

(This is written for a situation where the light comes from a region far away compared to the size of the massive object, such that asymptotes can be defined).

Similar velocity independent terms are present in other situations involving gravitational fields and matter or light waves, as highlighted in ref. 5 in the context of the Sagnac effect. In the context of the discussion in that paper, the relativistic part of the gravitational deflection is in fact the ratio of the local gravitational potential (generated by the massive body) and the gravitational potential due to all the masses in the universe. For a universe with critical density ($\rho \approx 2 \times 10^{-29} \text{ g/cm}^3$) and an effective causal size of $R_H \approx 10^{28} \text{ cm}$, the gravitational potential at every point is numerically close to the quantity c^2 . This clarifies why one part of the deflection is always given by an invariant factor, where, surprisingly, the velocity of light appears even while considering the gravitational deflection of other material particles or waves.

It is important to stress why this derivation gives a result identical to the full general relativistic result in which no wave aspect of light or particle is directly used. The non-Newtonian part of the deflection in general relativity comes from consideration of the curvature of the space-time in which the deflection occurs close to the massive body. The spatial coordinate system near the massive object is general relativistically distorted with respect to the asymptotic coordinate system in which the measurements are made. The gravitational factor that contributes to the additional deflection is same as the factor that is responsible for the gravitational redshift of a wave in the gravitational field. Therefore, whether we use an extended entity like a wave to include the variation of the time dilation factors in the gravitational field, or use the curvature of space-time caused by the mass, the results are the same. In other words, the plane wavefront is like a coordinate grid in the direction perpendicular to the wave vector, and the gravitational redshift and resulting bending are exactly like the curvature of any imaginary coordinate grid. What is important is to note that such a contribution is fundamentally different from the deflection obtained by applying the equivalence principle to a ray or a particle. This need not mean that general relativistic gravity is inconsistent without the quantum nature and wave aspect of particles to which the theory applies. However, one may argue that point particles without a quantum mechanical wave aspect are not fully consistent with general relativity in a local analysis, since point particles are singularities of the field. This issue needs to be studied further. What general relativity needs is the relativistic changes of scales and clocks as the position is changed in the gravitational potential. These effects can be incorporated either by correctly taking into account of the transformation between coordinates as usually done in the general relativistic derivation of the deflection light, or by considering physical effects on spatially extended objects, like waves. Both are equivalent as far as the final result for deflection is concerned, though

there are important differences in the conceptual and physical aspects of the two approaches. The discussion presented here using explicitly the physical effects on waves in a gravitational field is by far the simplest, and most transparent.

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Preparation and characterization of magnesium ion conducting glass-polymer composite films

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The flexible glass-polymer composite film electrolytes of high magnesium ion conducting oxysulfide glass and the comb-shaped poly(oxyethylene) polymer (TEC-19) were prepared. The conductivity of the composite film with 2% (v/v) TEC-19 doped with $\text{Mg}(\text{ClO}_4)_2$ was $1.2 \times 10^{-3} \text{ S cm}^{-1}$ at 100°C and $3.5 \times 10^{-5} \text{ S cm}^{-1}$ at 30°C . The composite exhibited a 4V stable potential window versus Mg^{2+}/Mg . The flexible glass-polymer composite films prepared in this way are promising solid electrolytes for solid magnesium secondary batteries. The electrical conductivity for pelletized composite film was measured in a dry Ar atmosphere by the ac impedance method in the temperature range $25\text{--}250^\circ\text{C}$ and the frequency range 1 Hz–10 MHz. Temperature dependence of electrical conductivities of glass-polymer composites has been observed.

IONIC conducting polymers^{1,2} have been of considerable interest because of their commercial application as batteries, signal processing devices, vacuum tubes, semiconductors, fibre-optics, charge-transfer complexes, etc. Many workers³ have reported synthesis and other characteristic data on the

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simple conducting polymers. The discovery of conducting polyacetylene³ was recognized as a boon for search of new related conducting polymers for welfare of mankind.

The development of all solid state magnesium secondary batteries using solid electrolytes is strongly desired to improve safety and reliability of the widely popularized magnesium ion secondary batteries using liquid electrolytes. The Li₂S–SiS₂ based oxysulfide glasses prepared by melt-quenching^{4–6} have considerably high conductivity over 1.5×10^{-3} S cm⁻¹ at room temperature and a wide electrochemical window of greater than 10 V, suggesting that these glasses are one of the most promising solid electrolytes for solid-state-lithium-secondary batteries.

In order to obtain superior solid-state secondary batteries with good cyclife performance, solid electrolytes with flexibility, which can sustain volume changes accompanied by charge–discharge processes, are required^{7,8}. However, the glassy electrolytes are brittle and have poor mechanical flexibility. The addition of flexible polymer to a glassy electrolyte is efficient to overcome the lack of flexibility. The glass–polymer composite electrolytes are expected to have improved mechanical flexibility for sheet like flexible solid batteries.

Also, an increase in packing density of an electrolyte, with voids filled with polymers has shown an enhancement of conductivity due to a decrease of grain boundary resistance⁸.

Several composite materials with ion conducting inorganic materials and poly(oxyethylene) (POE)-based polymers have been reported^{7–10}. In the lithium ion conducting polymer electrolytes, a high molecular weight branched POE with LiClO₄ as lithium salts exhibited high conductivity over 1×10^{-4} S cm⁻¹ at room temperature^{11,12}.

In the present study, we have attempted to prepare the glass–polymer composite film from the magnesium ion conducting oxysulfide glass and those branched POE without magnesium salts to examine their electrical conductivity. Also, high magnesium ion conducting composite electrolytes of the oxysulfide glasses with an addition of small amounts of comb-shaped POE polymers with Mg(ClO₄)₂ have been prepared. Their electrical, electrochemical properties and thermal stability against magnesium metal have been investigated.

The 95 (0.6 MgS, 0.4 SiS₂) 5.0 Mg₂SiO₄ (Mol.%) oxysulfide glass was prepared from reagent-grade MgS and SiS₂ and crystalline Mg₂SiO₄ using a twin-roller quenching technique in a dry N₂-filled glove box [(H₂O) < 1 ppm]^{5,6}. The glass obtained was ground to fine powder using a planetary ball mill, the average size of the particles was a few μm in diameter. The structural unit mainly present in the oxysulfide glass^{13,14} is shown in Figure 1 *a*. The synthesized high molecular weight branched POE ($M_n = 1.3 \times 10^5$) with 19 mol% co-polymer units of branching, which is named as TEC-19 (Figure 1 *b*), was used as a polymer^{12,16}. The polymer with Mg(ClO₄)₂ as a magnesium salt was also prepared. The concentration of Mg(ClO₄)₂ was fixed to be [Mg]/[–O–] = 0.1 M, where –O– means the ethereal oxygen.

The glass–polymer composite films were prepared by mixing and grinding the mixture of *x*% (v/v), TEC-19 polymer (*x* = 2, 10, 18) and (100–*x*)% (v/v) oxysulfide glass powder in a mortar and pestle. The polymers were dried at 80°C under high vacuum over one week before use. The glass–polymer mixtures were pressed into pellets ($\phi = 10$ mm) under 5550 kg/cm² for five minutes and then kept at 80°C for 2 h to ensure the polymer flow into the voids among glass particles. The composite electrolytes obtained are flexible even in the case of the addition of only 2% (v/v) TEC-19 to the oxysulfide glass, suggesting that TEC-19 used in this study is a good polymer binder and introduces mechanical flexibility to the high ion conductive oxysulfide glass powders.

The electrical conductivity for the pelletized composite disk was measured in a dry Ar atmosphere by the ac impedance method in the temperature range 25–250°C at a constant frequency of applied ac signal which lies in the range 1 Hz–10 MHz. The temperature dependence of electrical conductivities of the glass–polymer composite films is shown in Figure 2. The conductivities of the bulk and pelletized 95 (0.6 MgS, 0.4SiS₂) 5.0 Mg₂SiO₄ oxysulfide glasses are also shown (Figure 2). Closed and open marks denote the composite films of TEC-19 with and without Mg(ClO₄)₂ respectively. The conductivity value of the bulk glass is found to be 1.02×10^{-3} S cm⁻¹ at 25°C and that of the pelletized glass^{6,15} is found to be 1.05×10^{-4} S cm⁻¹. The conductivity of the glass–polymer TEC-19 without Mg(ClO₄)₂ composites decreases with an increase in TEC-19 content from 2% to 18% (v/v). The conductivity values of the composite films with 2% and 18% (v/v) TEC-19 are, respectively, 1.1×10^{-5} and 3.2×10^{-6} S cm⁻¹ at 30°C. These values are one or two orders of magnitude lower than those of the pelletized glass without polymer. This is because the magnesium ion concentration in the composite films decreases with an increase in additional polymers without magnesium ion; these polymers must also prevent magnesium ion conduction. The Mg(ClO₄)₂ doping to TEC-19 increases the conductivity of the composite films. The composite consisting of 98% (v/v) oxysulfide glass and 2% (v/v) TEC-19 with Mg(ClO₄)₂ remaining glass exhibit conductivities similar to the pelletized glass in the high temperature range

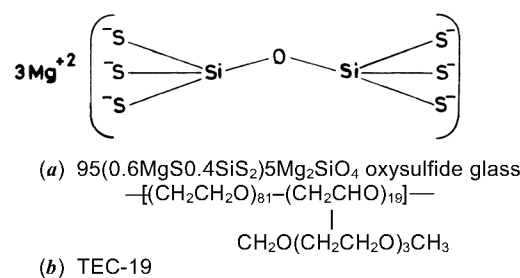


Figure 1 a, b. *a*, Main structural unit in the oxysulfide glass; *b*, Chemical structure of TEC-19 polymer.

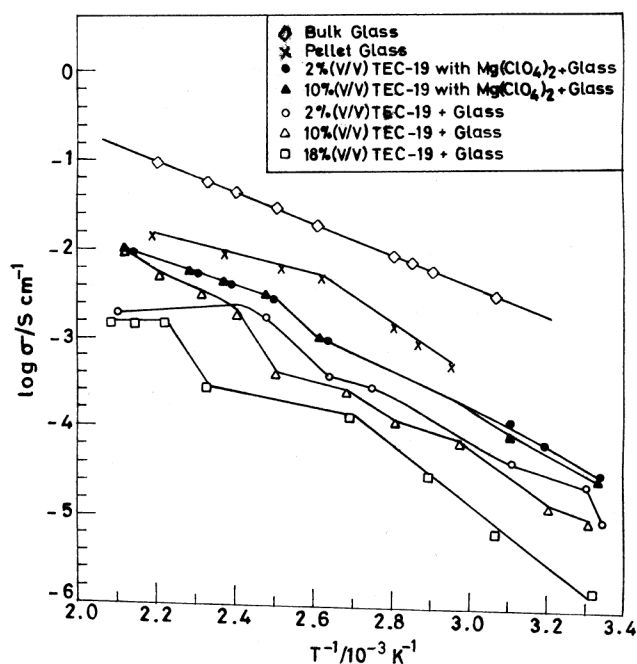


Figure 2. Temperature dependence of the electrical conductivities of the glass–polymer composite electrolytes of the 95 (0.6 MgS, 0.4 SiS₂), 5 Mg₂(SiO₄) oxysulfide glass and TEC-19 polymer with or without Mg(ClO₄)₂.

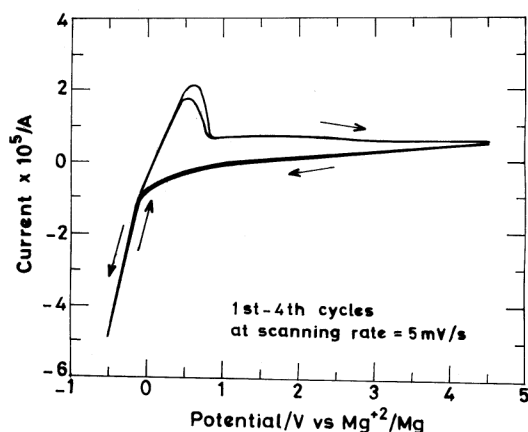


Figure 3. Cyclic voltammograms for the glass–polymer composite electrolyte with 2% (v/v) TEC-19 doped with Mg(ClO₄)₂.

over 85°C; the conductivities of this composite are 1.10×10^{-3} at 100°C and 3.15×10^{-5} S cm⁻¹ at 30°C. The conductivities of the composite with 10% (v/v) TEC-19 with Mg(ClO₄)₂ are almost the same as those with 2% (v/v) TEC-19. The conductivities of the bulk and pelletized glasses follow the Arrhenius equation, while the temperature dependence of the glass–polymer composites exhibits convexly curved profiles. These profiles are usually observed in the amorphous polymer electrolytes which are expressed semi-quantitatively by the WLF or VTF equation¹¹.

$$\log f = \log f_0 + C_1(T - T_0)/C_2 + (T - T_0),$$

where C_1 and C_2 are WLF parameters, f and f_0 are frequency parameters and T and T_0 are temperatures.

WLF equation has been used to evaluate the thermally stimulated depolarization current (TSDC). The TSDC technique can be used to determine the glass transition of a polymer sample. This TSDC glass transition temperature has been shown to be similar to that obtained from differential scanning calorimetry (DSC). However, the actual difference between these two values depends on the heating rates used with each technique. TSDC data can also be combined with AC dielectric data to produce a data set, which possesses a wide frequency range. Finally, individual TSDC relaxation peaks can be fit with the Williams–Watts distribution function¹¹ to obtain an estimate of their distributions. Therefore, the total conductivity of the composites is mainly controlled by the magnesium ion conduction in the TEC-19 polymer added to the oxysulfide glass.

Cyclic voltammetry was performed with a scanning rate of 5 mV/s for electrochemical cell with the pelletized composite as a solid electrolyte, a stainless steel (SUS) plate as a working electrode, and a magnesium foil as a counter electrode, which is also used as reference electrode. Figure 3 shows the cyclic voltammograms for the glass–polymer composite with 2% (v/v) TEC-19 doped with Mg(ClO₄)₂. The measurements were performed from the rest potential to the cathodic direction and then to the anodic direction to 4.6 V vs Mg²⁺/Mg. The cathodic current due to magnesium deposition and the anodic one due to magnesium dissolution are observed at -0.5 to IV. The composite exhibits good cycling performance in the potential range -0.5 to 4.2 V for 4 cycles. The large anodic current was observed in the potential over 5 V and the cycling performance became worse, suggesting that this composite has at least a 4 V stable potential window vs Mg²⁺/Mg.

In conclusion, the flexible glass–polymer composite films materials were obtained from the oxysulfide glass powder and TEC-19 polymer. The composites exhibited the conductivity over 10^{-5} S cm⁻¹ at room temperature and a 4 V stable potential window vs Mg²⁺/Mg. The flexible glass–polymer composites prepared in this study are promising solid electrolytes for solid state magnesium secondary batteries.

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Polyethersulfone supported titanium complexes as ethylene polymerization catalysts

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Polyethersulfone has been used as the support to anchor TiCl₄ or Cp₂TiCl₂ through dative 'O-Ti' bond. The supported complexes in combination with methylaluminoxane are effective ethylene polymerization catalysts. The polyethylene made by the supported catalysts, especially the titanocene-derived catalyst, has low polydispersity indicating single site character.

NOVEL catalysts for the manufacture of polyethylene are of great current research interest¹. While most of the commercial heterogeneous catalysts are based on silica-supported chromium, or magnesium chloride-supported titanium species, in recent years metallocene and non-metallocene transition metal complexes, the so-called single site catalysts, have attracted significant attention^{1,2}.

From the point of view of practical application anchoring of catalytically active titanium complexes onto a suitable support, by a simple synthetic procedure, and with minimum alteration of the ligand environments is a challenge^{3,4}. The supported catalyst at the molecular level must be well-defined and when used in polymerization reactions, should approximate single-site behaviour. TiCl₄ and Cp₂TiCl₂ are two of the most easily available and widely used precursors for magnesium chloride-supported Ziegler-Natta and single-site metallocene catalysts respectively. Thus from the point of view of potential application, it is highly desirable to find a polymer that without functionalization is capable of tethering TiCl₄ and titanium metallocene complexes through well-defined chemical bonds. Unlike other supported homogeneous catalysts, the purpose of anchoring is therefore not the easy separation of the catalyst, but to impart single site character to a supported catalyst. Furthermore such supported catalysts can be easily used in fluidized bed reactors.

In this communication we report that polyethersulfone (PES) is a versatile support material on which TiCl₄ and Cp₂TiCl₂ could be easily anchored through dative 'O-Ti' bond. The supported complexes in combination with methylaluminoxane (MAO) are effective ethylene polymerization catalysts. The polyethylene made by the supported catalysts, especially the titanocene-derived catalyst, has low polydispersity indicating single site character.

Triethylaluminum (AlEt₃) (Scherings, AG, Germany), titanium tetrachloride (TiCl₄) (Merck, Germany) and bis(cyclopentadiene) titanium dichloride (Cp₂TiCl₂) (Aldrich, USA) were used as received without further purification. Polyethersulfone (average $M_n \sim 20,000$) was a gift sample from Gharda Chemicals, India. All operations unless stated otherwise were carried out under an inert atmosphere of nitrogen or argon. GPC chromatograms (140°C, trichlorobenzene as solvent) were recorded on a Polymer Laboratory 220 instrument.

A solution of Cp₂TiCl₂ (1.7 GM) in dichloromethane (20 cm³) is added drop wise under nitrogen to a dichloromethane (200 cm³) solution of PES (5 GM) at 25°C and stirred for 2 h. Pale yellowish precipitate of **1** separates out from the clear solution, which is isolated by filtration and washed repeatedly with dichloromethane and stored under dry nitrogen. This material is used for all subsequent experiments with **1**.

Catalyst **2** is prepared and isolated by a similar procedure by using TiCl₄ (1.3 GM) and PES (5 GM). Catalyst **4** is prepared by mixing dichloromethane solutions (100 cm³ each) of TiCl₄ (1.3 GM) and dimethyl sulfone (0.1 GM), stirring the solution for 4 h, removing the solvent under reduced pressure and washing the residue with toluene (1 ml) and hexane.

All polymerization experiments were carried out in a double-jacketed three-necked glass reactor of one-litre capacity, in toluene (200 ml) at 27°C for 60 min. In all the experiments the cocatalyst used was MAO (30%), the amount of

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