Polyorganodisulfide electrodes for solid-state batteries and electrochromic devices

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The use of polyorganodisulfides in a variety of solid-state batteries and electrochromic devices is discussed. Cycling data is presented for solid-state batteries using sodium and sodium-lead alloy negative electrodes with polyethylene oxide electrolyte and polymeric thiazole positive electrodes. Rate capabilities are comparable to that for analogous lithium batteries, but cells show continual deterioration with extended cycling. The use of polyorganodisulfide electrodes as optically passive counter electrodes for electrochromic devices is also described. Solid-state devices consisting of molybdenum doped WO₃, amorphous polyethylene oxide electrolyte (aPEO), and a polyorganodisulfide counter electrode colored rapidly from a pale yellow to a deep blue-green, upon application of 1.2 V dc. The photopic transmittance changed from 61 to 9%, and the solar transmittance from 45 to 5% during the coloration process.

1. Introduction

The tremendous demand for advanced battery systems for both the consumer and electric vehicle market has inspired fundamental and technical breakthroughs in non-aqueous and solid-state battery technology. Still, ongoing refinement of conventional secondary battery technology including nickel/cadmium and sealed lead/acid as well as innovations such as the nickel/metal-hydride battery continues to challenge the anticipated advantages of future technologies. Advanced battery systems must demonstrate strong improvements in terms of volumetric and gravimetric energy and power density over nickel/cadmium and nickel/metal-hydride systems and still offer comparable reliability in terms of cycle life and safety. In this vein, a good deal of effort has been directed towards lithium battery systems [1]. The use of lithium metal negative electrodes offers distinct advantages in terms of specific energy and power. However, unresolved issues regarding the safety of rechargeable lithium batteries using non-aqueous electrolytes have raised serious doubts concerning the viability of such systems. Alternatives include the use of lithium-carbon anodes, Li₁ₓC₆, or the use of solid polymer electrolytes (possibly both). The use of Li₁ₓC₆ anodes in so-called Li-ion batteries, or rocking-chair batteries, has received much attention in the last two years [2–5]. The substitution of Li₁ₓC₆ for Li metal electrodes appears to greatly improve the cycleability of the negative electrode and dramatically increases the safety of rechargeable batteries based on Li₁ₓC₆ technology. Furthermore, the volumetric energy and power density of Li-ion systems are almost as high as for Li metal anode batteries, although the gravimetric energy density for the system is compromised to an extent that electric vehicles may be an unrealistic goal. Alternatively, the high gravimetric and volumetric energy density of Li metal systems can be realized through the use of solid polymer electrolytes such as polyethylene oxide (PEO). Since their inception by Armand [6], solid polymer lithium batteries have captured the interest of numerous researchers. Much of the early work on solid polymer electrolytes was carried in the temperature range of 60 to 100°C, where polyethylene oxide has suitable ionic conductivity. Since then, a number of groups have reported solid polymer electrolytes with acceptable conductivity at ambient temperature [7], significantly broadening the scope of applications for solid polymer electrolytes.
The approach in this laboratory has included the use of solid polymer electrolytes in combination with polymeric organodisulfides and/or polythiols. These materials are termed solid redox polymerization electrodes (SRPE’s) to reflect the dynamic process of polymerization/depolymerization that occurs as these electrodes are oxidized and reduced. Chemical synthesis of the polymers is easily accomplished by oxidation of di- or tri-mercaptans by an appropriate oxidant as shown below:

\[ nHS-R-SH + nH_2O_2 \rightarrow (SRS)_n + 2nH_2O, \]

where R is an organic group such as ethyl, phenyl, etc. The synthesis of a number of such polymers has been described earlier [8-10]. The polymers are very inexpensive (≈$3-4/lb), are non-toxic and biodegradable. Among the advantages of the polymeric organodisulfides is the tremendous chemical flexibility in altering the physical, chemical, and electrochemical properties of the polymers through synthetic means. In addition to moderation of properties through the choice of the organic group R, copolymers are easily generated through oxidation of a mixture of mercaptans,

\[ xHS-R-SH + yHS-R'-SH + (x+y)H_2O_2 \rightarrow (SRS)_x(SRS)_y + 2(x+y)H_2O, \]

or through reaction of the polymers in the solid state [11]. The redox process for SRPE’s can be represented by,

\[ (SRS)_n + 2ne^- \rightarrow 2n^-SRS^-, \]

for a simple linear polyorganodisulfide. The polymerization/depolymerization of polyorganodisulfides and polythiols can be represented schematically as shown in fig 1. If the redox process for the polyorganodisulfides proceeds in a linear fashion, the average molecular weight of the polymer is a function of the percent oxidation of the monomer as described below:

\[ L_{12}(SRS) + yL_{12} = (1-y)L_{12}(SRS)_{11/(1-y)} + 2yLi, \]

and as shown for polydimercaptothiapiazole, X1 in fig 2. Clearly, the average molecular weight is fairly low until oxidation of the monomer is greater than 85% The mechanism for assembly/disassembly of the polymer in the positive electrode has not yet been established. The formation of dimeric anions, \(-SRS^- - 2e^- \leftrightarrow RSSRS^-,\) appears to play an important role. The presence of dimeric anions is evidenced in the discharge curves for Li/PEO/SRPE cells by a slight drop in the discharge voltage at approximately 50% of the discharged capacity [8-10]. If reduction of the polymer proceeds by snipping discrete units off the ends of the polymer chain, i.e., removal of monomer, dimer, or trimer end groups, high molecular weight polymer could persist up to 50% reduction of the polymer (fig 3). However, the average composition would still follow fig 1. For the case of polythiols (fig 1b), the molecular weight of the polymer is not affected by the redox process.

For the SRPE’s where R is a small organic group such as CH₂CH₂, the equivalent weight of the polymer can be as low as 46 g/equivalent making these materials attractive for use in high energy density batteries (table 1). Furthermore, a number of polyorganodisulfides and their corresponding thiolate salts are essentially transparent in the visible spec-
trum Accordingly, polyorganodisulfides can function as transparent, optically passive, counter electrodes in electrochromic devices.

11 Use of SRPE’s in batteries

A number of solid redox polymerization electrodes have been prepared and described in terms of solid-state lithium battery performance [8–11]. The majority of these batteries have used polyethylene oxide as the solid polymer electrolyte, although, for ambient temperature testing, oxymethylene-linked polyethylene oxide [7] (amorphous PEO) was found to exhibit acceptable ionic conductivity as well as good mechanical properties. Since polyorganodisulfides are not electronically conductive, carbon black is also dispersed in the positive electrode. In principle, SRPE’s can function as positive electrodes for a number of metal negative electrodes. In fact, early tests on SRPE’s were done using liquid sodium electrodes and β”-alumina electrolytes [9] Sodium negative electrodes offer advantages over lithium including greater abundance, ease of processing, and much lower cost. The theoretical energy densities shown in table 2 for the sodium/SRPE cells are somewhat lower than for the lithium cells, but are still in excess of the requirement for electric vehicle and/or consumer electronic devices. Other possibilities include solid-state rocking chair technologies using SRPE positive electrodes and appropriate insertion of intercalation electrodes. Li/SRPE cells using liquid electrolytes have demonstrated high discharge rates [12], however, thiolate anions generated on cell discharge may have appreciable solubility in non-aqueous solvents leading to lower cycle life. It is possible, in principle, to construct a rocking-chair battery entirely from SRPE’s, and thus have an all polymer battery, although the 1 V OCV (table 1) hardly leads to inspiring energy densities. Polyorganodisulfides could be used in combination with LiC6 anodes (table 3) with acceptable volumetric energy densities, however, the gravimetric energy densities may not be acceptable for electric vehicle...
Table 1
Nomenclature for polyorganosulfide electrodes, and energy densities of lithium solid polymer batteries based on them

<table>
<thead>
<tr>
<th>ID</th>
<th>SRPE</th>
<th>Description</th>
<th>E W equiv/g</th>
<th>mAh/g</th>
<th>mAh/cc</th>
<th>$V_{nom}$ vs Li</th>
<th>Wh/kg</th>
<th>Wh/£</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>lithium (SCH$_2$CH$_2$OCH$_2$CH$_2$S)$_n$</td>
<td>clear, viscous liquid</td>
<td>7</td>
<td>3,829</td>
<td>2,045</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X0</td>
<td>(SCH$_2$CH$_2$OCH$_2$CH$_2$S)$_n$</td>
<td>pale, yellow powder</td>
<td>76</td>
<td>353</td>
<td>564</td>
<td>2</td>
<td>646</td>
<td>885</td>
</tr>
<tr>
<td>X1</td>
<td>(N - N) C C C S S</td>
<td>pale, yellow powder</td>
<td>74</td>
<td>362</td>
<td>652</td>
<td>2 8</td>
<td>990</td>
<td>1,384</td>
</tr>
<tr>
<td>X5</td>
<td>(N - N) C C C S S</td>
<td>pale, yellow powder</td>
<td>58</td>
<td>462</td>
<td>739</td>
<td>3</td>
<td>1,237</td>
<td>1,629</td>
</tr>
<tr>
<td>X8</td>
<td>(SCH$_2$CH$_2$S)$_n$ white powder</td>
<td></td>
<td>46</td>
<td>583</td>
<td>932</td>
<td>2</td>
<td>1,012</td>
<td>1,281</td>
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Table 2
Theoretical energy densities of sodium solid polymer batteries having polyorganosulfide cathodes

<table>
<thead>
<tr>
<th>ID</th>
<th>E W equiv/g</th>
<th>mAh/g</th>
<th>mAh/cc</th>
<th>$V_{nom}$ vs Na</th>
<th>Wh/kg</th>
<th>Wh/£</th>
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<tr>
<td>sodium</td>
<td>23</td>
<td>1,165</td>
<td>1,142</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X0</td>
<td>76</td>
<td>353</td>
<td>564</td>
<td>1.7</td>
<td>460</td>
<td>642</td>
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<tr>
<td>X1</td>
<td>74</td>
<td>362</td>
<td>652</td>
<td>2.7</td>
<td>746</td>
<td>1,121</td>
</tr>
<tr>
<td>X5</td>
<td>58</td>
<td>462</td>
<td>739</td>
<td>2.7</td>
<td>894</td>
<td>1,212</td>
</tr>
<tr>
<td>X8</td>
<td>46</td>
<td>583</td>
<td>932</td>
<td>1.7</td>
<td>660</td>
<td>873</td>
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</table>

Table 3
Theoretical energy densities of representative battery systems

<table>
<thead>
<tr>
<th>Electrode</th>
<th>E W equiv/g</th>
<th>Capacity mAh/cc</th>
<th>$V_{nom}$ vs Li</th>
<th>$V_{nom}$ vs C$_x$</th>
<th>Lithium (Wh/kg)</th>
<th>LiC$_{12}$ (Wh/kg)</th>
<th>Lithium (Wh/£)</th>
<th>LiC$_{12}$ (Wh/£)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1 (4 1)</td>
<td>28</td>
<td>511</td>
<td></td>
<td></td>
<td>494</td>
<td>205</td>
<td>1900</td>
<td>558</td>
</tr>
<tr>
<td>LiC$_{12}$</td>
<td>196 a)</td>
<td>246 a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiNiO$_2$</td>
<td>195</td>
<td>686</td>
<td>3.6</td>
<td>3.2</td>
<td>494</td>
<td>205</td>
<td>1900</td>
<td>558</td>
</tr>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>181</td>
<td>740</td>
<td>3.9</td>
<td>3.5</td>
<td>578</td>
<td>216</td>
<td>2182</td>
<td>551</td>
</tr>
<tr>
<td>SRPE (X1)</td>
<td>74</td>
<td>652</td>
<td>2.8</td>
<td>2.1</td>
<td>930</td>
<td>208</td>
<td>1384</td>
<td>375</td>
</tr>
</tbody>
</table>

a) Equivalent weight and volumetric capacity of composite having 60 vol% active carbon

Furthermore, it is unclear whether L$_1$L$_6$ electrodes will function properly with solid polymer electrolytes as it appears that either propylene or ethylene carbonate is necessary for passivation of the carbon electrode surface for extended cycling [2–5]. Assuming that solid polymer technologies avoid the safety problems associated with cycling alkali metal electrodes in non-aqueous electrolytes, the most desirable configurations for SRPE's appear to be in solid polymer cells using either lith-
Fig 4 Calculated gravimetric capacity and energy density for Li (4:1 excess) and composite Li$_x$C$_6$ electrodes (60 vol% active material) (a) gravimetric capacity, (b) gravimetric energy density for representative battery systems

Fig 5 Schematic representation of solid-state electrochromic device consisting of transparent indium-doped tin oxide (ITO) current collectors, solid polymer electrolyte, and complementary metal oxide electrochromic layers
one electrode, even if the electrodes were matched initially. The device then becomes unbalanced and is unable to bleach fully. One way to avoid this problem is to use an optically passive ion storage electrode that undergoes redox without an associated color change. Since the majority of the known electrochromic electrodes reversibly insert (or intercalate) cations, a suitable redox electrode would possess electroactive anions such as the organothiolates. The pertinent half-reaction for coloring and bleaching WO₃ can be represented as,

$$\text{WO}_3 \text{ (bleached)} + ne^- + nLi^+ \rightarrow \text{Li}_n\text{WO}_3 \text{ (colored)}$$  \hspace{1cm} (5)

and for the SRPE,

$$nLi_2 (\text{SRS}) \leftrightarrow (\text{SRS})_n + 2nLi^+ + 2ne^- \text{ (passive)},$$ \hspace{1cm} (6)

giving a cell reaction for the electrochromic device as

$$\text{WO}_3 \text{ (bleached)} + nLi_2(\text{SRS}) \leftrightarrow (\text{SRS})_n + L_i_{2n}\text{WO}_3 \text{ (colored)}$$ \hspace{1cm} (7)

In the case of an optically passive SRPE, the capacity need not be matched to the electrochromic electrode, but rather would be formulated with excess capacity. A diagram of such a device is shown in fig 6. Since the polyorganodisulfides are not electronically conductive, the redox reaction must take place in the vicinity of the transparent current collector. Fortunately, the amount of charge needed to reversibly color and bleach many electrochromic electrodes is quite small, in the range of 25 to 40 mC/cm², and can be achieved with polyorganodisulfides in the absence of conductive additives.

Fig 6 Solid-state electrochromic device based on solid redox polymerization electrodes. Coloring/bleaching reaction occurs only at metal oxide electrode. SRPE is optically passive and functions only as redox active ion storage electrode.
2. Experimental

2.1 Na/PEO/SRPE cells

Alkali metal purification and cell assembly/testing was carried out in an inert atmosphere glove box with less than 1 ppm O₂ and H₂O. Reagent grade sodium was treated with sodium oxide at 350°C to remove calcium, then filtered with stainless wool to filter out the oxides. Roughly purified sodium was then reacted with titanium sponge at 400°C to remove oxygen. Sodium-lead alloy, Na₃₋₇₅Pb, was directly made by melting the appropriate amount of purified sodium and lead in an α-alumina crucible. Polyethylene oxide (PEO) of molecular weight 1 × 10⁶ and NaSO₃CF₃ (Na ethylene oxide ratio = 1.8) were dissolved in acetonitrile and cast on release sheets in suitable volumes to give 10 to 40 micron films after solvent evaporation. Electrolyte films were dried under vacuum for four days prior to testing in solid-state cells. Composite positive electrodes with surface capacities of 2 to 6 C/cm² were cast from solutions of PEO, NaSO₃CF₃ (Na/EO = 1.20), and carbon black and dried as above. Positive electrodes having no carbon black were used for cyclic voltammetry experiments. Assembled cells were cycled galvanostatically under software control.

2.2 WO₃/aPEO/SRPE electrochromics

Molybdenum doped tungsten oxide films were deposited potentiostatically from a bath consisting of tungsten and molybdenum metal dissolved in aqueous hydrogen peroxide onto conductive indium tin oxide (ITO) coated glass electrodes (Donnelly Co., Holland, MI), using a BAS potentiostat/coulometer (model CV-27). The ITO electrodes were ultrasonically cleaned, dipped in ethyl alcohol, dipped in 10–20% sulfuric acid, rinsed in distilled water and dried with nitrogen prior to the deposition. After deposition, the electrodes, approximately 3×5 cm in size, were rinsed in distilled water and dried with nitrogen. Ion conducting layers were cast onto the coloring electrodes from solutions of high molecular weight amorphous PEO and lithium triflate (Li ethylene oxide ratio = 1.20) in acetonitrile (2–4 wt% solids) and allowed to dry completely. These films were estimated to be less than 10 μm thick. Ion storage counter electrodes were cast directly onto the dried ion conductor layers from solutions of amorphous PEO (aPEO), lithium triflate and the lithium dithiolate salt of the polyorganodisulfide being tested. Upon drying of the SRPE films, the polymer electrodes were either colorless or pale yellow, depending on the choice of thiolate salt. Electrochromic cells were assembled as shown in fig 6. After drying, another ITO coated glass electrode was placed on top of the ion storage layer, such that the active area of the device was 3×3 or 9 cm². The edges were sealed with a hot melt adhesive, and care was taken to prevent contact of the glue with the internal components during the curing. Devices were colored and bleached by application of a controlled potential from a custom dc power supply with current regulation. A Cary 14 UV-visible spectrophotometer was used to take optical transmittance spectra. WO₃ was used as the electrochromic material for this study. Intercalation cations upon reduction (application of potential to the device) and deintercalates cations upon oxidation (reversal of the potential). Molybdenum is added to the WO₃ to alter the color from bright blue to gray-blue, but does not participate in the redox process. In situ spectrophotometry on the WO₃/Mo electrode was performed using a special quartz cell with a micro-calomel reference electrode, a platinum foil counter electrode, and a potential of -0.7 V versus S C E. was applied to the electrochromic electrode in order to color it.

3. Results and discussion

3.1 Na/PEO/SRPE and Na₃₋₇₅/PEO/SRPE cells

The solid-state cyclic voltammogram for polydimercaptothiadiazole (X1) is shown in fig 7. The CV exhibits the chemically reversible and kinetically quasi-reversible behavior characteristic to organodisulfides [13,14] and polyorganodisulfides. In fact, polydimercaptothiadiazole exhibits the fastest electrode kinetics of any of the organodisulfides or polyorganodisulfides examined so far. The relatively slow electrode kinetics of the disulfides are compensated by the use of high surface area carbons in the formulation of positive electrodes. Shown in fig 8 are the discharge curves of a Na/
30 wt% X1 in aPEO

Fig 7 Solid-state cyclic voltammogram of polydimercaptotriazole in amorphous PEO electrolyte at 90°C. 30 micron lithium reference and counter electrodes were used in the solid-state cell.

PEO/X1 cell operated in the temperature range of 70 to 85°C. The cell shown in fig. 8 was initially cycled at shallow depth (10 to 20% of available capacity for 60 cycles) to improve the Na/PEO interfacial contact. Preliminary impedance spectroscopy studies of Na/PEO/Na cells in this laboratory have shown that the quality of the interface depends critically upon impurities in the sodium electrode, and in the PEO electrolytes (moisture and/or residual solvent); Li/PEO cells were not found to be as sensitive to contaminants. This cell achieved over 90 cycles, with 30 cycles between 40 to 60% of available capacity, although gradual deterioration of cell performance was observed with cycling. Clearly, the rate capability of Na/PEO/X1 cells at this temperature is not as good as that of Li/PEO/X1 cells [8-11]. Na/β"-alumina/SRPE cells operated at 130°C have demonstrated very high rate capability [9]. However, the melting point of sodium, 97°C, sets the upper limit of the operating temperature of all-solid-state Na/PEO/SRPE cells.

Sodium-lead alloy has been reported to perform well as a negative electrode for sodium batteries [15], and is not limited by a low melting point. The cycling behavior of a Na₃.₇₅Pb/PEO/X1 cell operating at 90°C is shown in fig. 9. The rate behavior of the
Fig 8 Charge/discharge curves for Na/PEO/X1 cells operating at 70 to 85°C. First 60 cycles involved shallow discharges (10 to 20% of available capacity) to condition cell.

cells is clearly improved by the higher operating temperature. The first 15 cycles of this cell look promising, however, subsequent cycling shows consistent deterioration. Four probe dc measurements using current-pulse techniques have correlated this deterioration to increasing resistance at the Na/PEO or Na$_{3.75}$Pb/PEO interface. The degradation of the Na/PEO interface may be due to either water or solvent present in the PEO electrolytes, or possibly due to migration of thiolate anions towards the sodium negative electrode, and subsequent reaction. Lithium electrodes are less prone to interfacial degradation due to their superior ability to form passivation films.

3.2 $WO_3/a$PEO/SRPE cells

Amorphous PEO (aPEO) electrolytes were found to have good dimensional stability and excellent optical properties. The optical transmittance of an aPEO electrolyte is shown in fig. 10. The electrolyte films appear completely transparent to the human eye. The spectral properties of an SRPE/aPEO film are shown in fig. 11, the electrode is faintly yellow to the human eye. Tungsten oxide, $WO_3$, intercalates cations upon reduction (application of potential to the device) and deintercalates cations upon oxidation (reversal of the potential) as described in eq (5) The visible transmittance spectra for $WO_3$ Mo in both the bleached and the colored state are shown in fig 12. The photopic transmittance ($T_p$) changes from 0.83 to 0.19 when a voltage of -0.7 versus S.C.E. is applied to the electrochromic electrode in a 0.1 M $H_2SO_4$ solution.

The current-voltage characteristic of an ITO/$WO_3/a$PEO/SRPE/ITO device is shown in fig 13. When a voltage of about 1.3 V is applied between the $WO_3$ Mo and counter electrode for this example, current flows and the device rapidly colors to a deep blue-green, indicating that Li ions are intercalating into $WO_3$ as it is being reduced. Concurrently, the dithiolate salts in the ion storage layer are oxidized to disulfide polymers and release Li ions. When a potential of about -1.0 V is applied to the colored device, rapid and complete bleaching to the original pale yellow occurs, the electrochromic electrode is reox-
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Fig 9 Cycling of a Na$_{3.75}$Pb/PEO/X1 cell at 90°C

The optical spectra of the device in both the colored and the bleached states are presented in fig 14. The photopic transmittance, $T_p$, changed from 61 to 9% and the solar transmittance, $T_s$, from 45 to 5%, upon coloring. The optical properties and switching times vary somewhat depending upon the compounds used in the ion storage layer, but the results presented above are fairly typical. The devices remain stable in both the colored and bleached states, and cycle well, laboratory cells have demonstrated several hundred switching cycles thus far.

4. Conclusions

Polyorganodisulfide electrodes have unique advantages as positive electrodes in solid-state alkaline metal batteries and as optically passive counter elec-
Fig 10 Optical transmittance of an aPEO electrolyte layer. The solid line shows the spectrum of the substrate and dotted line that of the aPEO layer.

Fig 11 Spectral optical transmittance of lithium 2,5-dimercaptotet-rene-1,3,4 thiadiazole salt in aPEO. Film thickness is approximately 10 microns. The electrode is faintly yellow to the human eye.

Fig 12 Normal transmittance for an electrochromic WO₃ Mo/ITO/glass electrode in a liquid cell (0.1 M H₂SO₄) in the bleached and colored states. Coloration occurs at a voltage of −0.7 V versus an SCE.
Polyorganodisulfide electrodes function well as ion-storage electrodes in solid polymer electrochromic devices. Amorphous PEO appears to be a good electrolyte for this solid-state device, exhibiting adequate ionic conductivity at room temperature and good mechanical stability. The use of aPEO electrolytes and SRPE ion-storage electrodes allows construction of a stable, completely solid state window with excellent optical properties and switching times. Because the new ion storage layer does not change color as a function of redox state, there is no need to match the capacity to that of the WO₃ electrodes. This greatly simplifies the assembly process, and thus represents a potential saving in manufacturing cost.

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References