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Short communication

Adipic acid assisted, sol–gel route for synthesis of $LiCr_xMn_{2-x}O_4$ cathode material

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Abstract

Spinel $LiMn_2O_4$ and $LiCr_xMn_{2-x}O_4$ ($x = 0.00-0.20$) have been synthesized by a soft chemistry method using adipic acid as the chelating agent. This technique offers better homogeneity, preferred surface morphology, reduced heat-treatment conditions, sub-micron sized particles, and better crystallinity. The synthesized spinel materials are characterized by X-ray diffraction, scanning electron microscopy, cyclic voltammetry, and charge–discharge testing. It is found that chromium substitution alleviates capacity fading in the 4-V region and improves the structural stability of $LiMn_2O_4$ spinel upon repeated cycling.

Keywords: Spinel $LiMn_2O_4$; Chromium substitution; Adipic acid; Sol–gel synthesis; Intercalation reaction; Electrochemical properties; Lithium ion battery

1. Introduction

$LiMn_2O_4$ spinel is a promising cathode material for rechargeable lithium batteries because of its low cost and environmentally benign nature. Although $LiMn_2O_4$ cycles well at room temperature, prolonged cycling at higher temperatures is accompanied by an unacceptable fading of capacity [1,2]. This phenomenon has been attributed to several factors such as electrolyte decomposition, slow dissolution of $LiMn_2O_4$ [3], unstable two-phase reaction, i.e., Jahn-Teller distortion [4], lattice instability [5], and particle disruption [6]. Ohzuku et al. [7] have studied a series of 5-V positive-electrode (cathode) materials obtained by substituting the Mn in $LiMn_2O_4$ with third transition metals such as Co, Cr, Cu, Fe, Ni, Ti and Zn, which are effective in suppressing capacity fading on cycling. These materials have operating voltages above 4.8 V, as also reported by Lee et al. [8].

It is well known that the physical as well as the electrochemical properties of any cathode depend upon the method of synthesis and the type of precursors employed. In recent years, several low-temperature preparation methods, such as sol–gel synthesis [9,10], precipitation [11], the Pechini process [12], and a hydrothermal method [13] have been used to prepare $LiMn_2O_4$. In this work, an attempt has been made to stabilize the $LiMn_2O_4$ spinel structure by a sol–gel method that employs adipic acid as a chelating agent with Cr as a dopant. This soft chemistry technique offers many advantages such as better homogenity, low calcination temperature, shorter heating time, regular morphology, sub-micron sized particles, less impurities, large surface area, and good control of stoichiometry.

2. Experimental

$LiCr_xMn_{2-x}O_4$ ($x = 0.00$, 0.01, 0.02, 0.05, 0.10, 0.20) powders have been synthesized by a sol–gel method using adipic acid as a chelating agent, see Fig. 1. Stoichiometric amounts of lithium nitrate, manganese nitrate, and ammonium dichromate were mixed thoroughly and dissolved in de-ionized water. The solution was stirred continuously with mild heating to ensure homogeneity. The 50 ml of 1 M adipic acid was added to the homogeneous solution and resulted in the formation of precipitate. Simultaneously, the pH of the solution was adjusted to between 7 and 8.5 and stirring and heating was continued until a gel was obtained.

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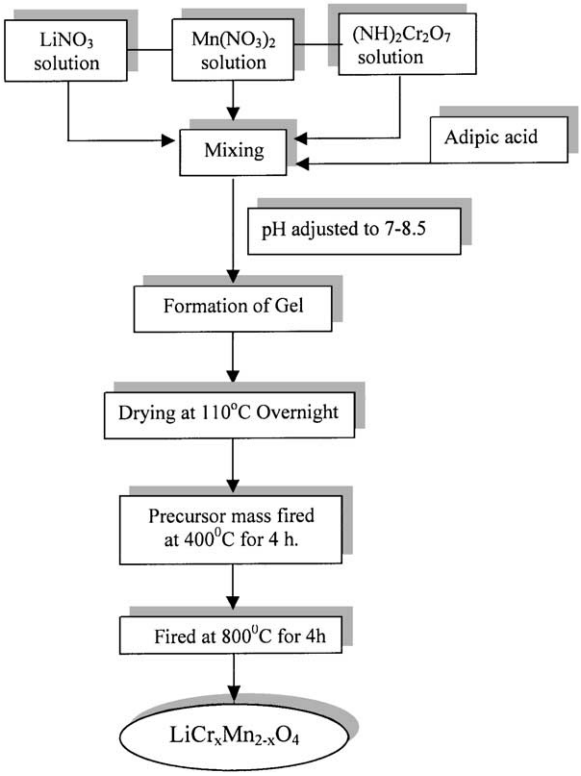

Fig. 1. Flow chart for synthesis of $LiCr_xMn_{2-x}O_4$ via adipic assisted, sol–gel route.

The gel thus obtained was heated initially in an oven at 110 °C overnight and then in a furnace at 400 °C for about 4 h. Finally, the powder was heated at 800 °C for 4 h to ensure good purity and crystallinity. Ultimately, the resulting powders were subjected to physical as well as electrochemical characterization.

2.1. Coin cell preparation

Standard 2016 coin cells were assembled using lithium metal as the anode, a Celgard 2400 separator, and a 1 M solution of $LiPF_6$ in a 50:50 (v/v) mixture of ethylene carbonate and dimethyl carbonate as electrolyte. The cathode was an aluminium disc (diameter 1.8 cm) that was spread-coated with a 80:10:10 slurry of the cathode active powder, graphite and polyvinylidene fluoride in *N*-methyl-2-pyrrolidone. The loading of active material in the cathode varied from 0.087 to 0.098 g. Charge–discharge studies were carried out between 3 and 4.5 V by wears of an in-house charging facility.

Phase characterization studies were undertaken on a Jeol JDX 8030 X-ray diffractometer with nickel-filtered Cu Kα radiation, in order to examine the crystalline phase of the synthesized spinel. The surface morphology was investigated with a JEOL JSM 1200 EX II scanning electron microscope (SEM). Charge–discharge studies were performed with a TOSCAT-3000 V, battery testing unit. The cells were assembled in an argon-filled glove-box (MBraun) with moisture and oxygen levels maintained at less than 1 ppm.

3. Results and discussion

3.1. X-ray diffraction analysis

The X-ray diffraction patterns of Cr^{3+}-doped samples show striking similarity to that of pure $LiMn_2O_4$ (space

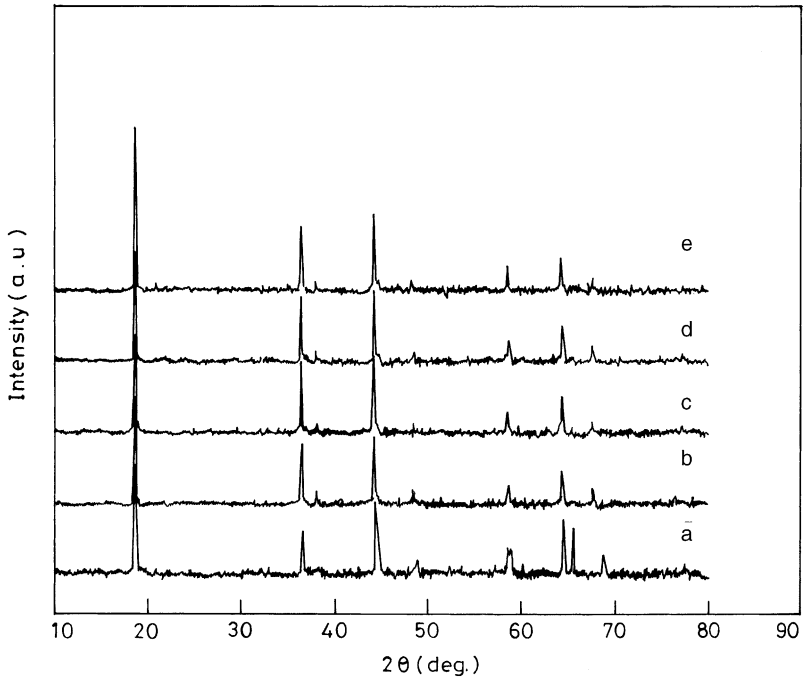

Fig. 2. XRD pattern for $LiCr_xMn_{2-x}O_4$ samples calcined at 800 °C for 4 h: (a) $x = 0.00$, (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.05$, (e) $x = 0.10$.

group Fd3m) in which the manganese ions occupy the 16d sites and the O^2-ions occupy the 32c sites (Fig. 2). That the chromium-doped compounds have cubic spinel structure has been demonstrated by several workers [14–16]. In fact, the lattice parameters of $LiCr_xMn_{2-x}O_4$ are very close to those of $LiMn_2O_4$ [17–19]. Substitution of manganese by chromium should result in a shrinkage of the unit-cell volume. This is because, in the same oxidation state, chromium ions have smaller ionic radii than manganese ions, i.e., Cr^{3+}(0.615 Å), Mn^{3+}(0.68 Å), Cr^{4+}(0.58 Å), Mn^{4+}(0.60 Å) [20]. The decrease in cell volume should increase the stability of the structure during intercalation and de-intercalation of lithium [21–23]. The stronger Cr–O bonds in the delithiated state (compare the binding energy of 1142 kJ mol^{-1} for CrO_2 with 946 kJ mol^{-1} for α-MnO_2) may also be expected to contribute to stabilization of the octahedral sites.

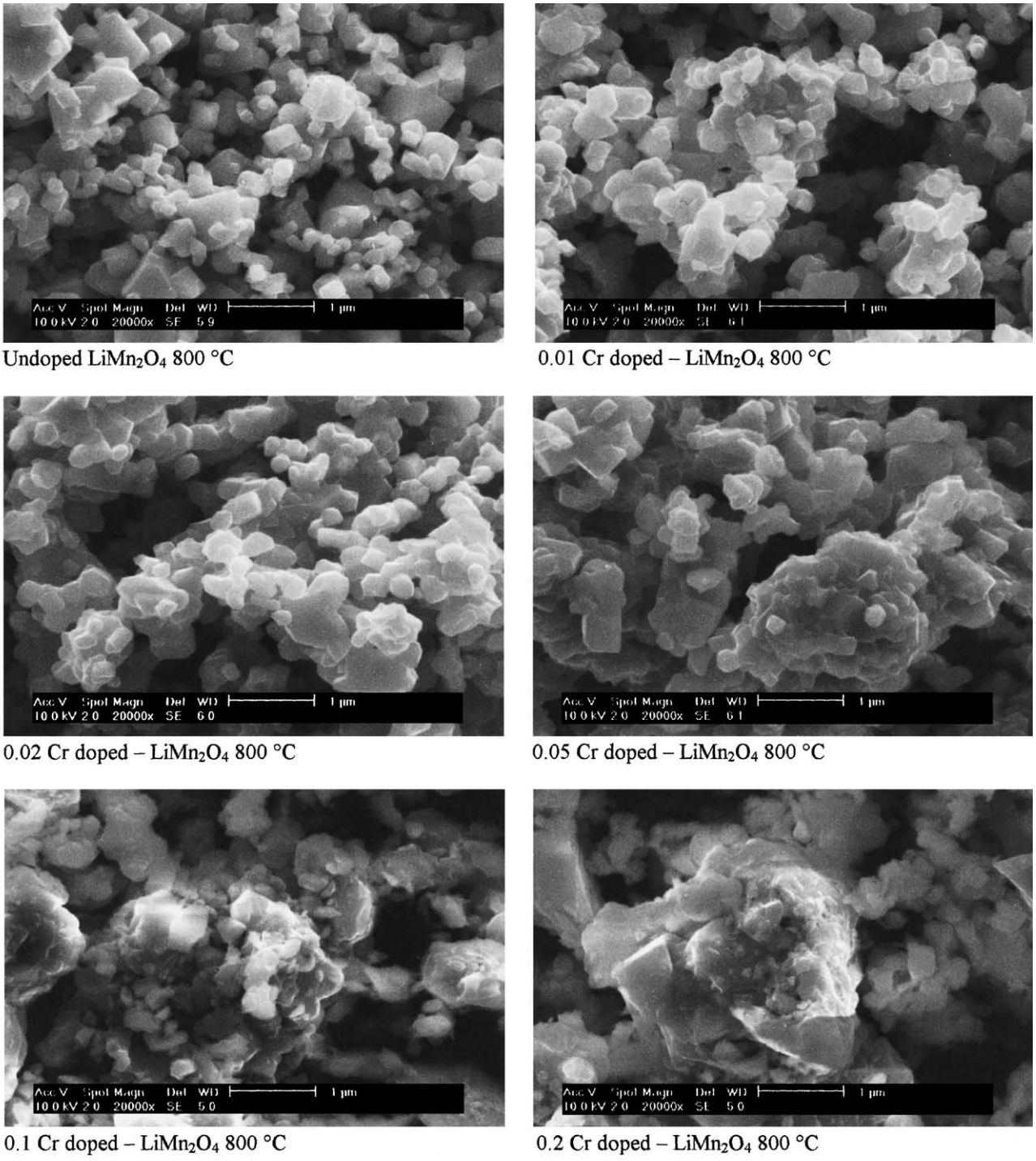

Fig. 3. Scanning electron micrographs for sample calcined at 800 °C for 4 h: (a) $x = 0.00$, (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.05$, (e) $x = 0.10$, (f) $x = 0.20$.

The higher stabilization energy of Cr^{3+} ions for octahedral coordination is well known. Sigala et al. [21] have demonstrated the structural stability imparted by Cr^{3+} ions to $LiMn_2O_4$ spinels, and a similar effect by chemically modified Cr^{5+}–Cr^{6+} oxide has been observed by Zhang et al. [22]. It has also been found [23] that incorporation of Cr^{3+} greatly suppresses the dissolution of manganese ions in the electrolyte, which is one of the failure of mechanisms of $LiMn_2O_4$ cathodes.

3.2. Surface morphology

Surface morphology, one of the prime factors that govern the physical as well as the electrochemical properties of synthesized cathode oxides, has been studied by means of SEM analysis. The micrographs for a series of $LiCr_xMn_{2-x}O_4$ ($x = 0.00$, 0.01, 0.02, 0.05, 0.10, 0.20) samples are given in Fig. 3. It is evident that the presence spherical grains of an independent nature are obtained up to a dopant level of about $x = 0.02$. Slightly agglomerated particles are formed at higher dopant concentrations of $x = 0.05$, 0.10, 0.20.

It is interesting to note that the effect of a high calcination temperature results in the formation of highly sintered particles, as demonstrated by the micrographs. Nevertheless, particles of sub-micron size (<0.10 μm) are present throughout the series of solid solutions of $LiCr_xMn_{2-x}O_4$ ($x = 0.00$–0.20). The sintered nature of particles of uniformly distributed, sub-micron size is desirable for cathode materials as they enhance the electrochemical behaviour. Evidently, the present sol–gel approach, in which adipic acid is used as a chelating agent, has resulted in the formation of particles that possess preferred surface morphology.

3.3. Charge–discharge studies

Charge–discharge curves for $LiMn_2O_4$ and $LiCr_xMn_{2-x}O_4$ cells are given in Fig. 4. These cells were cycled between 3 and 4.25 V at the 0.1 °C rate. The two-step intercalation–de-intercalation process for chromium-doped $LiMn_2O_4$ can be represented as follows:

$$Li[Cr_y{}^{3+}Mn_{1-y}{}^{3+}Mn^{4+}]O_4 \overset{4\,V}{\leftrightarrow} 1-yLi_y[Cr_y{}^{3+}Mn_{2-y}{}^{4+}]O_4 + (1-y)Li^+ + (1-y)e^- \overset{4.8\,V}{\leftrightarrow} [Cr_y{}^{4+}Mn_{2-y}{}^{4+}]O_4 + yLi^+ + ye^-$$

During the first cycle, the $LiMn_2O_4$ spinel exhibits a specific capacity of 128 mA h g^{-1}, whereas 0.01 Cr-doped material gives a slightly lower capacity. Replacement of Mn^{3+} ion by Cr^{3+} and the oxidation of a similar amount of Mn^{3+} to the Mn^{4+} state leads to an increase in the average oxidation state of manganese. The diminished Mn^{3+} ion concentration causes a reduction in the unit-cell volume of the spinel, which results in increased structural stability. The capacities obtained correspond to oxidation of Mn^{3+} to Mn^{4+}. The oxidation of Cr^{3+} to Cr^{4+} occurs at 4.8 V [24–27].

3.4. Cycleability studies

The cycleability curves for pure $LiMn_2O_4$ and chromium-doped spinel are shown in Fig. 5. It is seen that 0.01 chromium-doped $LiMn_2O_4$ exhibits a constant capacity up to 100 cycles. The superior cycleability of the doped variety is due to increased stability caused by the higher octahedral site stabilization energy of Cr^{3+}. The effect of chromium is more pronounced in reducing the capacity fade. On the other hand, the cycleability of undoped $LiMn_2O_4$ decreases drastically. Undoped $LiMn_2O_4$ delivers an initial capacity of 120 mA h g^{-1}, whereas 0.01Cr gives a constant capacity of 110 mA h g^{-1}.

3.5. Cyclic voltammetric studies

Cyclic voltammograms (sweep rate: 0.02 mV s^{-1}) for cells with $LiMn_2O_4$ and $LiCr_{0.01}Mn_{1.99}O_4$ are presented in Fig. 6a and b, respectively. Despite electrolyte decomposition is a possibility at the high voltage that is used there is no evidence for this in the voltammograms. Indeed, $LiPF_6$-based electrolytes, such as that used were

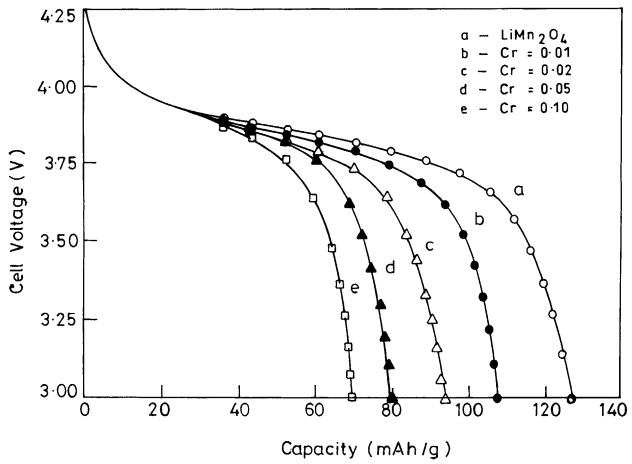

Fig. 4. Charge–discharge behaviour of $LiMn_2O_4$ and $LiCr_xMn_{2-x}O_4$ cells: (a) $x = 0.00$, (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.05$, (e) $x = 0.10$.

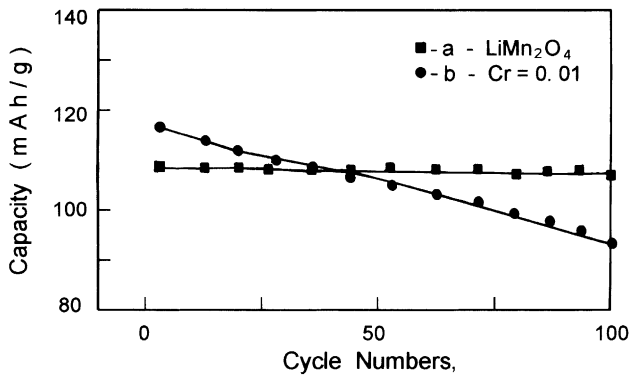

Fig. 5. Cycling performance of (a) $LiMn_2O_4$ and (b) $LiCr_{0.01}Mn_{1.99}O_4$ cells.

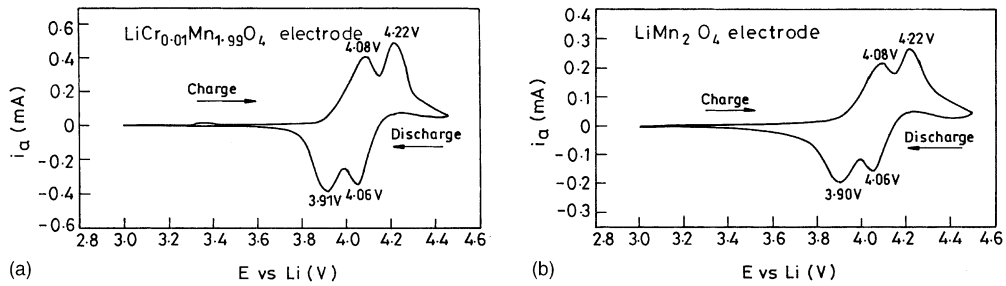

Fig. 6. Cyclic voltammograms for (a) $LiMn_2O_4$ and (b) $LiCr_{0.01}Mn_{1.99}O_4$ Li at sweep rate 0.02 mV s^{-1}.

fairy tolerant to high voltages [28]. Generally, the anodic and cathodic peaks on the voltammograms are related to the intercalation and de-intercalation of lithium ions into from the spinel. The peak around 4.08 V corresponds to this process at the 8a tetrahedral sites associated with the Mn^{4+}/Mn^{3+} couple, while the other peak at 4.22 V corresponds to the oxidation–reduction of Cr^{3+} ions [29,30]. The voltammogram for the chromium-doped spinel reveals that there is an increase in both the anodic and the cathodic peak current. This observation suggests that chromium-doped spinel enhances both reversibility and rate capability.

4. Conclusions

The above study has resulted in the following sentences:

(i) A new route for the synthesis of $LiMn_2O_4$ and $LiCr_xMn_{2-x}O_4$ has been demonstrated via an adipic acid assisted, sol–gel method. This method offers several advantages, i.e., a pure spinel phase, lower calcination temperature, shorter processing time, sub-micron sized particles with a narrow particle-size distribution.
(ii) XRD and SEM studies confirm high phase purity and well-defined particles with improved morphology, respectively.
(iii) Charge–discharge studies have established the possibility of enhancing the structural stability of $LiCr_xMn_{2-x}O_4$ spinels through Cr doping.
(iv) Cyclic voltammetric experiments disclose the enhanced reversibility and rate capability of Cr^{3+}-modified spinel as compared with undoped spinel.
(v) The synthesis of $LiCr_xMn_{2-x}O_4$ ($x = 0.00, 0.01, 0.02, 0.05, 0.10, 0.20$) has resulted in a structurally stabilized spinel with enhanced electrochemical properties.

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