

Chemical stability enhancement of lithium conducting solid electrolyte plates using sputtered LiPON thin films

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Abstract

Sputter deposition of LiPON films directly onto high Li^+ conductivity solid electrolyte plates has been investigated as a means to minimize the reactivity of the plates to metallic Li. The LiPON films were shown to effectively passivate the plates in contact with metallic Li, in contrast to unpassivated plates that reacted immediately in contact with Li metal. The conductivity of the passivated solid electrolyte plates was measured to be $1.0 \times 10^{-4} \text{ S cm}^{-1}$, with Arrhenius activation energy of 0.36 eV and an electrochemical stability window of at least 0–5.0 V versus Li/Li^+ . The passivated solid electrolyte was capable of supporting electrochemical plating and stripping of Li metal, as demonstrated by EIS and CV measurements. These high chemical stability, high Li^+ conductivity solid electrolyte plates will be useful for solid-state batteries employing Li anodes.

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1. Introduction

Many research groups have pursued a viable solid-state inorganic Li^+ solid electrolyte since the 1970s for application in solid-state lithium batteries. This research and development has been driven by the numerous benefits offered by a solid-state electrolyte-based lithium battery. Perhaps most importantly, a battery with a solid-state electrolyte can, in principle, employ a Li anode without the deleterious dendritic formation with multiple charging that is typically associated with lithium cells that employ liquid organic electrolytes. The lithium anode has a far superior theoretical specific capacity of 3800 mAh g^{-1} compared with the state-of-art lithium-ion graphitic anodes with 372 mAh g^{-1} . However, historically there have been serious limitations associated with inorganic solid electrolytes, notably low ionic conductivity relative to liquid organic electrolytes, as well as poor chemical stability at the anode.

The thin film solid electrolyte developed at Oak Ridge National Laboratories (ORNL) in the 1990s exemplifies the advantages of an inorganic solid-state electrolyte. The ORNL group reports thin film batteries employing the lithium phosphorous oxynitride (LiPON) electrolyte, LiCoO_2 cathode, and Li metal anode are capable of over

20,000 charge/discharge cycles with 0.001% capacity loss per cycle [1]. These cells have extremely low self-discharge rates, with charged cells losing only a few hundred millivolts over several years. Metallic Li is stable in direct contact with LiPON, and the electrolyte film has electrochemical stability from 0 to 5.4 V versus Li/Li^+ . Although LiPON has relatively poor ionic conductivity of ca. $2 \times 10^{-6} \text{ S cm}^{-1}$, typically no more than a few microns of sputter-deposited electrolyte is needed for thin film batteries.

Unfortunately, LiPON has been used exclusively as an electrolyte for thin film batteries with footprints of no more than about 1 cm^2 with $10 \mu\text{m}$ thicknesses. These batteries are not readily scaled to sizes that can deliver capacities on the order of hundreds milliamperes-hours or greater. In contrast, bulk electrolyte powders, pellets, and plates are much more amenable to fabrication of prismatic or cylindrical lithium batteries with sizes commensurate with conventional consumer applications (e.g. cellular telephones and laptop computers). Recently, high Li^+ conductivity solid electrolytes have been offered commercially by Ohara Inc. in rigid plates, rolls of flexible sheets, or powdered form with room temperature Li^+ conductivities of 10^{-3} to $10^{-4} \text{ S cm}^{-1}$ [2]. Ohara Inc. has patented these glass-ceramic Li^+ conducting solid electrolytes, which consist of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5-\text{TiO}_2-\text{GeO}_2$, with a NASICON-type crystalline phase [3]. The solid electrolyte is stable in moist air, but it is not chemically stable in

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contact with metallic lithium, thus precluding its use in direct contact with a Li anode. It should be noted that the Li⁺ conducting solid plates supplied by Ohara are not available commercially, though the flexible sheets are anticipated to be manufactured in volume in the near future.

A possible solution to the chemical reactivity issue of the high conductivity Ohara electrolyte is to sputter deposit a thin passivating LiPON film directly on the Ohara electrolyte. Though others have examined thin film electrolyte passivation of electrodes [4–6], we report here a high conductivity composite electrolyte system consisting of a LiPON-coated solid electrolyte plate that is chemically stable with Li metal. The freestanding composite electrolyte has a conductivity of 10^{-4} S cm⁻¹ and is capable of direct electrochemical plating and stripping of metallic Li. These composite electrolyte plates will have applications in high specific energy solid-state batteries capable of employing Li metal anodes. Full cell Li battery studies using the LiPON-coated Ohara solid electrolyte plates are currently underway within our laboratories.

2. Experimental

The commercially supplied solid electrolyte plates (Ohara Corporation) were tested as received, without any annealing or drying steps. The plate dimensions were 50.8 mm × 50.8 mm and 0.47 mm thick. Deposition of the passivating films and metal electrodes onto the plates (except the Li electrodes) was carried out in a planar RF magnetron sputtering chamber. Details of the deposition processes and hardware are published elsewhere [7]. The thin film electrolyte of Li_{3.3}PO_{3.8}N_{0.22} (LiPON) was deposited onto the plates by sputtering a Li₃PO₄ target in N₂, after Yu et al. [8]. The Pt and Cu electrodes were sputtered through a metal shadow mask defining an area of 8 mm × 40 mm, while the Li electrodes were thermally evaporated onto the plates through

the same mask. For characterization of the LiPON films, test structures were deposited onto Si₃N₄-coated Si substrates.

The test cells were characterized via electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) techniques. The EIS and CV measurements were performed using a Solartron 1286 frequency response analyzer and a Princeton Applied Research 273A potentiostat, driven by Zplot and Corrware Software (Scribner Associates). Cyclic voltammetry measurements were performed with sweep rates between 0.1 and 5 mV/s. The applied AC signal for the EIS measurements was 20 mV, with frequencies between 65,000 and 0.1 Hz. The EIS data was fitted to equivalent circuit models by a complex least square fitting program, Zview (Scribner Associates). To calculate electrolyte conductivity values, the real component of the impedance at the high frequency inflection point or local minima in the EIS data was taken as film resistance.

3. Results and discussion

The solid electrolyte plates (Ohara Corporation) were smooth and featureless as received from the vendor. When a thin (ca. 1 μm) film of Li was evaporated onto the plates, the Li metal reacted immediately with the plate to form a dark nonmetallic layer that was electrically nonconductive. In contrast, when the plate was coated with a film of LiPON nominally 1 μm thick and then coated with an evaporated Li film, the Li film maintained a lustrous metallic color and was electrically conductive (Fig. 1A and B). It is interesting to note that dark spots in the Li can be discerned in Fig. 1B where pinholes in the LiPON allowed the solid electrolyte to directly contact the Li film and react as in the case of the uncoated electrolyte plates. These dark regions gradually grew in size and coalesced over several weeks, indicating the importance of deposition of pinhole-free LiPON for suitable electrolyte plate protection.



Fig. 1. Evaporated Li films on solid electrolyte plates. (A) Uncoated plate with Li showing dark reaction product of plate and Li; and (B) LiPON-coated plate with pristine unreacted Li metal. Pinholes in the LiPON and associated Li reaction product are discernible on the left end of the Li pattern in B.

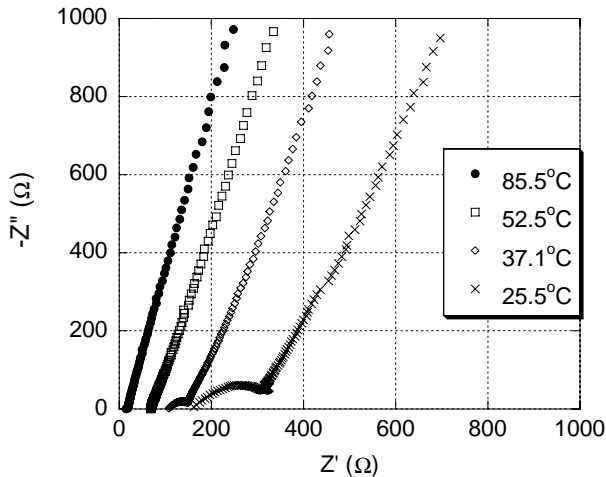


Fig. 2. Complex plane plots of Pt|LiPON|Pt test cell on Si_3N_4 -coated Si substrate at various temperatures.

However, the addition of the thin film of LiPON to the solid electrolyte plate increases the chemical stability of the plate at the cost of increased cell resistance. The Li^+ conductivity of LiPON was measured to be $5.6 \times 10^{-7} \text{ S cm}^{-1}$ with an activation energy of 0.46 eV as measured for a Pt|LiPON|Pt test cell (Figs. 2 and 3). In principle, a 0.5- μm thick LiPON film deposited on both sides of the electrolyte plate translates into an increase in electrolyte resistance of $180 \Omega \text{ cm}^{-2}$, whereas for a 0.5-mm thick plate with a conductivity of $10^{-4} \text{ S cm}^{-1}$, the resistance corresponds to $500 \Omega \text{ cm}^{-2}$. In our test results, we found the LiPON resistance was small relative to the overall test cell impedances. For a 0.47 mm solid electrolyte plate with 1.1 μm of LiPON on one side (cathode side) and 2.9 μm of LiPON on the other side (anode side), the composite electrolyte conductivity was $1.0 \times 10^{-4} \text{ S cm}^{-1}$, with activation energy of 0.36 eV (Figs. 4 and 5).

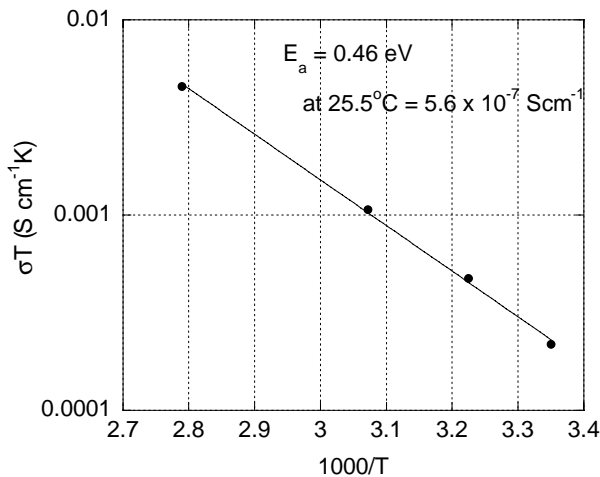


Fig. 3. Arrhenius plot of Pt|LiPON|Pt test cell on Si_3N_4 -coated Si substrate. The activation energy and room temperature conductivity were 0.46 eV and $5.6 \times 10^{-7} \text{ S cm}^{-1}$, respectively.

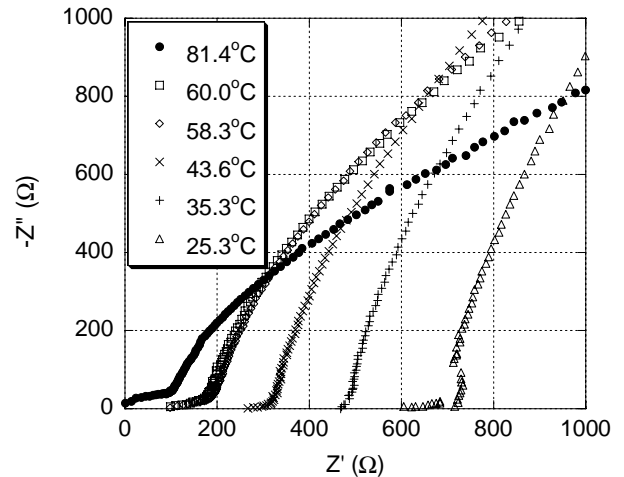


Fig. 4. Complex plane plots of Pt|LiPON-plate-LiPON|Pt test cells at various temperatures.

The LiPON-coated solid electrolyte plate displayed a wide electrochemical stability window, shown by the CV data in Fig. 6. For a test structure of the arrangement of Cu|LiPON-plate-LiPON|Li, the CV plot from -0.2 to 5 V, the test cell can be biased as much as 5 V without the onset of any appreciable oxidative current. A small anodic peak is observed at ca. 3.5 V and its conjugate cathodic peak appears at ca. 2.7 V. This pair of CV peaks does not likely originate from the LiPON film, shown in the featureless CV scan inset in Fig. 6 for a Pt|LiPON|Pt test structure. More significantly, though, is the performance of the LiPON-coated electrolyte plate at potentials near 0 V versus Li/Li^+ . The CV plots in Figs. 6 and 7 demonstrate plating and stripping of Li onto the Cu blocking electrode, facilitated by the LiPON passivating film on the electrolyte plate. In particular, the onset of Li plating at the Cu electrode is

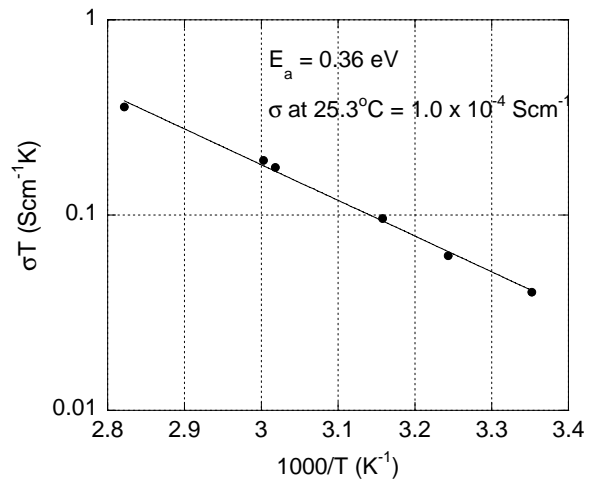


Fig. 5. Arrhenius plot of Pt|LiPON-plate-LiPON|Pt test cells. The composite activation energy and room temperature conductivity were 0.36 eV and $1.0 \times 10^{-4} \text{ S cm}^{-1}$, respectively.

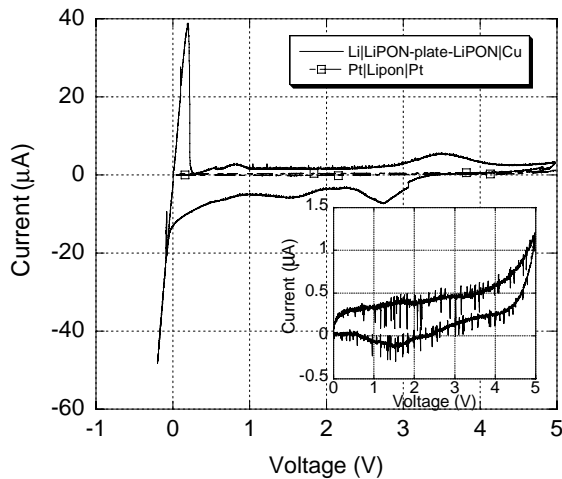


Fig. 6. Cyclic voltammetry scan of a Cu|LiPON-plate-LiPON|Li cell at 1 mVs^{-1} from -0.2 to 5 V . Inset shows the cyclic voltammetry scan of a Pt|LiPON|Pt cell at 1 mVs^{-1} , demonstrating the wide electrochemical potential window afforded by the LiPON electrolyte.

evidenced by the sharp increase in current at 0 V on the cathodic leg of the CV scan in Fig. 7.

The change in the EIS characteristics of the Cu|LiPON-plate-LiPON|Li test structures at different potentials further demonstrates the ability of the LiPON to successfully passivate the solid electrolyte plate for reversible Li deposition. At potentials greater than ca. 0.5 V , the test structure consists of an asymmetric electrode arrangement, with a single blocking Cu electrode and a non-blocking Li electrode. When the potential difference is lowered to 0 V or lower, Li metal is reduced on the Cu electrode, and the impedance spectrum changes from a blocking/non-blocking electrode response to a non-blocking/non-blocking electrode response. The latter spectrum is characterized by much lower impedance at the low frequency range (Fig. 8).

To model the EIS data for the various test structures, we start with the simple Pt|LiPON|Pt equivalent circuit model

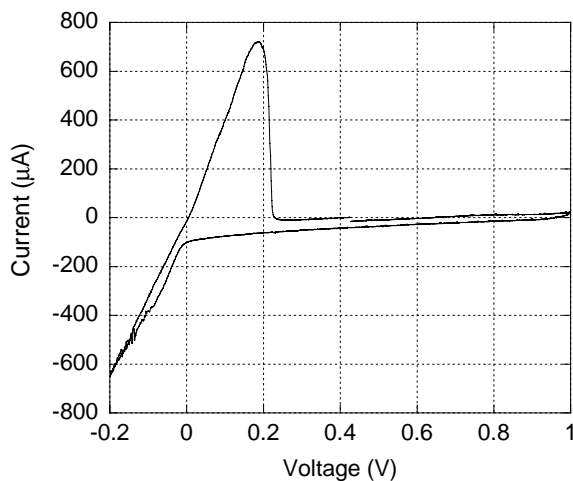


Fig. 7. Cyclic voltammetry scan of a Cu|LiPON-plate-LiPON|Li cell at 1 mVs^{-1} showing plating and stripping of Li between -0.2 and 1.0 V .

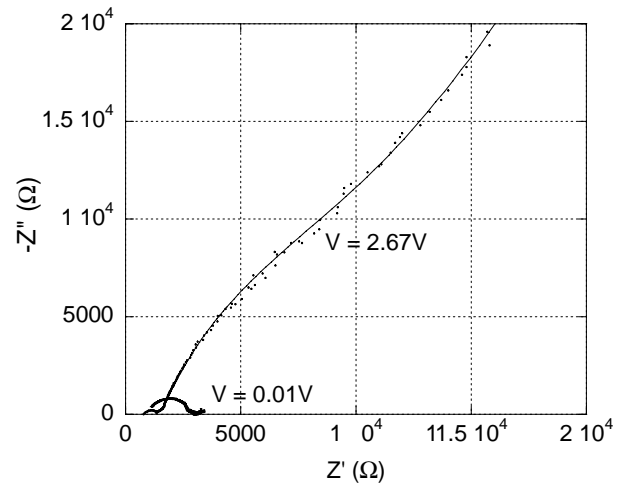


Fig. 8. EIS scans and data fits (solid lines) of a Cu|LiPON-plate-LiPON|Li cell at 2.67 and 0.01 V . At 2.67 V , the cell is modeled as a blocking/non-blocking electrode cell, while at 0.01 V the cell is modeled as a symmetric non-blocking electrode cell.

that has been discussed in detail elsewhere [8,9]. An inductive element has been added to the Pt|LiPON|Pt model to account for stray inductances arising from cabling and leads in the test circuit, shown in Fig. 9A. The LiPON electrolyte may be represented by a constant phase element $\text{CPE}_{(\text{el})}$ in parallel to an electrolyte resistance $R_{(\text{el})}$, where the impedance $Z_{(\text{CPE})}$ is given by

$$Z_{(\text{CPE})} = A(j\omega)^{-\alpha} \quad (1)$$

The fitting parameters were A and α , $j = (-1)^{1/2}$, and $\omega = 2\pi f$. A reaction layer at the Pt-LiPON interface is represented by a parallel $\text{CPE}_{(\text{rxn})}-R_{(\text{rxn})}$ pair, in series to the electrolyte terms. A small geometric capacitance $C_{(\text{g})}$ is placed in parallel to both the reaction layer and electrolyte terms. The interfacial $\text{CPE}_{(\text{int})}$ element accounts for the blocking response of the double Pt electrodes.

The equivalent circuit model describing a test structure consisting of a Pt|LiPON-plate-LiPON|Pt cell is very similar to the model above. The electrolyte plate simply adds another $\text{CPE}_{(\text{el})}-R_{(\text{el})}$ pair as a second electrolyte to the previous model. Although this test structure includes a second LiPON film, the model does not require a third electrolyte term since it will have the same relaxation time constant as the first LiPON film and will be indistinguishable in the EIS profile. Since the asymmetric blocking/non-blocking electrode arrangement will have very similar AC response as a double blocking electrode arrangement, the Cu|LiPON-plate-LiPON|Li may be modeled as shown in Fig. 9B. The increase in the thickness of the electrolyte from ca. $1 \mu\text{m}$ by the addition of the plate to ca. 0.5 mm decreases the geometric capacitance term by a factor of 500 and thus is neglected in the equivalent circuit modeling for 9B.

At a voltage of 2.67 V , the Cu|LiPON-plate-LiPON|Li test cell was fitted to the equivalent circuit model 9A using fitting parameters shown in Table 1. The cell was then

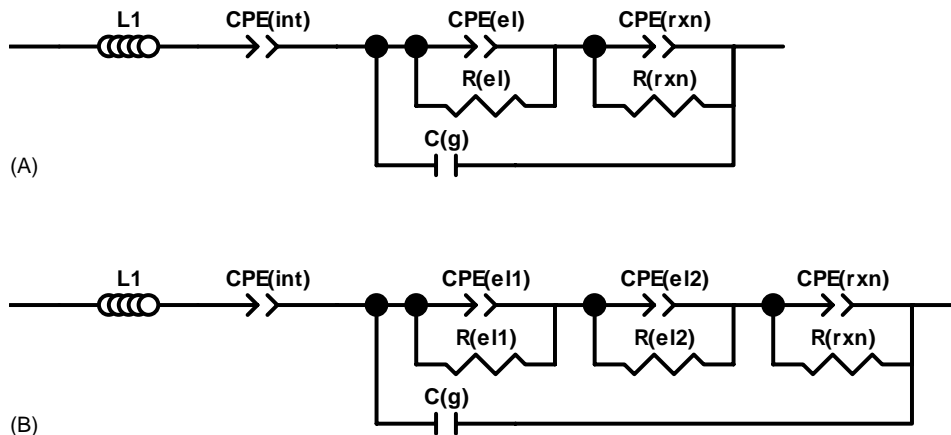


Fig. 9. Equivalent circuit model used to fit EIS data for the (A) Pt|LiPON|Pt and (B) Cu|LiPON-plate-LiPON|Li cells.

Table 1
Fitting parameters for the electrochemical impedance spectroscopy data

| Circuit element | $V = 2.67$ V | $V = 0.01$ V |
|----------------------|----------------------|----------------------|
| $CPE_{(int)}-A$ | 2.7×10^{-5} | – |
| $CPE_{(int)}-\alpha$ | 0.70 | – |
| $CPE_{(el1)}-A$ | 4.8×10^{-6} | 3.0×10^{-6} |
| $CPE_{(el1)}-\alpha$ | 0.95 | 0.95 |
| $R_{(el1)}$ | 89 | 120 |
| $CPE_{(el2)}-A$ | 6.2×10^{-9} | 4.0×10^{-9} |
| $CPE_{(el2)}-\alpha$ | 0.92 | 0.96 |
| $R_{(el2)}$ | 1400 | 1940 |
| $CPE_{(rxn)}-A$ | 2.3×10^{-5} | 1.1×10^{-4} |
| $CPE_{(rxn)}-\alpha$ | 0.92 | 0.15 |
| $R_{(rxn)}$ | 5718 | 1324 |
| L | 2.2×10^{-3} | 1.1×10^{-3} |

held at -0.2 V for several minutes to allow Li metal to deposit at the Cu electrode to yield symmetric Li electrodes at both sides of the composite electrolyte. The cathodic voltage was released and the cell voltage was allowed to stabilize slightly above 0 V, and the EIS scan was repeated. The EIS data for the cell held at 0.01 V was fitted by removing the capacitive element $CPE_{(int)}$ associated with blocking electrodes, and allowing the blocking electrode/electrolyte reaction layer terms $CPE_{(rxn)}$ and $R_{(rxn)}$ to vary. It is noted that other fitting parameters that ostensibly should be the same for both cases did vary somewhat between the two fits; we attribute the minor differences to the limitations of the model sensitivity for multiple overlapping relaxations.

4. Conclusions

Sputter deposition of LiPON films directly onto the high Li^+ conductivity Ohara solid electrolyte plates successfully passivated the plates to limit the reactivity to Li metal, in contrast to unpassivated plates that reacted immediately in con-

tact with Li metal. The conductivity of the composite passivated solid electrolyte plates was 1.0×10^{-4} S cm^{-1} , with Arrhenius activation energy of 0.36 eV and an electrochemical stability window of at least 0–5.0 V versus Li/Li⁺. The plates were capable of supporting electrochemical plating and stripping of Li metal, as demonstrated by EIS and CV measurements. These high chemical stability, high Li^+ conductivity solid electrolyte plates will be useful for solid-state batteries employing Li anodes, with full cell studies currently underway.

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