

Encapsulation for Improving the Efficiencies of Solar Cells

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1 Introduction

The urgency to increase the energy production in order to meet the present and future energy demands has led to explore various renewable energy resources [1]. Solar energy can be harvested and used by three basic mechanisms: solar to thermal/voltaic/chemical energy for various applications [2]. Even though solar energy has seemed to be the plausible solution in terms of sustainability, portability, and availability, it is not commercially viable in short term as compared to conventional fuels. This is due to inorganic semiconductor processing technologies and material supply limitations. With the introduction of thin film and organic photovoltaics, the feasibility of coating/printing solar devices conformally onto various flexible substrate surfaces has increased the hope of fabricating economically compliant solar devices [3–5]. The potential impact of the emerging polymer-based solar technologies could be on the niche of energy market due to their ability to work in diffuse light and promising large-scale scalability. For example, fabricating lighter, wearable, flexible devices with roll processability suitable for large areas and portable applications is possible [6, 7]. The expectations on the commercialization of organic-based solar devices can be realized only if some of the challenges involving efficiency and lifetimes of these devices are met. Photovoltaic power conversion efficiency of about ~12 % has been achieved in organic solar cells whereas it is about ~44 % in inorganic semiconductor devices [8]. Even though the parity in efficiencies is higher, other factors such as lower economy,

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aesthetic aspects, and suitability for domestic applications indicate organic solar devices as a better option over inorganic photovoltaics [4, 9]. Photoelectrochemical water splitting is another developing research field for production of solar-based fuels for industrial and domestic applications. Various semiconducting materials with suitable bandgaps matching with photocatalysts for water splitting reaction can be used to generate feedstock fuels for use in various industries and transportation [10].

2 Need for Encapsulation

Silicon-based solar cells are themselves brittle, apart from the glass encapsulation. The water vapor transmission rate (WVTR) to be possessed by the encapsulant for these solar modules is about $0.1\text{--}1\text{ g/m}^2/\text{day}$. Hence, polymers like ethylene vinyl acetate, poly (vinyl butyral), ionomers, polyolefins, and thermoplastic polyurethanes are commonly used as encapsulant and back sheets in standard commercial photovoltaic modules. The effective functioning of these materials is essential for corrosion-free solar module. The chemicals released due to degradation of the polymer corrode the metallic components in the module [11]. Hence, various filler materials like antioxidants, UV absorbers, permeation delaying components, and stabilizers are added to increase the performance of the encapsulant. Mono- and polycrystalline silicon-based solar cell have thickness of about $100\text{--}400\text{ }\mu\text{m}$ of which only the upper region comprising up to $15\text{ }\mu\text{m}$ can capture visible light by absorption. Hence, thin film-based solar devices provide a better solution as they are much thinner and flexible with the ability to absorb the light throughout the thickness ($<5\text{ }\mu\text{m}$). These materials include amorphous Si, cadmium telluride (CdTe), and copper indium gallium selenide (CIGS). However, the process complexity and continuous production strategies are further required to be explored for their commercialization. Even these thin film materials require a flexible, weathering, and UV-resistant encapsulant with WVTR of the range $<10^{-3}\text{ g/m}^2/\text{day}$ which is about three orders lower than the standard food packaging requirement [12].

The basic device architecture of an organic photovoltaic (OPV) device is given in Fig. 1. The incident light is absorbed by the photoactive layer, generating excitons, which dissociate at the donor–acceptor interface of the OPV device. In order to separate these excitons, a strong electric field is required for the conversion into final photovoltaic energy. As the exciton binding energies are higher in organic semiconductors than that in the inorganic materials, it helps in designing much thinner devices. The dissociated charges are transported to the electrodes where they are collected.

The device architecture, interfacial contacts at the electrodes, interfacial nanomorphology of the active layers, bandgaps of the materials used, and contaminant-free processing determine the organic device performance. Hence, organic chemistry and device physics helps choosing and engineering the suitable

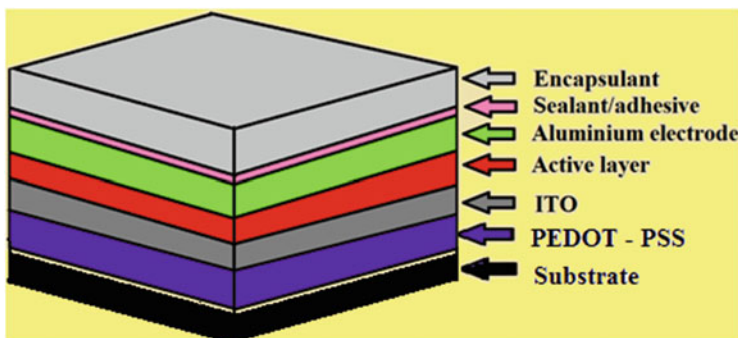


Fig. 1 Basic schematic for cross-sectional view of encapsulated organic solar device

active component materials for fabricating the organic solar device dynamically [13, 14]. However, the lifetime of the device is dependent on the effective working of the active materials in the fabricated device. Most of the active materials used in OPV devices are not stable under ultraviolet (UV) radiation and in humid environmental conditions. The major reasons include degradation of the active components, oxidation of electrodes, and delamination of the layers in the fabricated OPV device upon exposure to moisture, oxygen, or ultraviolet radiation. As the degradation in device performance is caused by external elements, the optimal solution would be to protect the device from interfering with such environments which can be achieved by encapsulating the OPV device with a high barrier material.

The encapsulant material must be capable of reducing the ingress of moisture, oxygen as well as remain resistant to UV radiation. The encapsulant ideally should be impermeable to moisture and oxygen or exhibit at least permeability with the acceptable transmission rates through the material being $<10^{-6}$ g/m²/day and $<10^{-5}$ cc/m²/day/atm, respectively [15]. The conventional encapsulant material that satisfies the prescribed transmission rates is glass [16]. However, it is brittle, heavy, and not suitable for large area and large-scale processing, leading to detrimental effect on the main features and advantages of organic solar devices. Thus, it is unsuitable for being used as an encapsulant. Hence, an easily processable, monolithic, flexible, high vapor and gas barrier material, which can conform into various surfaces and shapes, is required as an OPV encapsulant. This led to exploration of various organic, inorganic, and hybrid layers for their use as encapsulants. Along with the development of the material for encapsulation, suitable techniques to determine the ultra low transmission rates of water vapor and oxygen through the encapsulants are required for characterization.

3 Lifetimes and Performance of OPV Devices

The lifetime and performance is the key to the commercialization of the organic solar cells. Degradation of performance is one of the major limitations in OPVs. The problem lies in the appropriate understanding about the mechanisms of degradation that occur in OPV devices. Various degradation causes have been probed so far relating to degradation.

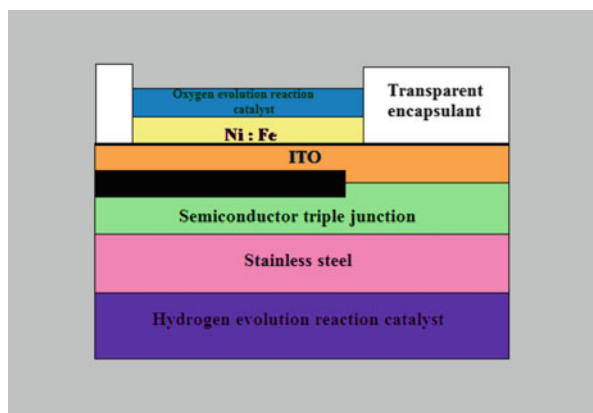
The active materials like P3HT and PEDOT-PSS oxidize in the presence of light and oxygen [17]. Moreover, the rate of oxidation increases in the presence of H₂O [18] as well as with an increase in temperature [19–21]. UV light-induced degradation of conjugated polymers has also been observed [22, 23]. The mobility and conductivity of fullerene/pentacene-based molecules decrease drastically because of their oxidation. Even the ingress of moisture decreases mobility of the charge carriers [24]. Organic materials and metal electrode materials such as aluminum are susceptible to reactions with oxygen and water, further leading to delamination of individual layers. The diffusion of oxygen through the electrode materials results in indium diffusion to the active layer through the ITO electrode [25].

In bulk heterojunction OPVs, interpenetrating donor–acceptor blends are used. The donor–acceptor interfacial stability changes with time due to either processing conditions or thermodynamic equilibrium [26]. The blend morphology also is affected with oxidation of blend components or the impurities. Sometimes, physical changes occur in active layer, changing the morphology due to thermodynamic instabilities [27].

Degradation of PEDOT: PSS layer is one of the major reasons in the failure of OPVs. The interfacial contact between the PEDOT:PSS and the electrode delaminates due to oxidation and absorption of water vapor [28–31]. Most of the residual oxygen and moisture during processing result in primary damage [25]. Mechanical stresses develop due to the bending/handling of solar modules. Hotspots were also evident in some cases resulting in electrical stresses. These stresses result in variation in the performance of the flexible devices [32–34].

As all the above discussed factors affecting the lifetime performance of the device are interlinked, it is difficult to clearly determine the actual degradation mechanism. In order to choose an appropriate encapsulant for the organic photovoltaic device, it is required to understand the cause for degradation and its mechanism. Internal factors affecting the performance of these devices include interfacial stability, active layer, and morphology which could be overcome by appropriate design and engineering of the device. The external factors are related to the ingress of moisture, oxygen, and UV radiation. The detrimental effects due to external factors can be subdued if the OPV device is encapsulated by an ultra-high barrier material. The barrier coating/composite/layered film used for device encapsulation must be able to restrict the diffusion of permeating molecules through the barrier material which initiate/increase the intrinsic/extrinsic degradation and filter UV light.

Fig. 2 Basic schematic of encapsulated photo electrode for water splitting reaction



The semiconductor photoelectrodes (schematic given in Fig. 2), photosensitive dyes (synthetic pigments and complexes), and other nano materials used for photocatalytic water splitting are prone to degradation either due to UV radiation or environmental deterrents. Hence, a suitable non-corrosive (on exposure to electrolyte), nonconducting, highly transparent barrier material is required for encapsulation of the device [35, 36].

4 Encapsulation of Solar Devices

The major applications of solar devices involve conformal coatings, battery charging, and solar lighting for domestic applications, automobile applications, as well as wireless instrumentation applications and wearable power devices on clothing, unmanned aerial vehicles for defense applications. Therefore, the barrier material should possess some of the crucial properties which help the effective functioning of these devices to be used in the previously discussed specific applications:

1. *Flexibility*: Encapsulant material must be flexible enough, along with the device substrate without the formation of cracks
2. *Hermetic*: It must be possible to seal the device completely isolating from external environment, protecting from external deterrents of degradation like O_2 , H_2O , chlorofluorocarbons, and UV light
3. *Ultra low gas permeability*: The encapsulant should provide sufficient barrier to penetrating gases like oxygen and moisture
4. *Stability*: The encapsulant must be dimensionally, chemically (non-corrosive), thermally, and electrically stable
5. *Ease of processing*: Processing compatibility with the final product for integration is a major requirement in terms of energy and economy minimization

Hence, in order to satisfy these specific requirements various organic and inorganic materials are being investigated for their use as encapsulants. As the present conventional methods cannot measure below 10^{-4} g/m²/day for WVTR, suitable techniques for determining ultra low permeabilities have to be explored.

5 Characterization of Barrier Properties of Encapsulants

Available techniques to determine WVTR through the barrier films are discussed in this section:

1. Gravimetric-based technique
2. Capacitance/resistance/coulometric moisture sensor-based measurement
3. Tritium-based radioactive technique
4. Optical/electrical calcium degradation test
5. Spectroscopy-based techniques

1. *Gravimetric-based technique*: ASTM E96/E96M–12 technique includes two basic methods, the desiccant method and the water method. The sample to be tested is placed in between two cells with different humid conditions in both the cases. The variation is in the service conditions on the high humidity (wetted) and the low humidity sides of the specimen. In the desiccant method, the sample is sealed on the top of the test cell with a dry desiccant and the setup is placed in a controlled humid environment. Anhydrous calcium chloride is used as the desiccant. Periodically, the weight of the desiccant is determined to measure the WVTR through the sealed test cell. In the water method, the test cell contains distilled water instead of the desiccant and the periodic weights determine the WVTR through the specimen from the water to the controlled atmosphere [37, 38].

In ASTM E398–03 dynamic relative humidity method, the sample is mounted between two chambers with variation in humidity. After conditioning and isolation of the chamber, the rate at which the transmission of moisture increases is measured within the relatively lower relative humidity chamber over a predetermined range of interest. This rate is further compared to the WVTR of a calibration sample, which is calibrated gravimetrically initially to determine the WVTR of the barrier sample [39]. In another method, the dried sample film is placed in a controlled humid environment and then transferred to the test cell which is equipped with a halogen lamp. The heating of the sample releases moisture and the amount is measured gravimetrically [40]. However, these techniques based on gravimetry cannot be used for reliably for determining WVTRs below 1 g/m²/day.

2. *Capacitance/resistance/coulometric moisture sensor-based measurement*: In this technique, the sample is placed in between two chambers of a test cell with different, controlled humid environments. The water vapor is transmitted through the sample due to the relative difference in pressure or concentration of humidity on either side of the sample film. Thus, the WVTR from higher humid condition to lower humid condition is sensed by using a capacitive/resistive/coulometric-based

humidity measurement sensor. Even when the initial sensitivity of the sensors is good, the saturation of these sensors due to oxide layer formation cannot fulfil long time accurate measurements [41–43]. In commercialized techniques like MOCON, Permatran, and Aquatran techniques, coulometric sensors are used where the change in concentration of the analyte is used for sensing. Theoretical limits of measurement are very low but practical values of about $\sim 10^{-3}$ g/m²/day have only been achieved till date.

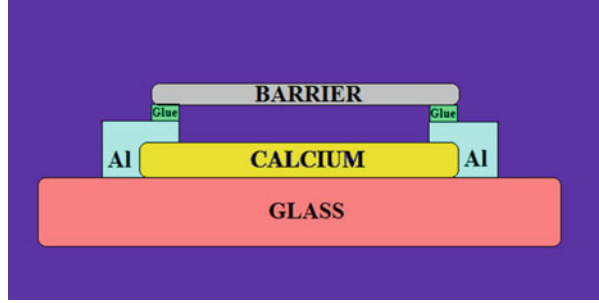
3. *Tritium-based radioactive technique*: In this technique, H₂O doped with Tritium is used on one side of the test material. The transmitted HTO is monitored with time to determine the WVTR. Two methods are used for quantification of HTO. The permeated HTO is swept with a carrier gas to an ionization chamber. In the other case, HTO is collected by a hygroscopic salt and then analyzed for the tritium concentration by scintillation. Though these radioactive-based techniques can be used for WVTRs in the range of $\sim 10^{-6}$ g/m²/day, they are not economical, environmental friendly and it is not possible to differentiate the signals due to permeated elemental tritium and HTO [44].

4. *Optical/electrical calcium degradation test*: In the calcium degradation test to determine the WVTR, calcium is deposited onto a clean, highly impermeable substrate like glass. Stable metal electrodes like aluminum, silver, or gold are deposited to provide electrical contact for measuring the resistance of calcium, as shown in the schematic. Then the calcium on the substrate is sealed with the sample barrier films to be tested using a sealant/glue over the edges. The sealed calcium-based moisture sensing device is placed in an environmental chamber with controllable temperature and humidity. The water vapor permeates through the barrier film and reacts with calcium deposited on the substrate. This results in the change of optical transmittance, as determined from optical microscopy and an increase of resistance (R) which can be measured as a function of time (t) using a programmable digital multimeter. When calcium reacts with moisture, the thickness of calcium deposited decreases with time, when uniform surface oxidation of the calcium thin film is assumed. Hence the measured transmittance/resistance of calcium film varies with time as it gets oxidized and this change in optical/electrical property is correlated to the change in thickness, which further gives the value of WVTR [45, 46].

In optical calcium degradation test, optical images are saved periodically using an optical microscope from which oxidized areas are estimated. Quantification based on visual analysis cannot be as exact as in the electrical calcium test (Fig. 3).

In electrical calcium degradation test, the change in thickness results in change of resistance which gives the amount of calcium reacted [47]. The resistivity of calcium (ρ) is independent of calcium film thickness only above 100 nm [48]. Hence, the change in resistance, over the calcium thickness variation from an initial thickness of h to 100 nm is used for calculation. As one molecule of calcium can react with two molecules of H₂O forming Ca(OH)₂, the water vapor permeated through the barrier film over calcium is determined using Eq. (2) where molecular weight of water is $M_{\text{H}_2\text{O}}$ (18) and that of calcium is M_{Ca} (40). If the

Fig. 3 Schematic for calcium degradation test



density of calcium is ∂ for a film thickness of h , with deposition area being $l \times b$, the WVTR through the sealed barrier film is given by:

$$\text{WVTR} = -2 \frac{M_{\text{H}_2\text{O}}}{M_{\text{Ca}}} \partial \rho \left(\frac{1}{b} \right) \frac{d(1/R)}{dt} \quad (1)$$

WVTR in the range $\sim 10^{-5}$ g/m²/day can be determined using this method. However, the assumption of uniform oxidation of calcium, permeability through the glue used for sealing and constant resistivity of calcium, which changes with film thickness, limit the long-term testing of the material for barrier property.

5. *Spectroscopy-based techniques*: In infrared sensor-based technique, ASTM F1249–06, the dry side is separated from the wet side of the test chamber both of which are under controlled conditions of temperature and humidity by the sample barrier material to be tested. The water vapor passing through the sample film from wet to dry side of the diffusion cell is carried to a pressure-modulated infrared sensor. The fraction of infrared energy absorbed by the water vapor is measured by the sensor and an electrical signal is produced, whose amplitude is proportional to water vapor concentration. This amplitude is then compared to the signal produced by the initial measurement of a calibration film of known WVTR, from which the value of transmission rate is determined for the sample film [49]. WVTR values up to 10^{-3} g/m²/day have been determined using this method.

In mass spectroscopic-based measurement technique, the sample to be tested is mounted onto a diffusion cell where both sides of the film are evacuated. One side of the sample is exposed to a constant flow of water vapor at constant pressure. The water vapor permeated through the film is swept by inert flow gas to a gas chromatogram for water vapor quantification [50, 51]. Even though the lower limit of detection for WVTR is $\sim 10^{-6}$ g/m²/day, the system is complex (with leak-free chambers) and is not economical.

Oxygen transmission rate: There are three major techniques by which oxygen permeated through the barrier film material can be determined:

1. Coulometric-based technique
2. Calcium degradation test
3. ASTM 3985

1. *Coulometric-based technique*: OTR is primarily determined by using a coulometric sensor similar to the procedure discussed previously for determining WVTR. This method can be used by following two procedures; one is a manometric method where pressure difference is maintained and the other is a volumetric method where concentration difference is maintained with no difference in total pressures on either side of the film [52].

2. *Calcium degradation test*: The setup for calcium degradation test is the same as used for WVTR determination. Instead of placing the sealed calcium device in a humid environment, it is placed in oxygen environment with controllable humid conditions. The change in resistance gives the amount of calcium reacted with oxygen which finally gives OTR through the sealed test film [46].

$$\text{WVTR} = -0.5 \frac{M_{\text{O}_2}}{M_{\text{Ca}}} \partial \rho \left(\frac{1}{b} \right) \frac{d(1/R)}{dt} \quad (2)$$

3. *ASTM 3985*: This method is for determining oxygen vapor barrier measurement of flexible materials, which is under validation by ASTM. It is very similar to the ASTM 1249 method and apparatus as previously discussed except that it has a micro fuel cell with oxygen sensor instead of humidity sensor [53].

5.1 Materials for Encapsulation

In order to design the encapsulant requirement for organic-based devices, basic differences between the permeation mechanisms through organic and inorganic materials must be discussed. The inorganic thin film materials offer high barrier towards permeant penetration. The presence of defect sites and the pin holes in the homogeneous thin film provide the pathway for the penetrant. But in the case of organic materials like polymers, permeation of gases/vapors follows standard mechanism of solution-diffusion. The permeant first gets adsorbed onto the surface and then dissolve in the polymer matrix. The available free volume between the molecular chains, provide the pathway for diffusion of the dissolved permeant. Then the permeant is desorbed on the other end of the polymer.

Therefore, defect-free inorganic thin films materials are brittle, and are not crack resistant even though they offer high barrier towards moisture permeation. Organic polymer encapsulants are suitable in terms of flexibility, processability, and conformability. But the permeation rates of gases through polymers are quite higher. Hence, a combination of both organic and inorganic materials has been the choice to meet the requirement of flexibility as well as high gas barrier in multilayered architecture as it provides redundancy and tortuosity. Various approaches for organic solar device encapsulation by single layered/curing/composite/multilayered films, etc. have been used by various research groups.

Hence, alternate coatings of inorganic and organic materials have been chosen as an apt solution for retaining the barrier property of inorganic material as well as the flexibility and crack resistance of organic material. The inorganic oxides were coated onto polymeric substrates by either physical or chemical vapor deposition techniques in layer-by-layer method to achieve ultra low permeabilities. In this technique, the base film surface quality is critical for inorganic oxide deposition to achieve defect-free thin film and much higher barrier.

1-(3-methoxycarbonyl) propyl-1-phenyl[6,6]C61 (PCBM)-based solar cells were encapsulated using a flexible and transparent poly(ethylene naphthalate) (PEN)-based ultra-high barrier material which is fabricated by plasma enhanced chemical vapor deposition (PECVD). Five inorganic and organic bilayers, SiO_x and PECVD-deposited organosilicon, were grown sequentially on the PEN film, which resulted in about 500 nm thick layer. This encapsulation raised the shelf lifetime by 50 % of the initial efficiency of solar cells from tens of hours to beyond 3,000 h [54]. Barrier material based on alternate coatings of polyacrylate/ Al_2O_3 was used for organic device encapsulation. It followed a multistep process where organic monomer is flash evaporated, cured by incident UV radiation and then coating of inorganic material on organic layer by reactive sputtering. A WVTR of 2×10^{-6} g/m²/day at 20 °C and 50 % RH was achieved from calcium degradation test of the barrier material [55, 56]. Similarly in another work, barrier material was fabricated by atomic layer deposition (ALD) of Al_2O_3 onto a PEN substrate, which showed a WVTR of 1.7×10^{-5} g/m²/day at 38 °C and 85 % relative humidity (RH) [57]. $\text{SiO}_x/\text{Al}_2\text{O}_3$ /parylene layers were used for device encapsulation where WVTR was found to be $\sim 10^{-5}$ g/m²/day [58]. Series of organic and inorganic layers were used in Barix™, Vitex technology, assuming the offset of defects due to the presence of organic layer over inorganic oxides [59]. Hermenau and group used different encapsulations for small molecule organic solar cells and observed that a loss of 50 % of initial efficiency is observed when 0.01 g/m² water entered the device either through the encapsulant or the electrode. PET with 245 nm sputtered ZTO had shown the better performance next to the glass-encapsulated device [60].

Diamond like amorphous carbon was used by high energy sputter deposition along with silicon and oxygen over polymer substrates with multilayered architecture for encapsulating organic devices [61]. Polymer multilayered stacks were used along with nitride, oxide, and oxy-nitride layers over a PET substrate for achieving WVTR < 0.005 g/m²/day [62]. Deposition of inorganic oxides like SiO_2 , AlO_x by techniques like ALD, thermal co-evaporation, sputtering, PECVD techniques can be used for OPV encapsulation, as discussed above. Defects caused by particles and surface imperfections were found to have major detrimental effect on the barrier properties in such multilayered coatings [63]. A model was proposed for defect-mediated permeation in oxide-coated gas barrier films. This model accounts for diffusion through the amorphous inorganic oxide lattice, nano-defects within the lattice, and macro-defects. Even though no defects could be detected from microscopic measurements, the permeation data through the barrier films indicate the presence of defects. It was estimated that macro-defects (>1 nm), nano-defects (0.3–0.4 nm), and the lattice interstices (<0.3 nm) exist in such coatings and all of

them contribute to the total permeation [64]. However, due to the presence of pinholes and defects in these inorganic layers, they could not suffice the need for ultra low permeable material. Moreover, the deposition techniques are quite expensive and lack scalability. Hence, alternate materials with simplified, economic processing methodology are still a major requirement.

Polymer nanocomposites and blends are used as conventional encapsulants in food and pharmaceutical industries. But they are not sufficient for being used for organic solar device encapsulation. Generally various inorganic micro- and nano fillers are used in the polymer to increase the permeation pathway. As the permeation through polymers follows the solution-diffusion mechanism, the choice of the matrix polymer and the filler material determines the solubility of H_2O in the composite and the geometry of the filler determines the diffusion pathway. Moreover, the filler and polymer can be chosen in such a way that would decrease the free volume available for permeant penetration through the composite if they interact favorably. Nano platelet-structured morphologies of the fillers with parallel orientation to the film in the composite would provide more tortuous pathway for the permeant to penetrate. Generally composites are prepared by solution casting, blending, or in situ polymerization techniques, which are more energy intensive as compared to physical and chemical vapor deposition, sputtering-based encapsulation techniques. Further, various composite films can be used in multilayered architecture to achieve further reduction in permeability.

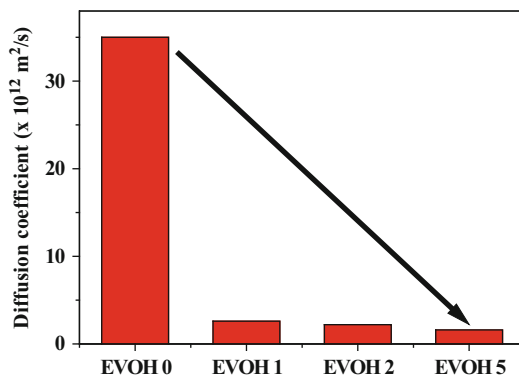
The optimization of sodium-montmorillonite clay (MMT-Na) content in poly (vinyl alcohol) (PVA) nanocomposite to obtain the properties required for organic solar cell encapsulation was discussed. These nanocomposites were fabricated by following an environmentally friendly processing of aqueous solution by casting technique. The nanocomposite layer was used for encapsulating organic solar cells and the increased device stability was observed [65]. Saran-based boron nitride nanotube composites were reported as barrier material for OPV devices [66].

Functionalized acrylic UV curable hard coat materials with silane functionalized silica particles were discussed for solar cell encapsulation with a WVTR of 10^{-1} g/m²/day [67]. The use of polyurethane as encapsulant for polymer solar cells has been explored in eight different countries in different weather conditions. Reduction in degradation of the performance of solar device was observed. The average efficiencies with at least 40 % of the initial values were observed up to 4½ months of outdoor exposure [68].

Polymer nanocomposites were fabricated using SiO_2 , Al_2O_3 , and ZnO as filler materials in different polymer matrices for their use as OPV encapsulants. Nano SiO_2 and Al_2O_3 were functionalized by coupling with different siloxane functional groups to increase the compatibility with the polymer [69–71]. PVA/ZnO-based composite was optimized for barrier property from calcium degradation test and organic device encapsulation results. Encapsulation with this optimized composite material improved the device lifetime by four times compared to the lifetime of non-encapsulated organic device [72].

The presence of interactions between the filler and the polymer results in better compatibility and decreases the free volume availability in polymer composites.

Fig. 4 Decreasing trend of coefficient of diffusivities for water vapor through the neat polymer (EVOH 0) and composite (EVOH 1, 2, 5 compositions represent 1, 2, and 5 wt% of MMT in EVOH, respectively) films



Filler materials like clays with platelet geometry offer longer diffusion pathway to the permeant through the polymer than compared to one dimensional fillers. Clays are arranged as stacked sheets and hence the gallery spacing between the layers determine the diffusion pathway. When they are intercalated or exfoliated, the gallery spacing between the sheets increase and thus provide a more tortuous pathway to the penetrant through the polymer composite. Therefore, gallery spacing is higher in organically functionalized clays.

Poly (ethylene-co-vinyl alcohol) (EVOH)-based nanocomposite barrier films with dispersed montmorillonite clay surface modified with octadecylamine (15–35 wt%) and aminopropyltriethoxysilane (0.5–5 wt%) (MMT) were fabricated by solution casting technique. Due to the hydrogen bond and van der Waals interactions in the EVOH/MMT composite, helped forming a strongly interacting composite decreasing the available free volume for permeation and increasing the permeation barrier. The coefficient of diffusion for water vapor as determined from calcium degradation test decreased by more than one order for the composite material than that of the neat polymer (Fig. 4). These EVOH/MMT composite films exhibited WVTR in the order of $10^{-3} \text{ g/m}^2/\text{day}$. Moreover, the composite-encapsulated P3HT-based Schottky devices exhibited lifetimes that were ten times higher than the neat polymer-encapsulated devices [73].

Blending of two different polymers can be devised effectively to attain high barrier material. Two copolymers, namely poly (ethylene-co-methacrylic acid) (PEMA) and EVOH were melt blended with PEMA as the base component. Both the copolymers used for blending are capable of forming hydrogen bonds with permeating H_2O molecules. This helps in providing a strongly interacting environment for water molecules. The blend of ionomer and copolymer is compatible, because of the electrostatic interactions as well as hydrogen bonding, resulting in an interacting complex blend. These interactions decreased the free volume available for permeation (Fig. 5). Moreover, the theoretical molecular dynamics simulations have shown that the intersegmental motion of the polymer chains decreased in case of the blend system compared to that observed in the neat system. Hence, these blend films showed much lower permeability values (Fig. 6) towards moisture with WVTR of $10^{-4} \text{ g/m}^2/\text{day}$ than the neat polymer films. The diffusivity of H_2O

Fig. 5 Occupiable free volume of a unit cell of $340 \text{ \AA}^3$ for the neat PEMA and the blend system (10 wt % of EVOH in PEMA) with different solvent probe radii as determined from molecular dynamics simulations

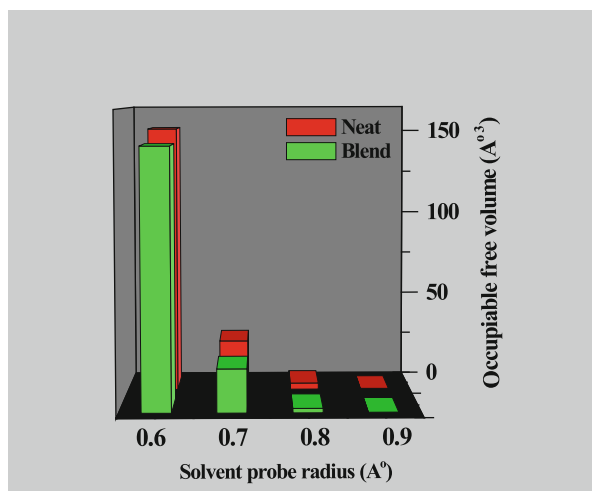
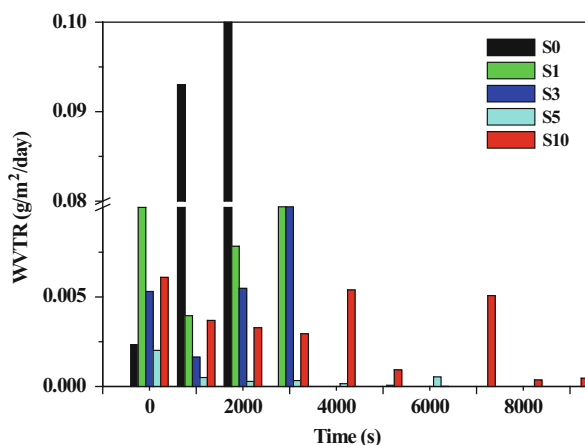


Fig. 6 WVTR for the neat PEMA (S0) and blend films (S1, 3, 5, 10 represent 1, 3, 5, and 10 wt% of EVOH in PEMA, respectively) calculated from calcium degradation test



decreased in the case of blend composition as determined from molecular dynamics simulations. The lifetimes of the encapsulated P3HT (also used in solar cells)-based Schottky organic devices increased by more than 20 times compared to the bare device [74].

Though, polymer-based composites and blends could not satisfy the barrier property as a single layer, the barrier property could further be improved when used as multilayered films. Moreover these organic-based encapsulants fabricated by simple processing techniques by casting, blending, etc. offer better economic solution as well as scalability for roll processing as compared to inorganic atomic layer, chemical vapor deposition techniques. Theoretical understanding and practical characterization of the interactions between the filler and the matrix in the

composite at the atomistic level would provide a better solution to design the barrier material satisfying all the requirements of an encapsulant for organic devices.

Sputter-deposited TiO_2 has been used as the transparent encapsulant for photoelectrode in solar-based water splitting application. Due to the change in potentials of the TiO_2 surfaces, oxygen evolution and other active corrosion reactions were observed. Hence, it was replaced with Master Bond polymer system EP39-2, a transparent epoxy polymer, which was designed specifically for electronics packaging application. It was found that it has good stability in KOH and was compatible with traditional printing techniques [75]. It can be conformally coated onto the planar photoelectrode structure, as required for water splitting applications. Therefore, polymeric encapsulants must be suitable for photoelectrode encapsulation application over inorganic materials.

6 Conclusions

The effective working of the solar photovoltaic device requires an effective encapsulant layer for protecting it from detrimental factors. The efficient functioning of the photoelectrodes used in solar-based water splitting technologies requires a non-corrosive, stable encapsulant. Of the various materials that have been explored so far, while some exhibit sufficient barrier to WVTR, they are difficult to process and are not economical. Therefore, various materials that are potential encapsulants are discussed. The characterization of the barrier property for WVTR and OTR is another issue for designing encapsulant materials with ultra-high barrier. Various techniques that are available for determining WVTR and OTR are discussed.

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