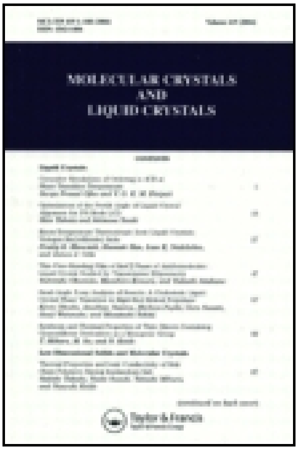

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Solid Redox Polymerization Electrodes and Their Use in All-Solid-State Batteries

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1 INTRODUCTION

The dramatic proliferation of products based on semiconductor technology is a strong testament to the predictability and reliability of solid-state technology. In a similar vein, advances in materials exhibiting high levels of ionic conduction in the solid state has led to worldwide efforts in the development of all-solid-state rechargeable batteries. Although higher current densities are achievable with liquid electrolytes, all-solid-state cells offer inherent advantages of negligible self-discharge, long cycle life, high reliability, and virtual absence of container corrosion. Elegant work on polycrystalline and vitreous electrolytes has led to solid electrolytes with suitable ionic conductivities for battery development,[1,2,3] however, the superior mechanical properties of elastomeric electrolytes combined with the simplicity of fabrication of thin separator films from these materials, has led to very active pursuit of solid-state cells based on solid polymeric electrolytes (SPE's). Although solid polymer electrolytes generally have lower ionic conductivities than their polycrystalline and vitreous counterparts,[4] the ability to cast thin films (10 to 100 μm) from dilute solutions, compensates somewhat for this limitation. While many polymeric electrolytes have been described in the literature, the best known SPE is undoubtedly polyethylene oxide (PEO) complexed with an appropriate electrolyte salt.[5] The operating temperature of SPE cells generally falls in the range of ambient to 100°C, with the highest levels of performance occurring in the elevated temperature regime, with claims of performance that meet the demands of electric vehicle application. Initial efforts towards ambient temperature operation of such cells were not promising due to the rapid decrease in ionic conductivity below about 60°C. However, further investigation into the nature of ionic conductivity in poly-

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meric electrolytes has led to the conclusion that ion transport is strictly through the amorphous regions of these polymers which tend to crystallize with decreasing temperature. It has been found that by lowering the glass transition temperature of the polymer electrolyte, either by structural modification or addition of plasticizing electrolyte salts, sufficiently high conductivities for ambient temperature operation can be achieved. Reported results for a number of such cells have indicated that high performance solid-state batteries are nearing commercialization. To date, the majority of these advanced lithium SPE batteries have utilized positive electrodes based on intercalation chemistry. However, work in our laboratory has led to the development of a novel class of solid-state, organic positive electrodes which not only operate on an entirely new principle for energy storage, but which have demonstrated performances exceeding those for intercalation electrodes in solid-state lithium and sodium batteries. These new electrodes have been termed **solid redox polymerization electrodes**, SRPE's, for reasons that will explained below.

1.1 Electrodimerization/scission

The introduction of redox polymerization electrodes was an extension of earlier work in this laboratory on advanced sodium/β″-alumina/organosulfur batteries[6,7,8] in which the cell reaction can be described as,

$$2Na + RSSR = 2NaSR,$$

where R is an organic moiety such as CH_3, C_6H_5, CF_3, etc. The redox mechanism for the positive electrode is in essence a redox dimerization/scission reaction which occurs in two steps as described below,[9]

$$2[RS^- - e^- = RS\cdot]$$

$$RS\cdot + RS\cdot = RSSR,$$

where the rate-limiting step is electron transfer, and the standard rate constant is a strong function of R with higher rates of electron transfer being observed with increasing electron-withdrawing nature of the organic moiety[10]; diffusion constants for the organosulfur species also follow the same general trend. Of course, the ability of the thio group to undergo reversible dimerization/scission can be extended to polymers where oxidation of the thio anion leads either to reversible inter/intramolecular crosslinking as in the case of protein folding, or to reversible electropolymerization.

1.2 Protein folding, redox resins, and solid redox polymerization electrodes (SRPE's)

One of the important mechanisms controlling the folding of proteins into their native conformation is the oxidation of pendant cysteine residues situated at various locations on the polypeptide chain (Figure 1). Although this mechanism occurs in

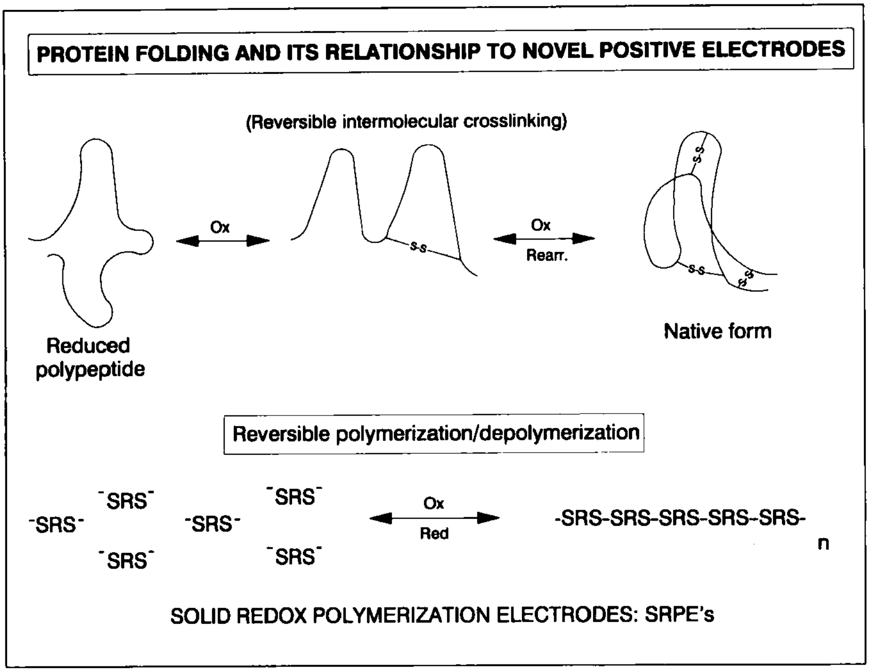
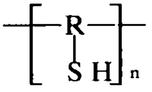


FIGURE 1 Formation of intermolecular S-S bridges during protein folding, and the related process of electropolymerization/depolymerization.

nature for configurational purposes, the same principle can be used for the storage of energy. In order to use this redox mechanism for battery applications however, a much larger proportion of $-SH$ groups must be present per monomer unit, otherwise the equivalent weight of the material and the rate of oxidation/reduction of the polymer would be uninteresting for real devices. In fact a number of synthetic polymeric thiols,



$$\left[\underset{\displaystyle \text{SH}}{\overset{}{\text{R}}} \right]_n$$

have been made and used as redox resins or electron exchangers[11,12]; they have also been used in the study of protein folding mechanisms,[13] and have been used as specific ion exchangers. The polythiols constitute an interesting class of redox materials. They are single-ion conductors in that the anions are locked in the molecular backbone. The equivalent weights of the materials can be quite low, depending of course on the R group in the polymer chain, leading to lithium cells with high theoretical energy densities. Furthermore, the electrode kinetics for these materials should depend on both electronic and steric factors; earlier work in this laboratory on the electrode kinetics for electrodimerization/scission has clearly shown a relationship between the nature of R and the standard electrochemical rate constant, and other studies have established a relationship between distance between adjacent thiol groups on the polymer chain and relative rates of oxidation/reduction.[14] It has also been established for the polythiols, that polymers with flexible chains are more readily oxidized,[15] similar to the trend for ionic conductivity in polymer electrolytes. A number of these polymers have been cycled chemically through oxidation and reduction with greater than 97% of the thio groups showing electroactivity.[16] The majority of the redox processes for these materials are clearly intermolecular, there is also evidence of intramolecular crosslinking on oxidation.[17] Although there is work currently underway in our laboratory on these interesting materials, the majority of data has been collected on a related class of organopolysulfides which undergo electropolymerization/depolymerization reactions.

Polydisulfide polymers, $-(SRS)-_n$, are a subset of the industrially important polysulfide polymers, $-(RS_x)-_n$, known for their excellent resistance to swelling by hydrocarbon fuels and impressive aging and weatherability properties. The industrial process for the production of polysulfide polymers involves the reaction between the appropriate dihalide and sodium polysulfide,

$$n\ Cl\text{-}R\text{-}Cl + n\ Na_2S_x = -(RS_x)-_n + 2n\ NaCl;$$

these reactions generally give rise to polymers having very high molecular weights, normally greater than 500,000.[18] Although there are a number of approaches one might use to generate polymeric disulfides, the route generally used in this laboratory involves the oxidation of dithio (or multi-thio) acids,

$$HS\text{-}R\text{-}SH + nI_2 = -(SRS)-_n + 2n\ HI.$$

The rate of reaction depends on a number of factors including the nature of the R group, and in some cases, polymerization is complete in a few minutes. However, in contrast to conventional polymers, in this case the polymerization process is completely reversible. It is this characteristic property of the polydisulfide polymers which allows them to be used as positive electrodes for energy storage. Since it is the polymerization/depolymerization process which is used to store energy, and these materials are generally used in (but not limited to) the solid state, they are termed **solid redox polymerization electrodes**.

An additional feature of the disulfide-based polymer electrodes is their inherent reversibility to many metal ions, in stark contrast to most intercalation compounds which demonstrate good reversibility only to lithium. Consequently, in principle a broad spectrum of solid-state batteries having various metal anodes can be constructed if the appropriate solid electrolytes are available. In this laboratory both solid-state lithium and sodium batteries have been successfully cycled using SRPE materials.[19,20]

2 EXPERIMENTAL

A large number of organodisulfide polymers were prepared and characterized; the polymerization of few representative thio acids is described here. Chemical polymerization was accomplished in a one step reaction with the appropriate oxidizing agent. The polymerization can be described as above by the general scheme,

$$n\ HS\text{-}R\text{-}SH + nI_2 = -(SRS)_n- + 2n\ HI.$$

All polymerization reactions were carried out in aqueous solution. Insoluble mercaptans were solubilized by first converting the thio acids to the corresponding akali metal salts. The aqueous monomer solutions were then polymerized by addition of the stoichiometric amount of iodine or other appropriate oxidant. In most cases the reaction proceeded instantaneously with precipitation of the polymeric organodisulfides upon addition of the oxidant.

Polymerization reactions carried out by the above route were accomplished in distilled water at room temperature. The thio acids 2-mercaptoethyl ether, $(HSCH_2CH_2)_2O$, 2,5-dimercapto-1,3,4-thiadiazole, and trithiocyanuric acid, were obtained from Aldrich Chemical Co. and used as received; reagent grade iodine was obtained from J. T. Baker and used as received. After reaction of the aqueous thio salts with the stoichiometric amount of iodine the insoluble polymers were thoroughly rinsed with distilled water and dried under vacuum for several weeks.

The density of the di-lithium salt of the thiadiazole compound and the density of the corresponding polymeric disulfide were measured by volumetric displacement in non-solvents and mass determinations. Thin film electrolytes and composite electrodes were cast from solution as described below. Anhydrous acetonitrile, chloroform, tetrahydrofuran, and crystalline polyethylene oxide (PEO) of various molecular weights ($3 \times 10^5, 9 \times 10^5, 4 \times 10^6, 5 \times 10^6$) were obtained from Aldrich and used as received. Thin films of PEO-based electrolytes (10 to 100 μm) were cast from mixtures of a solution of PEO in acetonitrile (or other suitable solvent) and solutions of appropriate lithium or sodium salts depending on which alkali metal anode was to be used in the battery. Thin films of the organic cathodes (6 to 15 mg/cm^2) with surface capacities of 1 to 6 C/cm^2 were cast from solutions of PEO and redox polymers (with or without electrolyte salts) in an appropriate solvent or mixed solvents with dispersed carbon black. The electrolyte and composite electrode solutions were cast into glass rings placed on polished Teflon plates and the solvents were allowed to evaporate in air. The thin films were then dried under vacuum at 50°C for 2 days and then kept under vacuum for a few weeks prior to testing.

Prior to testing the solid redox polymerization electrodes (SRPE's) in solid-state cells, the cyclability/reversibility of these positive electrodes was tested as described previously[20] in liquid sodium/β''-alumina/SRPE cells in order to eliminate possible complications at the alkali metal/polymeric electrolyte interface, and effectively isolate the performance of the SRPE for subsequent evaluation.

Battery grade lithium foil (thickness = 125 um) was obtained from Lithco Co. and stored in an argon atmosphere dry box. Reagent grade sodium was highly purified by a previously published method[21] prior to use. All-solid-state, thin film, alkali metal/SRPE cells were constructed by sandwiching a polymeric electrolyte between the thin film composite SRPE cathode and a thin foil of alkali metal; the battery being positioned between matching stainless steel plate current collectors.

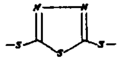
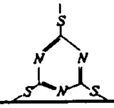
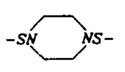
3 RESULTS AND DISCUSSION

The theoretical energy densities for lithium and sodium-based batteries using the solid redox polymerization electrodes are given in Table I. As can be seen from the values given, the equivalent weights of the polydisulfides can be quite low, leading to very high theoretical energy densities. Since the composite cathodes used in solid-state SPE (solid polymeric electrolyte) batteries are not 100% active materials, the low equivalent weights of the $(SRS)_n$ materials are an important factor in the realization of high practical energy densities for real devices.

The densities of one of the polymers and its di-lithium salt were measured by volumetric displacement. The density of the X1 polymer was determined to be 1.8 g/cm^3, and its corresponding salt was found to be 1.6 g/cm^3. Accordingly, the volumetric and gravimetric capacity of composite films based on X1, PEO, and carbon black, were calculated based on physical mixing of each component as a function of weight percent of active material in the composite electrode (the true values may be somewhat higher due to miscibility of X1 in PEO). The same calculations were performed for a representative intercalation electrode, TiS_2, for

TABLE I

Equivalent weights and theoretical energy densities of representative $(SRS)_n$ compounds.

MONOMER	Equivalent Weight	Energy Density (Wh/kg) Li/$(SRS)_n$ (OCV=3.0V)	Energy Density (Wh/kg) Na/$(SRS)_n$ (OCV=2.7V)	POLYMER NOMENCLATURE
$-SCH_2CH_2OCH_2CH_2S-$	76	870 (OCV=2.7 V)	600 (OCV=2.2 V)	X0
	74	990	750	X1
	58	1240	890	X5
	74	990	750	X6
TiS_2	112	560 (OCV=2.5 V)	—	

comparison. The results of these calculations are shown in Table II. The film capacities can then be used to calculate the thickness of the SRPE electrode as a function of surface capacity and loading level as shown in Table III (SRPE electrodes were generally loaded between 30 and 60 wt%). As can be seen from Table III, a composite SRPE electrode loaded with 30 wt% X1 with a surface capacity of 3 C/cm^2 would have a thickness of about 50 μm. If a cell is constructed with the above positive electrode and a 4:1 excess of lithium (16 μm), the total cell thickness including 10 μm for current collectors would be less than 100 μm.

The reversibility of the redox polymers X0 through X5 was tested in Na/β''-alumina cells operating above the melting point of sodium.[20] The sodium cells using SRPE's based on X1 and X5 showed highly reversible cycling and no evidence of thermal degradation over several months, whereas the X0 polymer rapidly polarized on discharge and the X6 polymer deteriorated on cycling (possibly due to the presence of impurities). Accordingly all-solid-state Li/PEO/SRPE and Na/PEO/SRPE cells were constructed and tested. The results of the all-solid-state sodium cells will be described elsewhere.

The X1 and X5 polymers were tested in all-solid-state, thin-film, lithium batteries from about 100°C to ambient.[19] All cells were cathode-limited in capacity as the thickness of the lithium electrode was 125 um (75 C/cm^2), and the surface capacity of the positive electrodes were in the range of 1 to 6 coulombs/cm^2. Shown in Figure 2 are the rate capabilities of the solid-state lithium cell based on the X1 polymer. As can be seen from the data in Figure 2 the Li/PEO/X1 battery is capable

TABLE II

Film capacities for composite positive electrodes having variable load of active material, 7 wt% carbon, and balance PEO.

Active Material	Loading Level Weight Percent	Density g/cm^3	Volumetric Capacity Density Ah/cm^3	Gravimetric Capacity Density Ah/g	Volumetric* Energy Density (vs. Li) Wh/cm^3	Gravimetric* Energy Density (vs. Li) Wh/g
X1	100	1.8	0.67	0.36	2.01	1.08
	50	1.5	0.25	0.168	0.75	0.504
	30	1.4	0.15	0.11	0.45	0.33
TiS_2	100	3.2	0.77	0.22	1.93	0.55
	50	1.77	0.18	0.10	0.46	0.25
	30	1.56	0.10	0.066	0.25	0.165
Lithium	100	0.534	2.0	3.8	—	—

*Volumetric and gravimetric energy densities calculated by multiplying the corresponding capacity densities by the estimated OCV vs. a lithium negative electrode (X1: 3.0 volts, TiS_2: 2.5 volts)

TABLE III

Film thickness and weight as a function of loading.

TABLE 3: FILM THICKNESS AND WEIGHT AS A FUNCTION OF LOADING

Active Material	Loading Level	Surface Capacity: 6 C/cm^2	
		Thickness	Weight
	Weight Percent	µm	**mg/cm^2**
X1	100	25	4.5
	50	67	10
	30	110	15.6
Lithium	100	8	0.45

of much higher current densities and better cathode utilization than is reported for analogous Li/PEO/TiS$_2$ cells. Even at a current density of 10 mA/cm^2 the nominal voltage and positive electrode utilization are higher for the SRPE cell than the intercalation based cell at 1/5th the current density (2 mA/cm^2). The high current densities achievable with the SRPE cells (12 c rate) translate to very high gravimetric and volumetric power densities. In order to achieve a direct comparison between SRPE electrodes and intercalation compound-based electrodes under identical test conditions, two positive electrode films of equivalent capacity and using the same

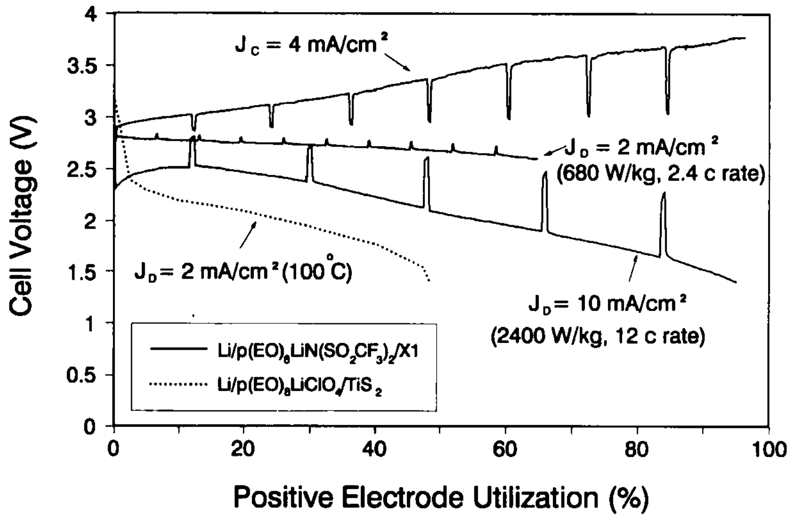


FIGURE 2 High rate discharge/charge curves for a Li/p(EO)$_8$LiN(SO$_2$CF$_3$)$_2$/X1 cell at 100°C (Li/PEO/TiS$_2$ comparison curve from literature).[22]

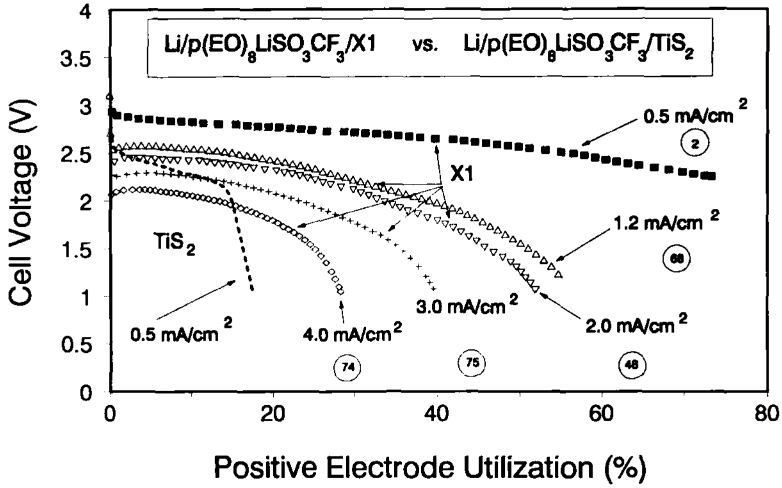


FIGURE 3 Positive electrode utilization and rate capability of Li/PEO/X1 and Li/PEO/TiS$_2$ cells prepared under identical conditions.

electrolyte salt were cast, one containing the X1 polymer and one containing TiS$_2$ powder‡; both electrodes were cycled in the same test cell. As can be seen from Figure 3 the SRPE cell again demonstrated superior rate capability and capacity utilization. Li/PEO/X1 cells were also subjected to extended cycling tests at a discharge current density of 0.5 mA/cm^2 (c/1.2) and a charge rate of 0.125 mA/cm^2 (c/4.8). At these current densities the cell was operating at a steady state energy density of approximately 260 Wh/kg and a steady state power output of 160 W/kg (not including current collectors or container). As can be seen from the cycling profiles in Figure 4, the first 83 cycles were virtually identical, with gradual loss of capacity upon further cycling. Cycling of the cell was terminated at approximately 40% of capacity on the 350th cycle. Li/PEO/X1 cells were also cycled at ambient temperatures at a current density of 250 μA to a film capacity of 0.5 C/cm^2. Optimization of the ambient temperature performance of these cells is presently underway.

In addition to Li/PEO/X1 batteries, all-solid-state Li/PEO/X5 cells also demonstrated high levels of performance,[19] however, the rate capability was lower than for SRPE's based on X1 polymers. The exceedingly low equivalent weight of the X5 polymer makes it very attractive for high energy density applications.

4 CONCLUSIONS

Solid redox polymerization electrodes constitute an interesting new class of materials for positive electrodes in solid-state lithium and sodium batteries. The

‡Battery grade powder obtained from Cerac.

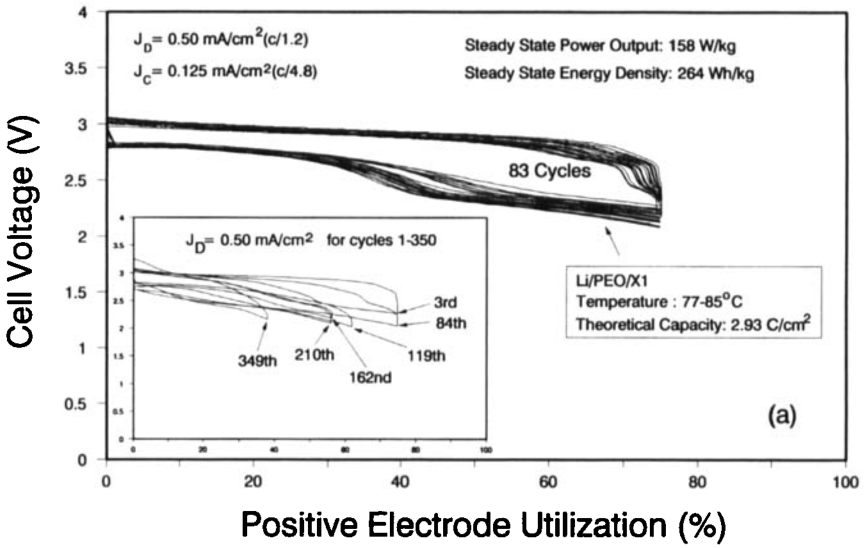


FIGURE 4 Cycling profile of a Li/p(EO)$_8$LiN(SO$_2$CF$_3$)$_2$/X1 cell operating in the temperature range of 77 to 93°C (power and energy densities shown do not include current collectors).

polydisulfide polymers have low equivalent weights leading to high theoretical energy densities and high practical energy densities. The generic nature of SRPE materials allows for molecular engineering of polymers for specific applications. Furthermore, some of the SRPE materials can be dissolved in suitable solvents prior to casting of the composite cathode, allowing for very homogeneous electrode structures. The rate capability and capacity utilization for solid-state cells based on SRPE materials is quite encouraging for eventual commercialization of these materials.

5 ACKNOWLEDGMENT

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