

The Gel Route to Transition Metal Oxides

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The so-called "sol-gel" process offers new approaches to the synthesis of transition metal oxides. Based on inorganic polymerization from molecular precursors, it leads to highly condensed species or colloids. These colloids are actually two-phase systems in which small oxide particles are dispersed in a liquid medium. A very large interface separates both phases and interfacial phenomena, at the oxide-water interface, lead to new features in the physics and chemistry of transition metal oxides. Ordered aggregation of oxide particles may occur, giving rise to colloidal crystals or anisotropic tactoids in which the mean distance between particles can be of about 0, 1 μm . This distance can be decreased leading to ordered solid aggregates. Transition metal oxide gels exhibit the physical properties of both phases, i.e., electronic properties arising from electron hopping through the mixed valence oxide network and ionic properties arising from proton diffusion through the liquid phase. Electronic and ionic properties appear to be strongly related through the very large interface. Large coatings can be easily deposited from colloidal solutions and transition metal oxide gels should be very useful for making microionic devices. © 1986 Academic Press, Inc.

I. Introduction

The so-called "sol-gel" processes have gained scientific and technological importance during the last few years (1). These processes offer new approaches to the preparation of glasses and ceramics. Starting from molecular precursors, they lead to the formation of a solid network. Most of the reactions occur in the liquid phase around room temperature, via hydrolysis and polycondensation (2). Therefore, the sol-gel process opens up a possibility of making homogeneous glasses and ceramics at low temperature. The special viscosity of the gel state is also particularly suitable for coating deposition (3) or fiber drawing (4).

Up to now, most publications dealing

with sol-gels involve oxides such as SiO_2 or Al_2O_3 . In this paper, we would like to show that the gel route to transition metal oxides could also open new possibilities in the field of materials science. Transition metal oxides are usually mixed valence compounds. Metal ions may exhibit several valence states so that electron hopping from low to high valence state can take place (5). This leads to specific electrical and optical properties; semiconducting coatings (6), switching behavior (7), or electrochromic devices (8).

Transition metal oxide gels can also be considered as particle hydrates. They can exhibit high proton conductivities (9) and some of them behave as inorganic ion exchangers (10).

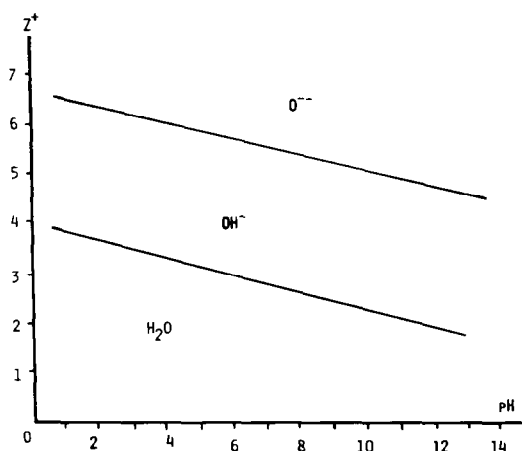
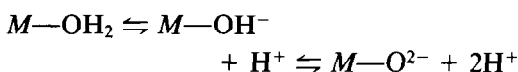


FIG. 1. pH intervals in which H_2O , OH^- , and O^{2-} are common ligands to a central cation of average size and of oxidation state z , according to (13).

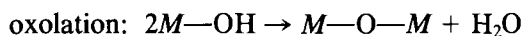
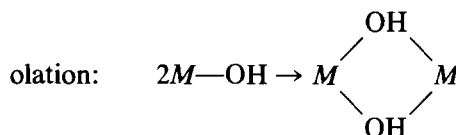
II. Inorganic Polymerization

Inorganic precursors. One of the simplest ways for making gels would be from aqueous solutions of inorganic salts. In such solutions, the M^{z+} cation is solvated by the dipolar water molecules. A $M\text{—OH}_2$ bond is formed in which an electron transfer occurs from the highest occupied σ bonding orbital of the water molecule toward the lowest unoccupied d orbital of the cation. This transfer weakens the O—H bonds leading to the following species:

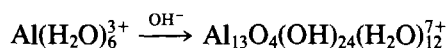


These equilibria mainly depend on the charge, z^+ , of the cation and the pH of the solution as shown in Fig. 1. For a given cation, we then have pH intervals in which water, hydroxide, or oxide are common ligands to the central ion (11). Usually $M\text{—OH}_2$ bonds are observed for low-valent cations in acidic medium, $\text{Fe}(\text{H}_2\text{O})_6^{2+}$, while $M\text{—O}$ bonds occur for high-valent cations in basic medium, WO_4^{2-} . In an intermediate pH, or oxidation state, range, $M\text{—OH}$ bonds are formed. One of the main proper-

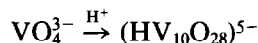
ties of these hydroxo ligands would be to lead to condensation reactions such as



Polycations can be obtained by increasing the pH of an aqueous solution of a low-valent ion such as Al^{3+} (12):



Polyanions can be obtained by decreasing the pH of an aqueous solution of a high-valent ion such as V^{5+} (13):

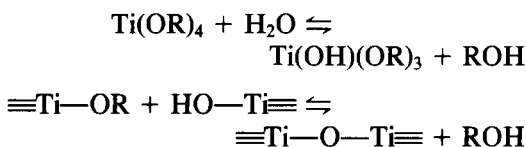


During these polycondensation processes, the total charge of the polyion, per metallic atom, progressively decreases and goes through a point of zero charge corresponding to the pH at which the precipitation of the oxide occurs (11). Al_2O_3 and V_2O_5 could then be considered as infinite polymers in which the total charge is zero. Stable colloidal solutions or gels can be obtained if the pH is kept near the point of zero charge. The condensed species then remain slightly charged and electrostatic repulsions prevent further collisions and flocculation (14).

Transition metal oxide gels can also be obtained through redox reactions. Colloidal MnO_2 , for instance, is formed when an aqueous solution of KMnO_4 is reduced by an inorganic or organic reagent (15).

Metal-organic precursors. The most versatile way for making oxide gels is undoubtedly the hydrolysis and condensation of metal alkoxides (16). One of the main advantages of this process is to allow an intimate mixing of the different precursors at a molecular level giving homogeneous multi-component glasses or ceramics (17). The chemical reaction involves two steps; a par-

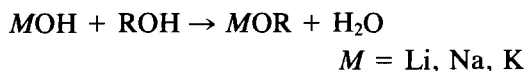
tial hydrolysis of the alkoxide introduces the active functional OH group which then reacts with other reactants to form a polymeric solution which further polymerizes to form a gel:



Hydrolysis is usually performed by slowly adding a water-alcohol mixture to an alcoholic solution of the alkoxide. Depending on the synthesis method, and especially on the kind of catalysis (acid or basic) the gelation process may change significantly (18). One can imagine processes all the way from condensation of colloidal particles to cluster growth and crosslinking of polymeric molecules (19).

It is however not always necessary to add water directly to the alkoxide solution. Water can be produced *in situ* through some chemical reaction. An organic acid R—COOH for instance can be added to an alcoholic solution of the alkoxide. The water produced by the esterification reaction gives rise to the hydrolysis of the alkoxide and leads to a transparent monolithic gel.

Water can also be produced by dissolving an alkaline base into an alcohol:



An alkoxide such as Ti(OR)_4 can then be added to the solution and a mixed hydrolysis of both metal-organic compounds occurs giving rise to titanates. The shape and the size of the particles strongly depend on the experimental procedure. It can vary from small spheres to long fibers.

Hydrolysis can also be performed by dissolving an hydrated salt into the alcoholic solution of an alkoxide. Monodispersed powders, particularly suited for sintering,

can be obtained for many different compounds such as BaTiO_3 or LiNbO_3 .

Mixed organic-inorganic polymers have recently been made. Methods of synthesizing materials for hard contact lenses were developed by hydrolysis and condensation of an epoxide substituted alkoxy silane and Ti-alkoxides. Polymethacrylates were incorporated as linear crosslinking elements using a methacryloxy substituted alkoxy silane as a hook between the siliceous network and the polymer chain (20).

These few examples show that the gel route from metal-organic precursors open a wide range of new possibilities.

III. Ordered Aggregation of Colloidal Particles

Colloids may be defined as two-phase systems in which solid particles are dispersed in a liquid medium. Because of the small size of the colloidal particles, a very large interface separates the two phases and, on surface energy considerations alone, the colloidal state should be thermodynamically unstable. The presence of electric charges at the interface and some form of structural interaction between the dispersion medium and the dispersed phase prevent flocculation and explain the stability of colloidal systems.

In the case of monodispersed spherical particles, these interactions can lead to a long-range ordering in which the charged colloidal particles are disposed along a periodic array as in a crystalline metal. Such systems are known as "colloidal crystals" (21). They are usually observed in organic or biological systems but they can be produced also with inorganic colloids such as suspensions of SiO_2 spherical particles (22). The natural "opals" are a well-known example of such a long-range ordering. They are made of tiny spherical silica particles cemented together into a regular packing. The voids between these spheres are

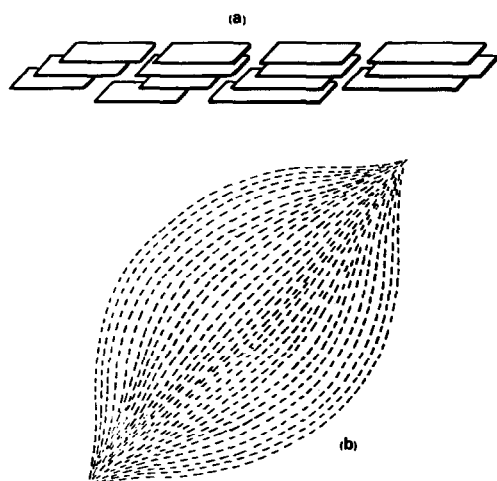


FIG. 2. Schematic illustration of colloidal particle ordering in (a) a smectic tactoid with platelet-like particles (WO_3) (24), and (b) a nematic tactoid with rod-like particles (V_2O_5) (26).

filled with a strongly hydrated form of amorphous silica and disposed in a long-range ordered lattice capable of providing specular light reflections. Because of the difference in refractive index between the spheres and the voids, the Bragg reflections of light make opals to "sparkle with flecks of pure spectral color" (23).

Ordered colloidal systems have already been observed a long time ago in transition metal oxide colloids. They are responsible for the iridescent aspect of tungstic acid and β - FeOOH sols. The smectic arrangement of monodispersed plate-like particles gives rise to the so-called "schiller layers" (24), Fig. 2a. The equilibrium distances between the associated particles can be as large as a few thousand Ångströms. Anisotropic ordered colloidal phases have also been observed with V_2O_5 gels. These gels are made of fiber-like particles that look like flat ribbons (25). Concentrated colloidal solutions separate, under suitable conditions, into a concentrated and a dilute phase. In the concentrated phase, the colloidal particles are arranged with their ma-

ior axis parallel to each other, giving rise to a nematic anisotropic structure called "tactoid" (26). These tactoids are dispersed in an optically isotropic dilute sol phase called "atactosol." The "football"-like shape of a tactoid arises from interfacial tensions between the concentrated tactoid and the surrounding dilute colloidal solution (Fig. 2b).

Ordered reversible aggregates change to ordered irreversible aggregates if the distances between the individual particles are carefully reduced. This can be done by suitable changes in or of the dispersion medium, or by its gradual removal. This leads to ordered solid aggregates called "crystalloids" in which all particles are mutually oriented (26). These crystallike bodies share with classical crystals the ability to "dissolve" on addition of a proper swelling agent, the product of dissolution being in this case colloidal particles instead of ions.

In the concentrated ordered tactoid phase, V_2O_5 ribbons are separated by water layers. On careful addition of coagulating electrolyte, V_2O_5 tactoids gradually shrink to a fraction of their original size maintaining and even enhancing their internal anisotropy (26). Such a shrinkage can also be observed when a V_2O_5 gel is deposited onto a glass substrate. After drying, a strongly anisotropic coating is obtained. X-Ray diffraction diagrams of these $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ xerogels exhibit a series of $00l$ peaks corresponding to a one-dimensional interlayer spacing arising from the stacking of the V_2O_5 ribbons along a direction perpendicular to the substrate (27). The hydration-dehydration process remains reversible as long as the amount of water does not go below $0.5 \text{ H}_2\text{O}$ per V_2O_5 . The basal spacing then depends on the water content and therefore on the partial water pressure above the sample. The basal spacing variation as a function of n was followed by X-ray diffraction and wide angle neutron scattering. The results are reported in Fig. 3. They show that, at low water content ($n <$

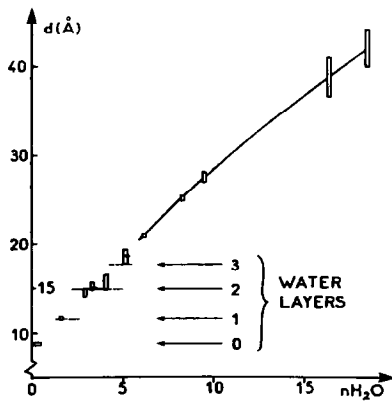


Fig. 3. Basal d spacing for $V_2O_5 \cdot nH_2O$ layers deposited from gels, as a function of the amount of water n .

5), the basal spacing d varies by steps of about 2.8 \AA each, corresponding to the intercalation of one water layer. This stepwise process is observed up to three water layers, beyond this value (for $n > 5$) a continuous swelling occurs leading to a more or less viscous gel. These observations are in agreement with the very simple model of 1D swelling of monodispersed plate-like particles. The d spacing is then inversely proportional to the solid volume fraction (28).

The formation of ordered aggregates in transition metal oxide gels opens new possibilities for making ceramics. A careful shrinkage of such aggregates, before sintering, would lead to a material in which all individual particles are mutually oriented. This could be very interesting for magnetic ceramics or anisotropic semiconducting coatings.

IV. Physical Properties of Transition Metal Oxide Gels

Gels are diphasic systems in which a liquid phase (water) is trapped in a solid network (transition metal oxide). Their physical properties therefore arise from both

phases, i.e., electronic properties of the transition metal oxide and ionic properties of the ionized water molecules. But, due to the very large interface between both phases, electronic and ionic properties are strongly related. Interfacial phenomena at the water-oxide interface must be taken into account in order to describe the physical properties of the gels.

Mixed conduction in V_2O_5 gels. The ac conductivity of a vanadium pentoxide gel, $V_2O_5 \cdot nH_2O$, deposited as a layer onto a glass substrate, strongly depends on the amount of water contained in the gel, and therefore on the partial water pressure above the sample, as shown in Fig. 4. The room temperature conductivity decreases from $1.5 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$ for a $V_2O_5 \cdot 1.8H_2O$ xerogel (basal spacing $d = 11.5 \text{ \AA}$) down to $4 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$ for a $V_2O_5 \cdot 0.5H_2O$ xerogel (basal spacing $d = 8.7 \text{ \AA}$). The $\Delta d = 2.8 \text{ \AA}$ variation of the basal spacing corresponds to the intercalation of one water layer between the V_2O_5 ribbons (28).

The dc conductivity of $V_2O_5 \cdot 0.5H_2O$ layers shows an ohmic behavior. A plot of $\log(\sigma T)$ versus T^{-1} gives an Arrhenius law around room temperature with an activation energy $E_a = 0.32 \text{ eV}$. Below 220 K

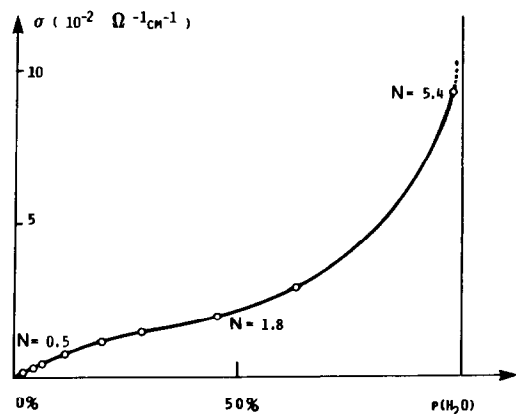


Fig. 4. Alternating current conductivity of $V_2O_5 \cdot nH_2O$ layers deposited from gels as a function of the partial water pressure above the sample.

however, a continuous decrease of the activation energy is observed which is typical of small polaron hopping in transition metal oxides (5). The dc conductivity depends on the amount of V(IV) ions in the gel. It increases up to $2 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ at room temperature for a reduced xerogel containing a V(IV)/V(V) ratio of 10%. More hydrated $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gels ($n > 0.5$) do not exhibit an ohmic behavior anymore. The dc conductivity does not vary with the V(IV) content. It remains quite high and a plot of $\log(\sigma T)$ versus T^{-1} shows two linear parts with a kink around -10°C . The activation energy is somewhat higher below this temperature ($E_a = 0.44 \text{ eV}$) than above it ($E_a = 0.35 \text{ eV}$). Such a behavior is typical of proton diffusion in hydrous oxides. The kink corresponds to the freezing point of the interstitial water (29).

These experiments show that $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gels behave as mixed conductors.

- Electronic conductivity arises from a small polaron hopping process along the vanadium ions in the oxide network. It can be observed when there is no water intercalated between the ribbons ($n < 0.5$) so that electrons could find a percolation pathway through the layer.
- Ionic conductivity becomes predominant when there is enough water intercalated between the V_2O_5 ribbons in order to provide a continuous pathway for proton diffusion ($n > 0.5$) through the liquid medium or along the water-oxide interface.
- Electrical properties of $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gels are strongly dependent on the interfacial phenomena. Their electrical conductivity appears to be higher than either the electronic conductivity of amorphous V_2O_5 or the ionic conductivity of pure water. A strong coupling between the electronic and ionic charge carriers has been observed by ESR and ENDOR spectroscopy (30). It has also been shown that the amount of water in equilibrium at a given water pressure increases upon re-

duction of the gel. It may then be suggested that the small polaron trapping energy is modified by the presence of water molecules at the interface, increasing, for instance, the dielectric constant of the material. Moreover, because V_2O_5 is an acidic oxide, water molecules are dissociated at the interface, increasing the number of free protons in the liquid phase. The pH of a colloidal solution can be as low as 2 (31).

Electrochromism of WO_3 gels. Electrochromic display devices based on amorphous WO_3 thin films have been extensively studied (32). About 10 years ago, Deb showed that such films could exhibit two stable states. One is transparent and highly resistive while the second one is blue and much less resistive. Fast reversible coloration can be obtained when the amorphous oxide is deposited onto a conductive electrode and placed in an electrochemical cell.

Amorphous WO_3 thin films are usually obtained by vacuum evaporation or sputtering. They could also be made by the sol-gel process (8). Colloidal tungsten oxide can be obtained upon polymerization of tungstic acids arising from the acidification of a tungstate aqueous solution (13). Acidification can be very easily performed with a proton exchange resin (8). The colloidal solution is then deposited by spin-coating or spraying onto a conductive transparent electrode (ITO, indium tin oxide-coated glass). The solvent readily evaporates within a few minutes and the coating is ready for use without any further treatment.

Electrochromic properties of colloidal tungsten oxide layers were studied in a ITO/ $\text{LiClO}_4(\text{M})$ -PC/Pt cell. With such a device, a deep blue coloration is obtained within 0.3 sec by applying a negative voltage of -4 V . The blue coloration remains for days after the voltage has been removed. The initial transparent state can be

restored within 0.4 sec upon application of a reverse positive voltage of +4 V. Under these conditions, the energy consumption for coloration and bleaching corresponds to about 8 mC/cm² for an optical density of 0.3. The process appears to be very reversible, coloring and bleaching cycles have been repeated over 10⁶ times without failure. Again, as for V₂O₅, the physical properties of WO₃ gels involve both electron diffusion through the oxide network and ion diffusion through the liquid phase.

Compared with usual amorphous WO₃ thin films, colloidal tungsten oxide exhibits several advantages:

The first one is due to the special viscosity of gels. Layers can be very easily deposited at room temperature on any kind of substrate. The sol-gel process should then be much cheaper than vapor deposition or sputtering.

The second one is due to the chemical composition of the gel itself that, even after drying, still contains some water molecules trapped in the solid network. According to the literature, the electrochromic properties of amorphous WO₃ strongly depend on the method of preparation. It has been shown, for instance, that some water has to be incorporated into the WO₃ film in order to obtain a deep coloration. The presence of water greatly improves the characteristics of the electrochromic display device.

Ion exchange properties of transition metal oxide gels. Hydrous oxides belong to the so-called particle hydrate group (29). They are made of charged particles held together by water molecules and either H₃O⁺ or OH⁻ ions. They thus exhibit the typical properties of such compounds, i.e., fast proton conduction, easy densification by cold pressing and ion exchange behavior. In the case of V₂O₅, the lamellar structure of the gels gives rise to specific ion exchange properties that can be described as intercalation into a 2D lattice (10).

Ion exchange, with metallic cations, can

be readily observed at room temperature by dipping a layer of a V₂O₅ gel into an aqueous solution of an inorganic salt such as NaCl, for instance. We then observe that, while an infinite swelling occurs in pure water, leading to a colloidal solution, an equilibrium is rapidly reached when the solution contains some coagulating electrolytes. The pH of the solution decreases and about 0.3 M⁺ or 0.15 M²⁺ cations per V₂O₅ are intercalated into the gel. The basal spacing between the V₂O₅ ribbons depends on the nature of the metal cation, mainly its charge and ionic radius. Large monovalent cations (Na⁺, K⁺, Rb⁺, Cs⁺, NH₄⁺ . . .) lead to a *d* spacing of about 11 Å, while divalent cations (Ca²⁺, Mg²⁺, Mn²⁺, Fe²⁺, Co²⁺, . . .) or Li⁺ lead to a *d* spacing around 13.7 Å. The $\Delta d = 2.7$ Å between these two basal spacings corresponds to the thickness of one water layer. This suggests that, because of the competition between the hydration energy of the cation and the energy required for lattice expansion, weakly polarizing cations intercalate with one water layer only while more polarizing cations can intercalate with two water layers.

Larger ions, such as alkylammonium cations C_{*n*}H_{2*n*+1}N⁺(CH₃)₃ can also be intercalated into the layered structure of V₂O₅ gels (33). The competition then occurs between the electrostatic interactions of the oxide layers and the van der Waals attractions of the alkyl chains. This last one depends on the number of carbon atoms, therefore, depending on the value of "*n*," one or the other interaction prevails. Alkyl chain orientation in the interfoliar space can be deduced from the basal spacing variation with the chain length. It can be shown that the chains remain parallel to the layers up to C₇, minimizing the lattice expansion. They lie perpendicular to the layers, and therefore parallel to each other, beyond C₁₁. In between, a transition state is observed where the chains make an angle ranging from 42° to 53° with the layers (33).

Intercalation of guest species into the lamellar structure of V_2O_5 gels does not involve ion exchange reactions only. Some reduction of the oxide usually occurs during the process. Intercalation of cobaltocene molecules $CoCp_2$ for instance give the same basal spacing as the cobalticinium ion $CoCp_2^+$. The reaction is only much slower. This suggests some electron exchange between the neutral molecule and the V_2O_5 lattice prior to intercalation, leading to a reduction of the oxide and the formation of cobalticinium ions (34). The intercalation of ferrocene appears to be impossible, while the ferricinium ion readily intercalates. This is probably due to the higher ionization potential of ferrocene (6.9 eV) compared to cobaltocene (5.6 eV) preventing the V_2O_5 reduction.

V. Conclusion

The sol-gel process offers a new approach for the synthesis of transition metal oxides. The numerous chemical possibilities given by the inorganic polymerization reactions should lead to a better control of the ultrastructure processing of ceramics, glasses, and composites together with the synthesis of new compounds in which organic and inorganic components are mixed.

The sol-gel process leads to a new form of matter, intermediate between a solid and a liquid that exhibits specific features. Ordered aggregates, for instance, could open new possibilities for processing ceramics or coatings in which all elementary particles are mutually oriented giving rise to an anisotropic material.

The special viscosity of gels, that look like paints, make them particularly adapted for depositing large coatings onto solid substrates by spraying, dip-coating, or even screen printing. The unusual ionic and electronic properties of these materials suggest that they could be very useful in the field of microionic devices. Several patents have

already been taken and we could imagine "all-gel" devices made by successive deposition of different layers, each of them having a specific property.

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