation or coating, which presents an obstacle to improving the performance of the material. Oxalic acid [17] is a low molecular weight acid that results in minimal carbon formation. Fig. 1 shows an example of a small organic acid in the form of a reductant in synthesis. The bonds of oxalic acid can be broken to form CO_2, CO, and H_2O, which immediately react to form H_2 [24,25]. One molecule of oxalic acid supplies two electrons, which can reduce two Fe(III) ions for the synthesis of $LiFePO_4$.

The aim of this work is to understand the reactions of organic acids in $LiFePO_4$ synthesis, which will help improve the reaction strategy in the synthesis of olivine cathode materials. The properties of carboxylic acids as reductants are discussed in terms of reducing power, bond dissociation, and reaction products for various acid structures.

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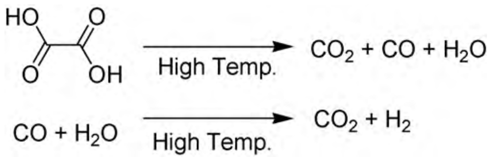

Fig. 1. Dissociation of oxalic acid.

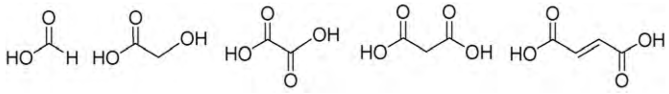

Fig. 2. Organic acids as reducing agents. The acids are formic, glycolic, oxalic, malonic, and maleic acids, from left to right.

2. Experimental

2.1. Chemicals and cell preparation

$LiOH{\cdot}H_2O$ (Aldrich, 98%), $FePO_4{\cdot}4H_2O$ (Junsei), formic acid (CH_2O_2, ACROS, 98%), oxalic acid ($(COOH)_2{\cdot}H_2O$, Kanto Chemical, 99.5%), glycolic acid ($C_2H_4O_3$, Aldrich, 70%), malonic acid ($HOOCCH_2COOH$, Junsei, 99%), and maleic acid ($C_4H_4O_4$, Daejung Chemicals & Metal, 99%) were used for this work. Fig. 2 shows the structures of the organic acids. The electron production mechanism of each organic acid may be different depending of the structure of the acids. In our work, we assume that each carboxylic group can produce one electron for reduction. $LiFePO_4$ was prepared by a solid-state reaction. For the reaction, $LiOH{\cdot}H_2O$, $FePO_4{\cdot}4H_2O$, and the selected organic acid were mixed by ball-milling for 24 h at 400 rpm in isopropyl alcohol. There was no color change observed during the ball-milling process, but some gas bubbles formed in the slurry. It was believed that the carboxyl groups in organic acids decompose to form CO_2. In the process, the organic acids lose electrons that reduce the other reactants. In order to compensate for the loss of organic acid during the ball-milling process, excess organic acid was added to the reaction. The reaction ratio of $LiOH{\cdot}H_2O$, $FePO_4{\cdot}4H_2O$, and organic acid was 1:1:1.2 for formic acid and glycolic acid, which are mono-carboxylic acids. For all of the bi-carboxylic acids, a ratio of 1:1:0.6 was used. The prepared reaction slurry was calcined at 700 °C for 3 h under argon. The temperature increased at a rate of 5 °C min^{-1}. Carbon coatings on the produced $LiFePO_4$ were made with stearic acid (DC Chemical) [4]. 3 wt.% of stearic acid was stirred with $LiFePO_4$ in isopropyl alcohol for 1 h. The prepared mixture was sintered for 1 h at 600 °C to form the carbon coating. The prepared $LiFePO_4$/C was mixed with carbon black (super P black, Timcal Carbon) and polyvinylidene fluoride (PVdF, Aldrich) at a ratio of 85:8:7 in *N*-methyl-2-pyrrolidone (NMP, Junsei) to make a slurry for the cathode. The slurry was spread on Al foil and dried overnight at 100 °C. The dried electrodes were hot roll-pressed to reduce the thickness by 20%. Li foil served as the anode. 2032-type coin cells (Hohsen Corp.) were prepared to monitor the performance of the materials. The electrolyte for the measurements was 1.0 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (EC/DEC) at a ratio of 1:1 by volume (Techno Semichem.). A 15-μm thick separator (5301 type, Celgard) was placed between the two electrodes. All cell preparations were performed in a dry room where the water content was maintained below 10 ppm.

2.2. Instruments and measurements

The thermal chemistries of the reaction slurries were investigated with a thermal gravimetric/differential thermal analyzer (TGA/DTA, Q600 TA instruments) and a differential scanning calorimeter (DSC, Q1000, TA instruments). TGA and DTA data were measured at a scan rate of 5 °C min^{-1} under N_2. The structure of the prepared $LiFePO_4$/C was examined by X-ray diffraction (XRD, PANalytical, model PW-3830) using monochromatic Cu Kα radiation at a scan rate of 0.04° min^{-1}. Prior to the performance measurements, such as the rate capability test and the cycle life test, the coin cells were cycled between 2.5 V and 4.3 V at a rate of 0.1 C so as to complete two formation cycles. A rate of *n* C corresponds to a full charge in 1/*n* h. All charge rates were 0.2 C, except for the 0.1 C discharge test for the rate capability test, which was charged at 0.1 C. Cell performance was measured using a TOSCAT-2100U tester (Toyo Systems Co.).

3. Results and discussion

3.1. Thermal analysis

Fig. 3 shows the TGA/DTA data of the synthetic reaction including oxalic acid. Two endothermic reactions occur below 200 °C. Rapid mass decrease is ascribed to the evaporation of crystalline water molecules and the water molecules created in the reaction as the reducing agent acts to form $LiFePO_4$. Reaction 1 shows the reactants and products. The products at this stage are amorphous [26,27].

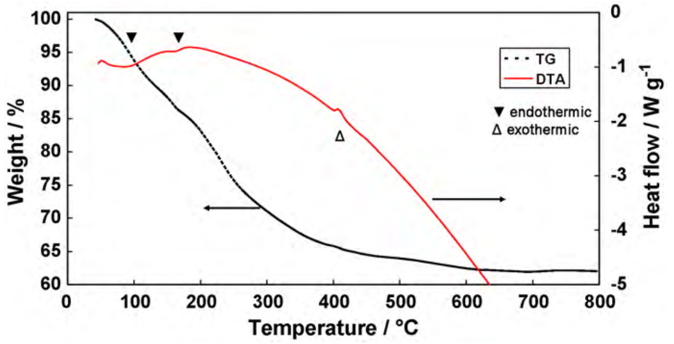

Fig. 3. TGA/DTA curves for the reaction slurry with oxalic acid.

$$LiOH{\cdot}H_2O + FePO_4{\cdot}4H_2O + 0.5C_2O_4H_2 = LiFePO_4 + 6H_2O + CO_2 \quad (1)$$

As the temperature increases, an exothermic peak is observed at 402 °C. At this point, mass change is negligible. Crystallization of $LiFePO_4$ occurs near this temperature [27,28]. DSC analyses were performed on all reaction slurries because DSC is more sensitive than DTA. All endothermic reactions were completed before 240 °C [26], as shown by the DSC measurements in Fig. 4. The reaction slurries with bi-carboxylic acids show more reaction steps or a higher intensity in their endothermic reactions than those with mono-carboxylic acids. Maleic acid shows the most complex DSC curves. If maleic acid decomposed to produce CO, which was described in Fig. 1, at least three sp^2–sp^2 carbon–carbon bond breakages are necessary. All others require fewer bond breakages. Mono-carboxylic acids require fewer bond cleavages than bi-carboxylic acids to produce carbon mono-oxide, which is utilized as a reducing agent. Bond cleavage can be a barrier for the reductants in the synthesis, which affects the reducing power of the acids. According to the DSC results, mono-carboxylic acids are better reducing agents when all other reaction conditions are kept the same. The crystallization temperatures of products formed with mono-carboxylic acids are higher than those of bi-carboxylic acids. The dependence of crystallization on the reducing agents is not yet understood and is beyond the scope of our study.

3.2. Relation between reducing power and impurities

The XRD data in Fig. 5 demonstrate the correlation between the reducing power of the acids and the creation of by-products in $LiFePO_4$. The diffraction peaks correspond to an ordered olivine, indexed by an orthorhombic structure with space group *Pnma*,

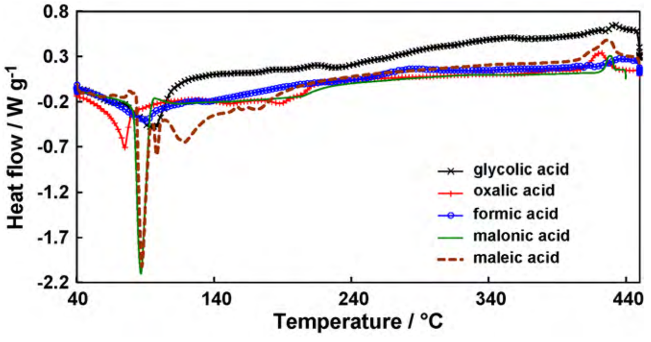

Fig. 4. DSC analysis of all reactions with organic acids.

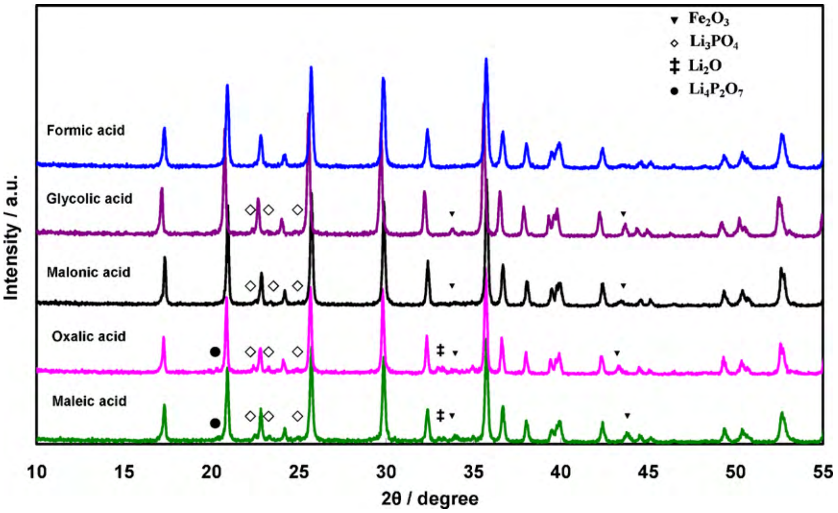

Fig. 5. XRD curves of $LiFePO_4$ powders.

except for some impurities that are indicated with symbols. Li_3PO_4 [29] and Fe_2O_3 [29,30] are the most common impurities, the formation of which is dependent on many reaction factors. When the reducing agents are weak, some of the Fe(III)PO_4 molecules remain un-reacted. Un-reacted Fe(III)PO_4 can exchange ions with LiOH to create Li_3PO_4 and Fe_2O_3 (Eqs. (2) and (3)) at high temperatures.

$$3LiOH + FePO_4 = Li_3PO_4 + Fe(OH)_3 \quad (2)$$

$$Fe(OH)_3 = 0.5Fe_2O_3 + 1.5H_2O \quad (3)$$

$$Li_3PO_4 = 0.5Li_2O + 0.5Li_4P_2O_7 \quad (4)$$

Products that contain a significant amount of Li_3PO_4 also show peaks for Li_2O and $Li_4P_2O_7$ (reaction (4)). As the product has more impurities, such as Li_3PO_4, Fe_2O_3, Li_2O, and $Li_4P_2O_7$, it produces a lower discharge capacity. In other words, the discharge capacity is directly proportional to the reducing power of the acid. According to the XRD results presented in Fig. 5, bi-carboxylic acids are weaker reductants than mono-carboxylic acids. The product from Fe(III)PO_4–formic acid shows the fewest impurities among the products. The performances of the products were evaluated by rate capability and cycle life tests. Fig. 6a and b shows that the active materials made with bi-carboxyl acids have low discharge capacities. The materials made with bi-carboxyl acids show poor performance due to their low reducing power, which causes more impurities. The discharge capacity at 0.1 C and the XRD data in Fig. 5 show that the reducing power of formic acid is stronger than that of the other acids. Even though formic acid has the strongest reducing power, it provides no carbon to the $LiFePO_4$ grains. Glycolic acid, another mono-carboxyl acid, which can give one carbon atom per acid molecule to $LiFePO_4$, shows a better rate capability than the material produced from formic acid. Fig. 6b shows the superior capacity retention in the cycle life test of the material from glycolic acid, which explains the effect of carbon on the material.

Fig. 7 illustrates the reducing power of ascorbic and mono-carboxylic acids. The production of hydrogen from ascorbic acid occurs through a keto–enol tautomer intermediate, which makes bond dissociation easier, as shown in Fig. 7b. Ascorbic acid can reduce Fe(III) materials to form Fe(II) materials, even at room temperature. When a formic acid is dissociated, a carbon monoxide and a water molecule are produced. A formic acid molecule provides two electrons. Fig. 6b shows a relative estimation of electron formation numbers from bi-carboxylic acids compared to mono-carboxylic acid. The amount of bi-carboxylic acid was half the amount of mono-carboxylic acid in the reaction. The discharge capacity values in Fig. 6b indicate that the capacity values of the products are roughly correlated to the amount of organic acid added. The results imply that only one of the two carbonyl groups in bi-carboxylic acids is involved in producing CO, although there are few variations among bi-carboxylic acids. Mono-carboxylic acids can form CO through thermal decomposition [31,32], as shown in Fig. 7c and d. It is much easier for mono-carboxylic acid to produce H_2 because H_2O is easily obtained in the molecule. On the other hand, bi-carboxylic acids follow a more complicated path to produce H_2 and H_2O, which can lead to multiple decomposition peaks, as shown in Fig. 4.

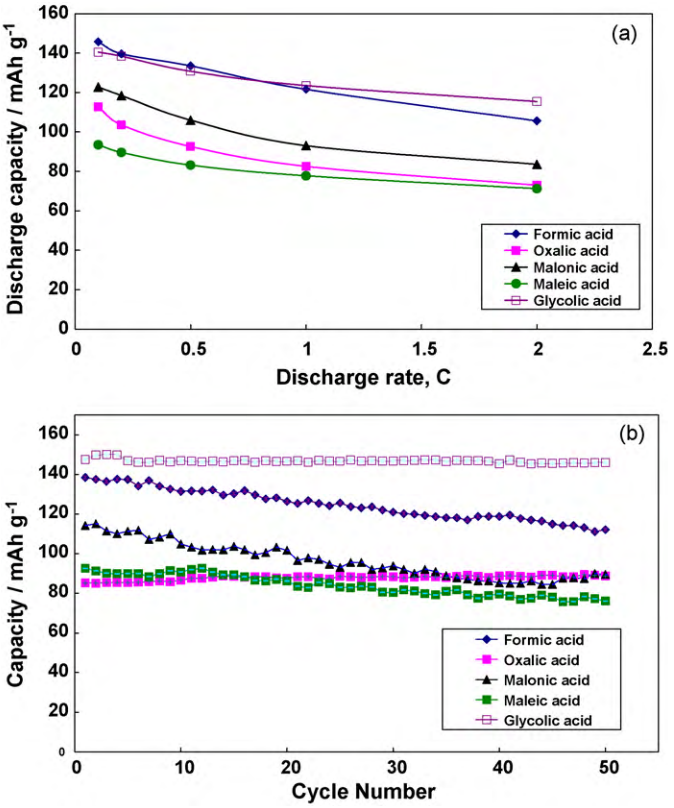

Fig. 6. Rate capability and cycle life tests with cathode materials. (a) Rate capability tests, (b) cycle life tests of $LiFePO_4$/C. The charge and discharge rates of the cycle life tests were 0.2 C.

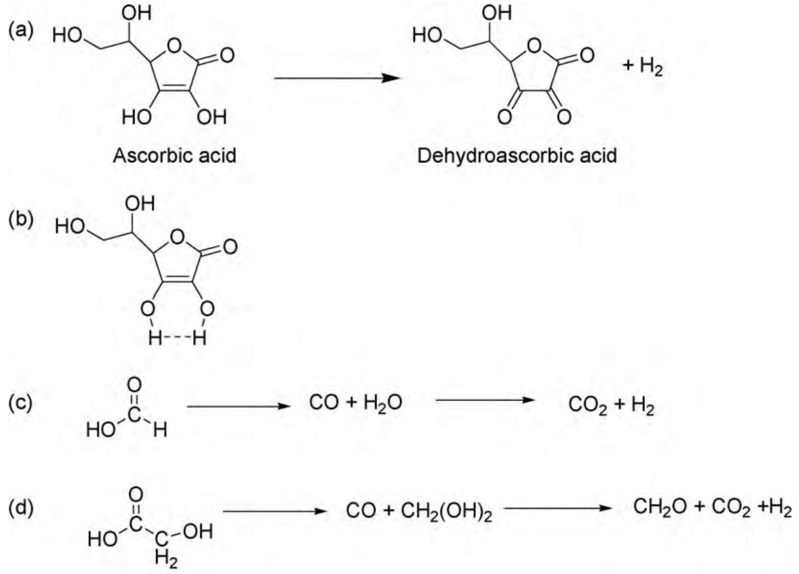

Fig. 7. Production of hydrogen from ascorbic and formic acids. (a) Hydrogen formation from ascorbic acid, (b) intermediates of ascorbic and formic acids for hydrogen formation, (c) thermal decomposition of formic acid, and (d) thermal decomposition of glycolic acid.

At the moment of reduction, there is competition between the reduction of Fe(III) and the ion exchange reaction to form Li_3PO_4 and Fe_2O_3. Depending on the strength of the reductant, the purity of $LiFePO_4$ varies. As an alternative to improving purity, the replacement of LiOH with Li(R) (R = alkyl group) was considered. Bond formation between Fe and the alkyl group is not feasible because the alkyl group is carbonized during synthesis, which can prohibit Fe(III) ions from forming $Fe(OH)_3$. As a result, the formation of Li_3PO_4 was limited. Even though XRD data from the $Fe(III)(NO_3)_3$–formic acid reaction showed negligible impurities, the capacity value implies that there were some undetected impurities. In some cases, impurities became measurable by XRD when further heat treatment was applied to the products. Because formic acid is volatile, loss of acid also decreased the reducing power. Unless a sealed reactor is not used, as in hydrothermal reactions, loss of the acid can cause impurities. Another way of improving reducing power is continuous addition of water vapor to the reaction. When the reaction mixture produces insufficient water, efficient usage of CO can be limited according to the reactions in Fig. 7.

4. Conclusions

It is believed that an organic acid molecule forms CO as the main reducing intermediate, which consequently leads to H_2 production. Mono-carboxylic acids have favorable decomposition mechanisms as reductants compared to bi-carboxylic acids. On the other hand, bi-carboxylic acids follow a more complicated path to produce H_2 and H_2O. Only one of the two carbonyl groups in bi-carboxylic acids is involved in producing CO, although there are few variations among bi-carboxylic acids. When temperature and time for the reaction are high enough for the reduction of $Fe(III)PO_4$, the products in the synthesis of $LiFePO_4$ are dependent on the amount of organic acid in the reaction. In order to utilize the reductant efficiently, a sealed reaction container was used because the organic acid and the reduction intermediates are volatile. When the required amount of acid is not able to participate in the reaction due to the evaporation, impurities can be found in the resultant $LiFePO_4$. Additionally, weaker reducing conditions leave more un-reacted $FePO_4$, which then reacts with LiOH to form Li_3PO_4, Fe_2O_3, Li_2O, and $Li_4P_2O_7$. The choice of a less volatile mono-carboxylic acid and Li(R) can lead to higher purity $LiFePO_4$.

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