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ARTICLE TYPE

LiCoO₂: Recycling from spent batteries and regeneration with solid state synthesis

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A green recycling process was designed and used to recycle spent LiCoO₂ batteries, and the recycled LiCoO₂ was regenerated after the solid state synthesis with Li₂CO₃. XRD results showed that the layered structure of LiCoO₂ was repaired after regeneration. The physical and chemical properties (XRD, morphology, tap density, average particle size, specific surface areas and pH value) and electrochemical properties (discharge capacity, attenuation rate of capacity, plateau retention at 3.6V and attenuation rate of plateau) of LiCoO₂ after regeneration were tested in detail and compared with commercial LiCoO₂. The test datas show that the regenerated LiCoO₂ at 900 °C can meet the commercial requirements for reuse.

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Introduction

The lithium-ion batteries (LIBs) are widely used in mobile electronic devices, electric vehicles and other fields, due to their high voltage, high energy density, low self-discharge, long cycle life, no memory effect, etc.¹⁻³ But along with the extensive use of LIBs, it must be noted that an increasing number of spent LIBs are generated. In these spent LIBs, there are many valuable chemicals, but many of them are harmful if they are released into the environment.⁴⁻⁶ So these spent LIBs must be disposed safely and properly recycled to avoid polluting the environment.

Because of their high energy density, high operating voltage and good electrochemical properties, LiCoO₂ batteries represent a very large proportion of the LIBs market. Therefore, the recycling process of LiCoO₂ batteries is an important focus area for spent LIBs recycling. Currently, the conventional recycling processes of LiCoO₂ batteries include extraction process, chemical precipitation process and electrolytic process, etc.⁷⁻²¹ The specific steps in these recycling processes are not identical, but the acid leaching step is common to all of them. After acid leaching, the cathode powders are dissolved with acid to form a solution containing Co²⁺, Li⁺, etc., and then the extraction process, chemical precipitation process or electrolysis process is used to recycle cobalt and lithium in the form of CoSO₄, CoC₂O₄, Co(OH)₂, Co, Li₂CO₃, etc. A large amount of acid solution or organic solvent is used in these recycling processes, which will create additional waste streams that need to be disposed of or recycled without causing harm to the environment. In addition, these recycling processes are complicated, difficult to operate and costly. Therefore, developing a novel, simple, comprehensive, environmental friendly and low-cost recycling process has obvious economic and social value.

In this paper, a green and efficient recycling process is developed to recycle spent LiCoO₂ batteries. Different from the conventional recycling processes, the structure of recycled LiCoO₂ is not destroyed and only the binder (PVDF) and conductive carbon (acetylene black) are removed during this recycling process. After recycling processes, the obtained LiCoO₂ is regenerated by solid state synthesis with Li₂CO₃. The properties of regenerated LiCoO₂ are tested and compared with commercial LiCoO₂ in detail.

Experimental

Recycling and regeneration

The spent LiCoO₂ batteries were recycled and regenerated as the process flow diagram shown in Fig. 1. The spent batteries were soaked in Na₂SO₄ saturated solution with iron powders for 24 h and completely discharged by electrolyzing water and short circuit, and then dismantled in a sealed glove box. The electrolyte waste gas in sealed box was released to air after three-stage spray purification with DMF, dilute alkaline solution and water in turn, and the electrolyte liquid remaining in the dismantled batteries was extracted and collected by centrifuging. After manual separation, washing and drying, the clean diaphragms and batteries outer shells were directly recycled, the clean cathodes and anodes needed to be further smashed.

The smashed cathodes were calcined in air at 400 °C for 1 h (to remove PVDF), and then most of the powders were separated from Al foils after sieving with 50 mesh screen. The Al foils were recycled after further washing. The cathode powders needed to be further calcined in air at 800 °C for 2 h (to remove acetylene black) after ball-milling and sieving with 400 mesh screen. The C, Li and Co mass contents of the cathode powders

were respectively 0.3 %, 6.4 % and 59.2 % (ICP), and the molar ratio of Li/Co was 0.92 after calculating. According to the data, 100 g cathode powders were mixed with the supplementary Li_2CO_3 powders (molar ratio of Li/Co in the mixtures was 1.05), calcined in air at 850-950 °C for 12 h, ball-milled, and sieved with 400 mesh screen. Finally, the regenerated LiCoO_2 was obtained.

The smashed anodes were further processed as the process flow diagram shown in Fig. 1. At last, clean Cu foils and the mixture of graphite and conductive additive were recycled.

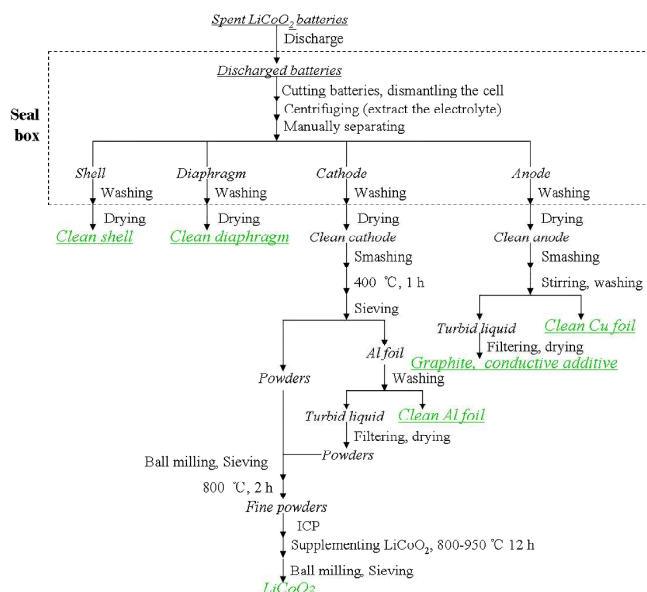


Fig. 1 Recycling and regeneration process flow diagram of spent LiCoO_2 batteries.

15 Physical and chemical properties measurements

The thermal gravimetric analysis was measured with Thermo Gravimetric Analyzer (TGA, EXSTAR6000, SEIKO). The total chemical composition was analyzed by an inductively coupled plasmas spectrometer (ICP, SPS 7800, Seiko Instruments, Japan).

The crystal structure and surface configuration were characterized by X-ray diffraction (XRD, Rigaku D/MAX-2500), scanning electron microscope (SEM, JMS-6700F, JEOL). The tap density was measured by ZS tap density meter (ZS-201) and the particle size distribution was measured with a particle size analyzer (OMEC, LS-POP (6)). The specific surface areas were measured with nitrogen adsorption/desorption isotherms (NOVA 2200e, Quantachrome Instruments).

After regeneration, the amount of the residual Li_2O and other alkaline compounds on the surface of particle, which was highly related to processability in a lithium battery system, was measured by the following method. Firstly, 1.000 g LiCoO_2 was added into 1000 mL redistilled water with continually stirring 0.5 h under a nitrogen atmosphere. Then, pH value of solution was measured by Mettler PE20.

35 Electrochemical properties measurements

For fabrication of cathodes consisted of 80 wt.% active materials, 10 wt.% acetylene black, and 10 wt.% PVDF, 3.2 g LiCoO_2 was mixed with 0.4 g acetylene black and 0.4 g PVDF in N-methyl-2-pyrrolidone (NMP). The electrochemical characterization of

electrodes was performed using CR2032 coin-type test cells with lithium foil as the anode and 1 M LiPF_6 in ethylene carbonate and diethyl carbonate (1:1 in volume) as the electrolyte. The cells were charged and discharged between 3.0 V and 4.3 V versus Li^+/Li by applying a current density of 30 mA g^{-1} at 25 °C.

Results and discussion

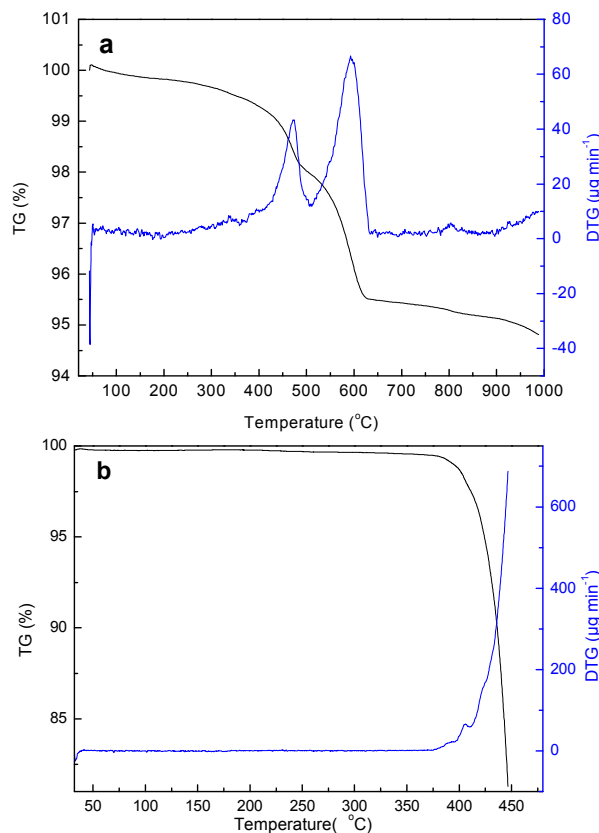


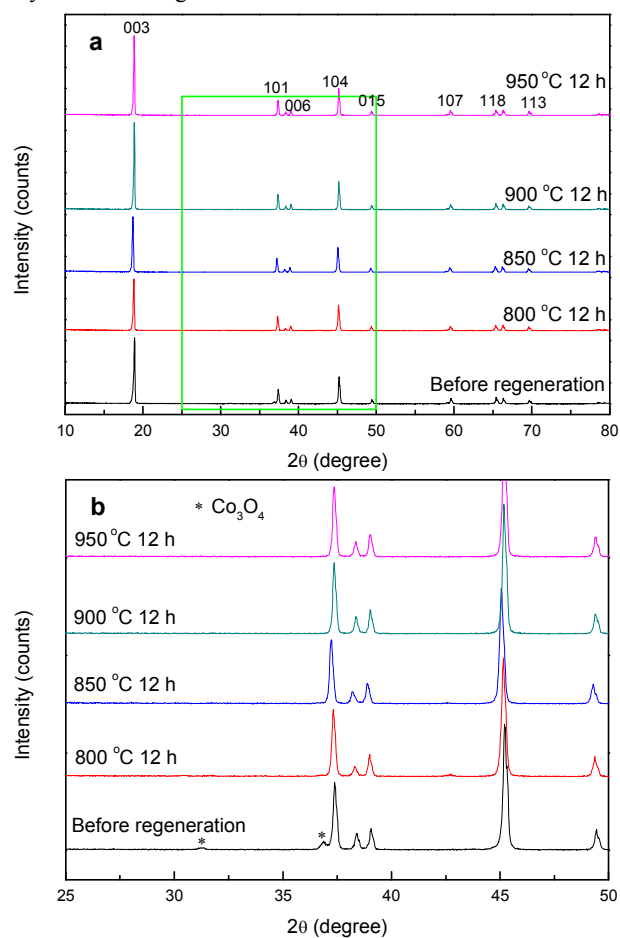
Fig. 2 (a) TG-DTG curves of electrode powders scraped directly from clean cathodes (b) TG-DTG curves of PVDF.

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Fig. 2 (a) shows the TG-DTG curves of cathode powders scraped directly from clean cathodes. There are two weight loss steps observed at 400-500 °C and 500-620 °C in the curves. Combining the TG-DTG curves of PVDF in Fig. 2(b), the first rapid weight loss step is attributed to the decomposition of the PVDF, while the second weight loss step is attributed to the oxidization of the acetylene black. Therefore, 400 °C is selected to remove PVDF (calcination at over 400 °C is more efficient but will accelerate the oxidization of Al foils) and 800 °C is selected to remove the acetylene black (calcination at 800 °C is more efficient than that at 620 °C). After calcination at 400 °C, the PVDF in recycled cathode powders can be removed completely, which is beneficial for the separation of powders and Al foils. After calcination at 800 °C, the acetylene black can be removed completely, which is beneficial for the further regeneration.

Fig. 3 shows XRD patterns of the recycled LiCoO_2 after regeneration at different temperatures. Before regeneration, there are some small diffraction peaks of Co_3O_4 observed at 32.2° and 36.8°, after regeneration at 800-950 °C, the diffraction peaks of Co_3O_4 disappear, and all the regenerated LiCoO_2 has $\alpha\text{-NaFeO}_2$ layered structure. It is generally believed that the higher I_{003}/I_{104}

is corresponding to the better layered structure of LiCoO_2 , which is of great advantage to the intercalation/deintercalation of Li^+ and the good electrochemical properties. It can be seen that I_{003}/I_{104} of LiCoO_2 before regeneration is 1.232, demonstrating the poor layered structure. After regeneration, I_{003}/I_{104} of LiCoO_2 increases obviously as regeneration temperature rises from 800 °C to 900 °C, demonstrating the repaired layered structure. I_{003}/I_{104} reaches the maximum of 2.554 at 900 °C, but decreases when the regeneration temperature further rises to 950 °C. It is known that too high temperature can result in some loss of lithium, thus can result in lattice defects and a decline of the crystallization degree.²²



Samples	I_{003}/I_{104}
Before regeneration	1.232
800 °C 12 h	1.671
850 °C 12 h	1.955
900 °C 12 h	2.554
950 °C 12 h	2.325

Fig. 3 (a) XRD patterns of LiCoO_2 after regeneration at different temperatures, and (b) the enlarged view of rectangle region.

SEM images of the recycled LiCoO_2 after regeneration are shown in Fig. 4. After regeneration, there are some small particles (residual Li_2O) attached to the surface of LiCoO_2 , but as regeneration temperature rises, these small particles decrease gradually until disappear completely. The similar phenomenon has been reported.²³ In addition, it can be observed that the particle size of regenerated LiCoO_2 is in the range of 5-20 μm and

increases a little as the regeneration temperature rises from 800 °C to 900 °C. The morphology and particle size of the regenerated LiCoO_2 are similar to those of commercial LiCoO_2 (5-20 μm).

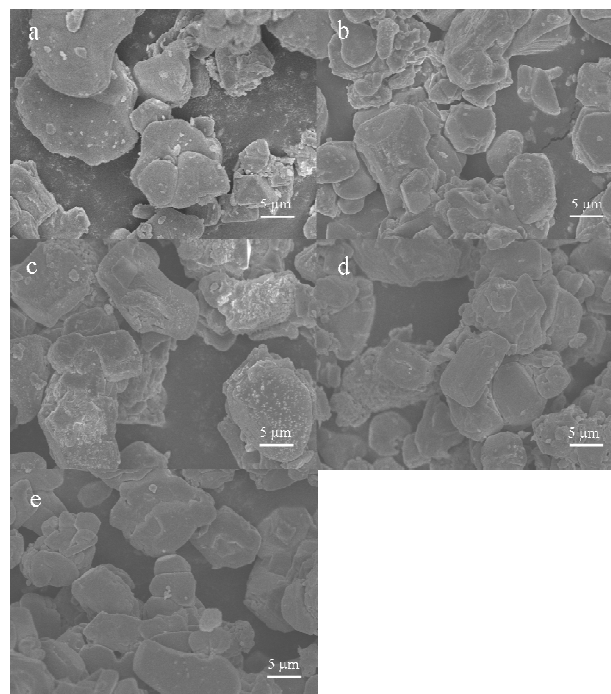
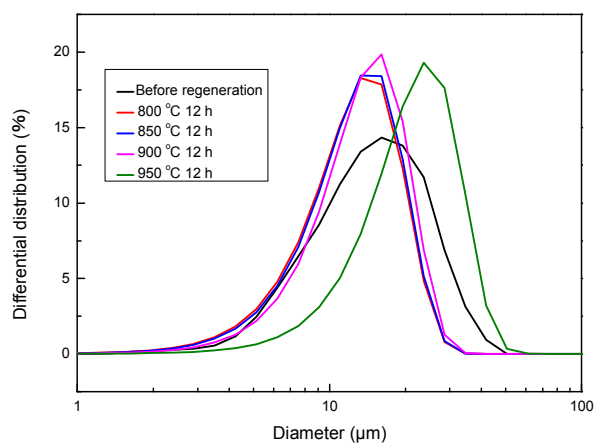


Fig. 4 SEM images of LiCoO_2 after regeneration at different temperatures. (a) before regeneration, (b) 800 °C, (c) 850 °C, (d) 900 °C, (e) 950 °C

Generally, high tap density of LiCoO_2 is corresponding to excellent processing properties in the battery production. Table 1 lists the tap densities of LiCoO_2 after regeneration at different temperature. The tap density of LiCoO_2 before regeneration is far from that of commercial LiCoO_2 (2.4-2.9 g ml^{-1}). As the regeneration temperature rises from 800 °C to 900 °C, the tap densities of regenerated LiCoO_2 increase gradually and reach the maximum of 2.366 g ml^{-1} at 900 °C, which is close to the level of commercial LiCoO_2 . However, when the regeneration temperature rises to 950 °C, the tap density reduces. These changes may be caused by material agglomeration at 950 °C, which is often observed in industrialized production of LiCoO_2 at this temperature.

Table 1 The tap densities of LiCoO_2 after regeneration at different temperatures.

Samples	Tap density (g ml^{-1})
Before regeneration	2.176
800 °C 12 h	2.311
850 °C 12 h	2.324
900 °C 12 h	2.366
950 °C 12 h	2.228



Samples	D50 (um)
Before regeneration	13.45
800 °C 12 h	11.50
850 °C 12 h	11.71
900 °C 12 h	12.49
950 °C 12 h	19.71

Fig. 5 Size distribution curves of LiCoO₂ after regeneration at different temperatures.

Particle size is also one of the important parameters related to processing properties. The size distribution curves of LiCoO₂ after regeneration at different temperature are shown in Fig. 5. The average particle size (D50) of LiCoO₂ is 13.45 μm before regeneration, but decrease to 11.50 μm after regeneration at 800 °C. As the regeneration temperature rises from 800 °C to 900 °C, the average particle size (D50) of regenerated LiCoO₂ increases gradually. However, the average particle size (D50) increases sharply from 900 to 950 °C, which is due to the material agglomeration occurs at 950 °C. Except for LiCoO₂ regenerated at 950 °C, the average particle size (D50) of other regenerated LiCoO₂ is within the scope of commercial LiCoO₂ (9-18 μm).

Table 2 The specific surface areas of LiCoO₂ after regeneration at different temperatures.

Samples	Specific surface areas (m ² g ⁻¹)
Before regeneration	0.747
800 °C 12 h	0.546
850 °C 12 h	0.506
900 °C 12 h	0.178
950 °C 12 h	0.191

Low specific surface areas is also conducive to good processing properties of LiCoO₂. Table 2 lists the specific surface areas of LiCoO₂ after regeneration at different temperature. Brunauer-Emmett-Teller (BET) specific surface areas of LiCoO₂ before regeneration is as high as 0.747 g ml⁻¹. As the regeneration temperature rises 800 °C to 900 °C, the specific surface areas of LiCoO₂ decrease gradually and reach the minimum of 0.178 g ml⁻¹ at 900 °C, which is within the scope of commercial LiCoO₂ (0.2-0.6 g ml⁻¹).

Table 3 The pH values of LiCoO₂ after regeneration at different temperatures.

Samples	pH values
Before regeneration	10.00

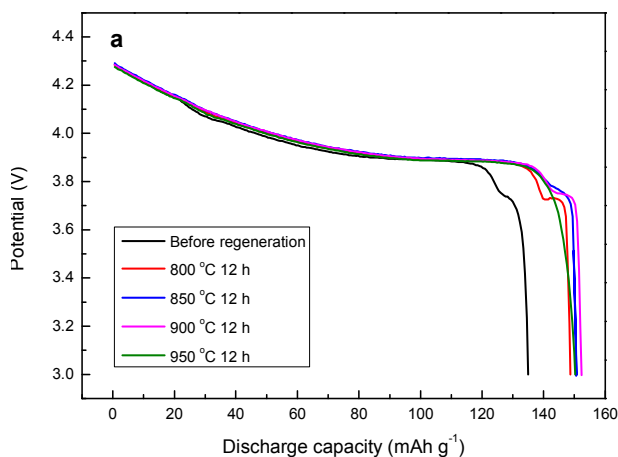
800 °C 12 h	10.15
850 °C 12 h	9.97
900 °C 12 h	8.89
950 °C 12 h	8.65

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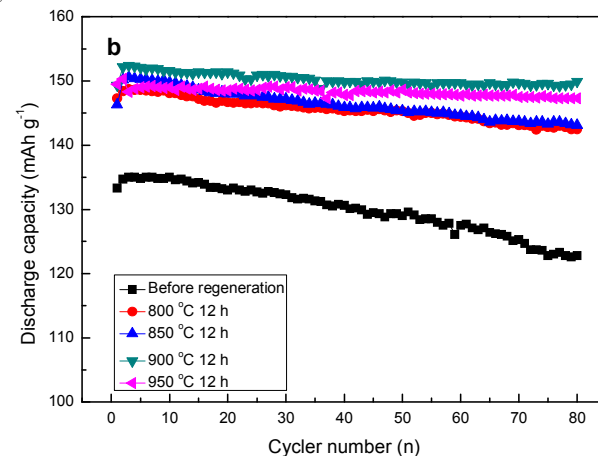
Low pH value is also conducive to good processing properties of LiCoO₂. Table 3 lists the pH values of LiCoO₂ after regeneration at different temperature. It can be seen that the pH value of LiCoO₂ decreases as the regeneration temperature rises. This phenomenon can be explained as follows, as the regeneration temperature rises, more added Li₂CO₃ reacts with fine powers and the less Li₂CO₃ is residual, so the pH value decreases. In addition, the pH values of the regenerated LiCoO₂ are all within the scope of commercial LiCoO₂ (9.5-11.5).

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Based the above test datas, the physical and chemical properties properties (XRD, morphology, tap density, average particle size, specific surface area and pH value) of LiCoO₂ after regeneration at 900 °C are all close to those of commercial LiCoO₂ and meet the commercial requirements for reuse.



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Samples	Discharge capacity (mAh g ⁻¹)	Attenuation rate of capacity during every cycle (mAh g ⁻¹)	Plateau retention at 3.6V (%)	Attenuation rate of plateau during every cycle (mAh g ⁻¹)
Before regeneration	135.0	0.1525	98.37	0.2713
800 °C 12 h	148.7	0.0775	99.19	0.1413
850 °C 12 h	150.6	0.0938	99.27	0.1300
900 °C 12 h	152.4	0.0313	99.08	0.0463
950 °C 12 h	150.3	0.0375	97.07	0.0225

Fig. 6 Electrochemical properties of LiCoO₂ after regeneration at different temperatures.

Fig. 6 displays the electrochemical properties of LiCoO₂ after regeneration at different temperature. It is obvious that the electrochemical properties of LiCoO₂ before regeneration are poor and not suitable for reusing. By contrast, the electrochemical properties of regenerated LiCoO₂ are improved obviously. Especially after regeneration at 900 °C, the discharge capacity could reach about 152.4 mAh g⁻¹ and the attenuation rate of capacity during every cycle is only 0.0313 mAh g⁻¹. The improved electrochemical properties of the regenerated LiCoO₂ are associated with the repaired layered structure, which is demonstrated by the increasing I₀₀₃/I₁₀₄ (in Fig. 3). The electrochemical properties of regenerated LiCoO₂ at 900 °C are close to those of commercial LiCoO₂ (140-155 mAh g⁻¹, coin cell) and meet the commercial requirements for reuse.

Conclusions

A green recycling process of spent LiCoO₂ batteries is developed in this paper. In this process, the spent LiCoO₂ batteries can be dismantled, separated and recycled without secondary pollution. After solid state synthesis with Li₂CO₃, the recycled LiCoO₂ is regenerated efficiently. The physical and chemical properties properties and electrochemical properties of LiCoO₂ after regeneration at 900 °C are all close to those of commercial LiCoO₂, and meet the commercial requirements for reuse. In general, the novel recycling and regeneration processes are simple, comprehensive, environmental friendly, low-cost and can be applied to a large scale in industrialization.

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Notes and references

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