

RISING THE MOLECULAR MOBILITY OF POLYVINYL BUTYRAL BY PLASTICIZERS: TOWARDS ENERGY STORAGE APPLICATIONS

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ABSTRACT. The versatile behaviour of poly-vinylbutyral (PVB) and its ability to form quasi-solid polymer electrolytes (SPE) with reliable ionic mobility, has been investigated over the temperature range from 120 K to 350 K, by mechanical and dielectric spectroscopic measurements. Enhancements in the polymer chain flexibility, due to the addition of low molar mass organic liquid plasticizers (acetonitrile, AcN, and methoxy-propionitrile, MPN) favouring the long-range motion of charge carriers, give rise to a room temperature ionic conductivity which in the hybrid PVB/MPN/LiI system increases of about 3 and 9 orders of magnitude with respect to the counterparts PVB/LiI and pure dry-PVB system, respectively. This result proves the existence of coupling between cooperative segmental motion and ion dynamics in such kind of materials.

1. Introduction

The pressing demand for a green electric power production together with the awareness of the finite supply of fossil fuels has aroused the need to explore alternative sources (*i.e.*, geothermal, wind, solar, etc.) to gain advances in the field of energy consumption and development of suitable storage systems. In this framework, solid-state devices based on solid-polymer electrolytes (SPEs) have been one of the hottest topics in the field of energy-storage research due to the several advantages they offer: (i) the exclusion of liquid electrolyte leakage, (ii) improvement of safety, (iii) reliable enhancement of energy/power densities, (iv) good mechanical strength and high chemical/thermal stability and (iv) potential application in flexible electronics.

Based on the discovery of ionic conduction in poly-ethylene oxide (PEO) by Wright (1975), and its first application to batteries by Vashishta *et al.* (1979) and Armand (1983), SPEs have been largely investigated as a safety-improving solution for energy storage applications and photoelectrochemical and electrochromic devices (Agrawal and Pandey 2008). Solid-polymer electrolytes comprise a polymeric thin film (*i.e.*, PEO (Li *et al.* 2011), polyvinylidene fluoride (PVDF) (Li *et al.* 2011), polymethylmethacrylate (PMMA) (Zhang *et al.* 2007) dissolving an inorganic salt (*i.e.*, NaSCN, LiI, etc.) with the host polymer acting as an immobile solvent.

Good SPEs require host polymers characterized by polar functional groups with electron donor character able to interact with alkaline cations, together with low molecular hindrances to allow chain conformational changes (bond rotation). On the other hand, inorganic alkaline salts with polarizing cations, large anions, well-delocalized charge and low lattice energy are additional further critical needs. In a such kind of structural arrangement that preserves the macroscopic mechanical features of a solid, at molecular level the polymer cooperative relaxation (α -relaxation) processes provide a liquid-like behaviour which assists the fast-ionic mobility. Thus, the ionic conductivity of the overall system will be the result of a coupling between the ions mobility as well as the polymer chain segmental motion. In this context, an enhancement of polymer amorphous phase with dissolved salt paired to an appropriate glass transition temperature (T_g) and a low crystallinity degree (χ_c) are to be preferred (Bartolotta *et al.* 2010). Many valuable investigations have focused primarily to lower the polymer T_g or to reduce its χ_c via various approaches such as blending (Baskaran *et al.* 2006; Li *et al.* 2018)], copolymerization [(Higa *et al.* 2010) and plasticization (He and Kyu 2016), the latter appearing the most simple, economic and effective viable processing route.

Plasticization can be achieved by: (i) the addition of side chains which, make weaker the inter-chain interactions due to hindrances induced by the additional substituent groups (internal plasticization) and promote the rise of extra free volume in the polymeric matrix, (ii) by the addition of low molecular weight compounds with low vapor pressure which interact with the polymer matrix by means of their solvent or swelling power (Immergut and Mark 1965). Generally, larger plasticizer molecules show lower vapor pressure (volatility) and greater permanence in the plasticized system. Usually, the depression of polymer's T_g is used as reliable tool to evaluate the plasticizer's efficiency (Immergut and Mark 1965).

In this study, we investigate the influence of acetonitrile (AcN) and methoxy-propionitrile (MPN), as liquid plasticizers of polyvinyl butyral (PVB) polymer films to produce a PVB/plasticizer/LiI electrolyte as potential candidates for photoelectric/photovoltaic applications (Aricò *et al.* 2005; Yang *et al.* 2008; Bhattacharya *et al.* 2009; Park *et al.* 2011). In particular, they will be used in dye sensitized solar cells (DSSCs), a type of photo-electrochemical devices inspired by the energy and electron transfer mechanisms in natural photosynthesis (McConnell *et al.* 2010).

Dye sensitized solar cells have attracted widespread interest as a credible alternative solution to mitigate the environmental and manufacturing issues associated with more conventional silicon based photovoltaic technologies. Typically, they consist of a mesoporous photoanode with dye-sensitized conducting oxide film, (Villamagua *et al.* 2015, 2017; Tehare *et al.* 2018), an electrolyte solution (the liquid conductor) and a counter electrode (Carini Jr. *et al.* 2015; Sinopoli *et al.* 2017). Unfortunately, the leakage and volatilization of the liquid components rise some technological limits to the device durability and restrict their large diffusion. Replacing the liquid electrolyte with a SPE has been suggested as an effective approach to solving the above-mentioned issues and, in some cases, interesting results have been obtained (Cho *et al.* 2014; Zhang *et al.* 2014; Rokesh *et al.* 2015). Among many polymers able to incorporate both liquid plasticizers and redox mediators in a SPE arrangement, PVB has been regarded as promising candidate for implementation of an ionically conductive polymer, due to its capacity to absorb and hold significant amount of plasticizers preserving a good optical transparency (Chen *et al.* 2013; Jauhari *et al.* 2018).

Polyvinyl butyral is a random copolymer with no apparent crystallinity, synthesized from polyvinyl alcohol and butyraldehyde in acidic medium with minor amount of acetyl moieties and predominant hydrophobic butyral and hydrophilic hydroxyl groups (see Fig. 1), which make it compatible with both hydrophilic and hydrophobic components. The percentage alteration of any monomer component can manipulate hydrophilicity or hydrophobicity of polymer (Zhang *et al.* 2017). Although mainly used as interlayer material in laminate automotive safety glasses to prevent glass fragments and to diminish the UV radiation effects, PVB shows a good capability to solvate inorganic/organic salts via its functional groups to form PVB-salt complexes which preserve the amorphous character of the host polymer and overcome the non-trivial crystallization issues that strongly influence the ionic mobility and the overall SPE performances. Mechanical and dielectric spectroscopic measurements on PVB/AcN and PVB/MPN mixtures provide evidence that these organic liquid plasticizers strongly influence the short- and long-scale segmental motions of the pure PVB, favouring the ion dynamics in hybrid PVB/plasticizer/electrolyte systems with a large enhancement of the room temperature conductivity (σ_{rr}). It has been found that the plasticizer addition keeps unchanged the polymer specific characteristics without any apparent degradation process. In addition, both the primary (α) and secondary (β) relaxations appear at lower temperatures with respect to the pure PVB, with the result of a growing cooperative character of both the processes.

2. Materials and methods

PVB (average Mw 40,000 ÷ 70,000), with about 80 wt% of vinyl butyral, 18 ÷ 20 wt% of vinyl alcohol and 0 ÷ 2 wt% of vinyl acetate, acetonitrile (AcN) and methoxypropionitrile (MPN) were purchased from Sigma Aldrich. Small amount of water (around 1.5%) in the as-received PVB (as-rec PVB) was determined by thermogravimetry analysis (TGA) and removed under vacuum of about 10^{-4} mbar at 318 K for 48 h. Fully dry polymer films (dry-PVB with thickness of 200 ÷ 300 μ m) were kept in an environment of AcN or MPN liquid plasticizers for the time necessary to ensure an equilibrium liquid content (about 36 h), determined by subsequent weighing of the samples until reaching a constant value. The liquid plasticizers content of layers was determined by thermogravimetric analysis (TG) at a constant heating rate of 5 K/min in a Setaram thermogravimetric analyser under a controlled nitrogen atmosphere. The study of thermal stability indicates the temperature range where the materials keep unchanged their specific characteristics without undergoing any degradation process, preserving their optical transparency as a clear evidence of uniform distribution of plasticizers in the host polymer.

The real and imaginary parts of the complex elastic modulus, $E^* = E' + iE''$ (E' and E'' being the storage and the loss moduli, respectively), and the related $\tan(\delta) = E''/E'$ were determined under a controlled nitrogen atmosphere over the temperature range between 120 and 373 K (heating rate: 2 K/min; frequency range 0.1 ÷ 30 Hz) by using a dynamic mechanical thermal analyser driven in bending mode with a fixed displacement ($\pm 20 \mu$ m) [8]. Dielectric permittivity (ϵ') and loss (ϵ'') together with the related $\tan(\delta) = \epsilon''/\epsilon'$ were also investigated over the same temperature interval (heating rate: 2 K/min; frequency range 0.3 Hz ÷ 30 kHz) in non-isothermal condition by using a Rheometric Scientific Dielectric Thermal Analyzer (DETA). Samples with cylindrical shape were sputtered by gold on both

sides for a better electrical contact polymer/capacitance bridge and kept between two plates (platinum electrodes, 30 mm diameter). The measurements were performed by increasing temperature under nitrogen atmosphere. Both mechanical and dielectric experiments have been performed on samples cut from the same layer and having rectangular and cylindrical shapes, respectively.

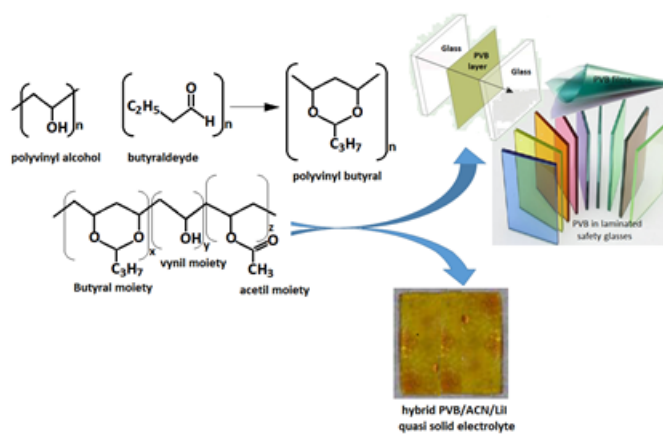


FIGURE 1. Synthesis of Polyvinyl Butyral, from polyvinyl alcohol and butyraldehyde, with illustration of some technological applications

3. Experimental results and discussion

The curves of internal friction $\tan(\delta)$ and storage (E') modulus for dry-PVB, PVB/AcN and PVB/MPN samples, at a selected frequency of 10 Hz, are plotted as a function of temperature in Figs. 2(a) and 2(b). For all the investigated samples, the α -relaxation arising from cooperative segmental motions of the amorphous chains at the glass transition appears at temperatures above 230 K, much higher than those of corresponding sub- T_g relaxation-peaks (β -relaxations). The storage modulus E' exhibits an inflection in the same temperature regions where the β -peaks are observed and a sharp fall, associated to the α -relaxation, at higher temperatures (Fig. 2(b)). Both β and α peaks shift to higher temperatures with increasing frequency (Fig. 3), as expected for thermally activated relaxation processes. Also, the significant temperature decreases of α -relaxation peaks of PVB/AcN and PVB/MPN samples (about 60 K) with respect to dry-PVB show the influence of the plasticizer on the segmental dynamics of the host polymer. In addition, in both PVB/AcN and PVB/MPN samples the β -relaxation strength is substantially larger (about a factor 3) than in dry-PVB, emphasizing a probable cooperative character of the relaxation.

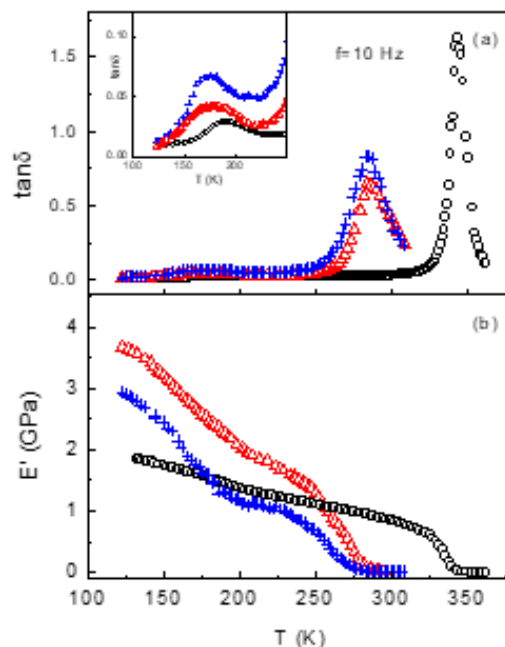


FIGURE 2. Comparison of (a) the internal friction $\tan(\delta)$ and (b) the storage modulus $E'(T)$ in PVB (O), PVB/AcN (Δ) and PVB/MPN (+) polymers at a frequency of 10 Hz. Inset of (a) shows $\tan(\delta)$ below 250 K in an expanded scale

The characteristics of mechanical relaxations, discussed above, are in parallel observed in dielectric measurements. Behaviours of the dielectric loss ($\tan(\delta)$) in dry-PVB and PVB/AcN are reported in Fig. 4, as typical. Observation of single mechanical and dielectric T_g over the explored temperature range indicates that these PVB/plasticizers systems can be regarded as homogeneous amorphous systems. Chain segmental mobility produces free space for alkali ion hopping, essential to promote fast ionic mobility above the polymer's T_g . Plasticizer addition, shifting the polymer T_g below room temperature, gives rise to an acceleration of the polymer backbone mobility, favouring the long-range motion of charge carriers which are cooperatively mobile within the elastic polymer matrix, but locally fluid above T_g . Good SPEs at room temperature require appropriate enhancement of amorphous phase paired to a T_g and a crystallinity degree (χ_c), as low as possible.

Polyvinyl butyral can be thought like a sponge able to keep considerable amount of liquid electrolyte while still remaining solid. In this respect, the plasticizer amount, its compatibility with the dissolved alkali ions as well as the most suitable temperature range for its permanence inside the polymer matrix are critical parameters, determining the SPE properties and its potential applications.

The liquid plasticizer uptake (LU(%)) in the dry polymeric matrix was derived by the relation:

$$\text{LU (\%)} = [(W_0 - W) / W_0]$$

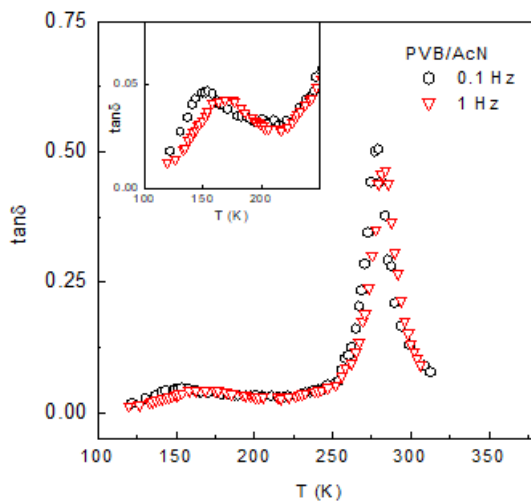


FIGURE 3. Temperature dependence of $\tan(\delta)$ in PVB/AcN polymer at frequencies of 0.1 Hz (O) and 1 Hz (∇). Inset shows $\tan(\delta)$ below 250 K in an expanded scale.

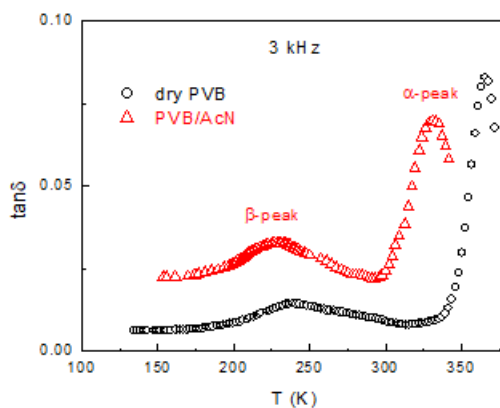


FIGURE 4. Comparison of the dielectric loss $\tan(\delta)$ in PVB (O) and PVB/AcN (Δ) polymers at a frequency of 3 kHz.

where, W_0 and W are the weights of the dry-PVB and PVB saturated with plasticizer (AcN or MPN), respectively. The percentage of desorbed plasticizers as well as their maximum rate of weight loss % were estimated by thermogravimetric analysis over the 298–473 K temperature range. It was found that, while for PVB/AcN the lost liquid is quite close to its LU ($\approx 8\%$), PVB/MPN shows a LU (about 26%) higher of 7% compared to that of the liquid desorbed, suggesting a possible molecular interaction plasticizer/host polymer. In the low temperature region, both mechanical and dielectric β -relaxations follow the same

Arrhenius behaviour, with average activation energies (E_β) and characteristic frequencies (ω_0) quite similar within the same sample (see Fig. 5 and Tab. 1), demonstrating that both the experimental probes are sensitive to the same local motion within the polymer chains.

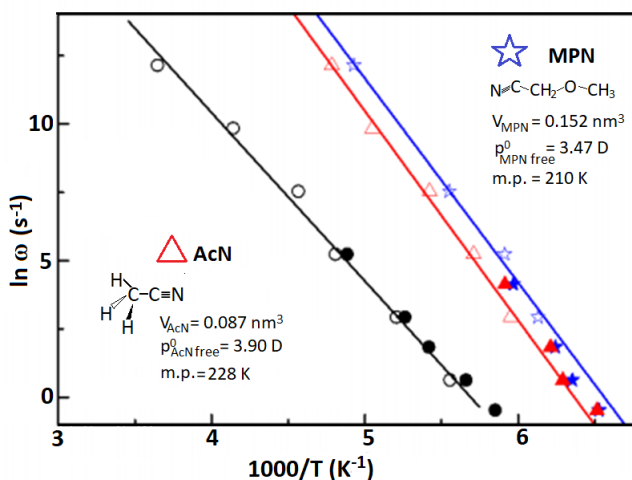


FIGURE 5. Arrhenius plots of mechanical (solid symbols) and dielectric (open symbols) β peaks for dry PVB (o), PVB/AcN (Δ) and PVB/MPN (*). Solid lines represent the linear fits to the data. The molecular structure of plasticizers together with some relevant physical parameters are also included.

Also, in dry-PVB, the obtained E_β and ω_0 values, lead to a quite small activation entropy ΔS^* (about 41 J/Kmol), suggesting very little intermolecular cooperativity of the β -local motion, justified by the small volume required for the rearrangements of the involved molecular units. These local motions which, have been suggested to arise from the $\text{CH-CH}_2\text{-CH}_2\text{-CH}_3$, side polar groups connected by two bridging oxygen atoms to the polymer chains (see the chemical structure of PVB in Fig. 1), are capable of local rotational motions around CH unit, also causing a local torsion of the main chain (Carini Jr. *et al.* 2018).

However, although in the dry-PVB the obtained E_β and ω_0 values lead to a quite small ΔS^* , marked differences with respect to PVB/plasticizer systems appear in the characteristic frequency ω_0 which increases of about 6 orders of magnitude. This result together with the strong decrease of T_g and the increase of the β -relaxation strength (see Fig. 2(a)) discloses a cooperativity in the motion of rearranging structural units. In fact, it is well recognized that high values of ω_0 are indicative of an inter-molecular cooperativity of the β -relaxation (Starkweather 1990), with an activation entropy ΔS^* due to the collective motion of side groups, as explained in the following.

TABLE 1. Average activation energies ($E_{\beta, \text{mech}}$ and $E_{\beta, \text{diel}}$) and characteristic frequencies ($\omega_{0, \text{mech}}$ and $\omega_{0, \text{diel}}$) of mechanical and dielectric β -relaxations of PVB/plasticizers polymers. The values of the activation entropy ΔS^* for both the processes are also included.

Samples	$E_{\beta, \text{mech}}$ (kJ/mol)	$E_{\beta, \text{diel}}$ (kJ/mol)	$\omega_{0, \text{mech}}$ (s ⁻¹)	$\omega_{0, \text{diel}}$ (s ⁻¹)	ΔS_{mech}^* (J/Kmol)	ΔS_{diel}^* (J/Kmol)
Dry-PVB	50.4	51.2	1.23×10^{15}	1.47×10^{15}	40.8	42.3
PVB/MPN	63.7	62.1	4.08×10^{21}	1.95×10^{21}	162.4	158.5
PVB/AcN	63.6	61.7	2.79×10^{15}	1.17×10^{15}	165.7	159.6

The Eyring's theory of absolute reaction rate relates the apparent activation energies E_{β} of relaxation processes to an activation enthalpy ΔH^* and entropy ΔS^* :

$$f = \frac{k_B T}{2\pi h} e^{-\frac{\Delta H^*}{RT}} e^{\frac{\Delta S^*}{R}} \quad (1)$$

The relationship between E_{β} and ΔH^* ($E_{\beta} = \Delta H^* + RT$) can be rearranged to derivate the following equation, which links E_{β} to the peak temperature (T_{peak}) of the mechanical (or dielectric) loss maxima at $f = 1$ Hz

$$E_{\beta} = RT_{\text{peak},1} \left[1 + \ln \left(\frac{k_B T_{\text{peak},1}}{2\pi h} \right) \right] + T_{\text{peak},1} \Delta S^* \quad (2)$$

The obtained values of ΔS^* for both mechanical and dielectric behaviours in PVD/plasticizers systems are reported in Tab.1 and point to the existence of a high degree of cooperativity characterizing the underlying local motions. This feature can be explained by considering that the local rotational motions of dry-PVB side polar groups, become cooperative extending their correlation range to several side groups via the plasticizer molecules which form links between OH polar groups of adjacent chains. The carbon atom of nitrile compounds, such as AcN and MPN (see Fig. 5), is an electrophilic centre, thus it is susceptible to nucleophilic addition reactions with hydroxylate moiety of the polymeric chain ($\text{R}-\text{C}\equiv\text{N}^{\delta-} \text{:} - \text{H}^{\delta+} + \text{O}^-$).

Below 200 K, mechanically stable bridges between plasticizer molecules and vinyl alcohol moieties, give rise to an increase in the modulus which becomes substantially larger in PVB/plasticizers than in dry-PVB. With increasing temperature, the mobility of additive molecules is expected to become growingly larger favouring the large-scale thermal motions of polymer segments via interchain interactions. Interestingly, the higher modulus observed in PVB/AcN than in PVB/MPN could be ascribed to a higher dipolar interaction plasticizer/polymer's active sites, due to both higher dipole moment and lower molecular volume of the former (data reported in Fig. 5).

Finally, in order to test the influence of plasticizer addition on ionic mobility of the polymer/electrolyte system, the room temperature ionic conductivity (σ_{rt}) has been measured in dry-PVB, in PVB/LiI (with a molar ratio 1:3 of PVB:LiI) and in PVB/MPN/LiI

quasi-SPE. The σ_{rt} of prepared films varied from less than 6.4×10^{-14} S/m in dry-PVB, through 1.5×10^{-8} S/m in PVB/Li, to 2.45×10^{-5} S/m in PVB/MPN/LiI.

The prominent increase of σ_{rt} by about 6 orders of magnitude by adding LiI to pure polymer and the significant growth by further 3 orders of magnitude due to the MPN addition, proves the strong coupling between the cooperative segmental motion and the ion dynamics in this kind of polymer electrolytes.

4. Conclusions

Solid polymer electrolytes are playing a critical role in the field of energy storage and/or conversion, where it is imperative to solve the issues linked to the liquid-electrolyte based devices. SPEs have the advantages of eliminating the electrolyte leakage and flammability, thus leading to higher safety. PVB, as robust and cheap polymeric material, has been used to satisfy a wide range of industrial applications, including photovoltaic circuits on glass sheets and electrochemical stable devices (Guinovart *et al.* 2014; Jauhari *et al.* 2018). In this experimental study, plasticized PVB-SPEs have been tested as promising candidates for the development of actual energy storage/conversion devices. Plasticizer addition shifts the polymer T_g below room temperature, enhancing the chain flexibility and the long-range motion of charge carriers. A growing degree of molecular cooperativity due to plasticizers affects both short- and long-scale segmental motions and gives rise to a huge increase of the ionic conductivity σ_{π} .

References

- Agrawal, R. C. and Pandey, G. P. (2008). "Solid polymer electrolytes: materials designing and all-solid-state battery applications: an overview". *Journal of Physics D: Applied Physics* **41**(22), 223001. DOI: [10.1088/0022-3727/41/22/223001](https://doi.org/10.1088/0022-3727/41/22/223001).
- Aricò, A. S., Bruce, P., Scrosati, B., Tarascon, J. M., and Van Schalkwijk, W. (2005). "Nanostructured materials for advanced energy conversion and storage devices". *Nature Materials* **4**, 366–377. DOI: [10.1038/nmat1368](https://doi.org/10.1038/nmat1368).
- Armand, M. (1983). "Polymer solid electrolytes - an overview". *Solid State Ionics* **9-10**, 745–754. DOI: [10.1016/0167-2738\(83\)90083-8](https://doi.org/10.1016/0167-2738(83)90083-8).
- Bartolotta, A., Carini Jr., G., Carini, G., Di Marco, G., and Tripodo, G. (2010). "Subglass Cooperative Mechanical Relaxations and Activation Entropy in Heterocyclic Polymer Networks". *Macromolecules* **43**(10), 4798–4804. DOI: [10.1021/ma100137w](https://doi.org/10.1021/ma100137w).
- Baskaran, R., Selvasekarapandian, S., Kuwata, N., Kawamura, J., and Hattori, T. (2006). "Conductivity and thermal studies of blend polymer electrolytes based on PVAc-PMMA". *Solid State Ionics* **177**(26-32), 2679–2682. DOI: <https://doi.org/10.1016/j.ssi.2006.04.013>.
- Bhattacharya, B., Lee, J. Y., Geng, J., Jung, H.-T., and Park, J.-K. (2009). "Effect of cation size on solid polymer electrolyte based dye-sensitized solar cells". *Langmuir* **25**(5), 3276–3281. DOI: [10.1021/la8029177](https://doi.org/10.1021/la8029177).
- Carini Jr., G., Bartolotta, A., Carini, G., D'Angelo, G., Federico, M., and Di Marco, G. (2018). "Water-driven segmental cooperativity in polyvinyl butyral". *European Polymer Journal* **98**, 172–176. DOI: [10.1016/j.eurpolymj.2017.11.016](https://doi.org/10.1016/j.eurpolymj.2017.11.016).
- Carini Jr., G., Parrino, F., Palmisano, G., Scandura, G., Citro, I., Calogero, G., Bartolotta, A., and Di Marco, G. (2015). "Nanostructured anatase TiO₂ densified at high pressure as advanced visible light photocatalysts". *Photochemical & Photobiological Sciences* **14** (9), 1685–1693. DOI: [10.1039/C5PP00149H](https://doi.org/10.1039/C5PP00149H).

- Chen, K.-F., Liu, C.-H., Huang, H.-K., Tsai, C.-H., and Chen, F.-R. (2013). "Polyvinyl butyral-based thin film polymeric electrolyte for dyesensitized solar cell with long-term stability". *International Journal of Electrochemical Science* **8**, 3524–3539. URL: <http://www.electrochemsci.org/papers/vol8/80303524.pdf>.
- Cho, W., Kim, Y., Song, D., Choi, H., and Kang, Y. S. (2014). "High-efficiency solid-state polymer electrolyte dye-sensitized solar cells with a bi-functional porous layer". *Journal of Materials Chemistry A* **2**(42), 17746–17750. DOI: [10.1039/C4TA04064C](https://doi.org/10.1039/C4TA04064C).
- Guinovart, T., Crespo, G. A., Xavier Rius, F., and Andrade, F. J. (2014). "A reference electrode based on polyvinyl butyral (PVB) polymer for decentralized chemical measurements". *Analytica Chimica Acta* **821**, 72–80. DOI: [10.1016/j.aca.2014.02.028](https://doi.org/10.1016/j.aca.2014.02.028).
- He, R. and Kyu, T. (2016). "Effect of Plasticization on Ionic Conductivity Enhancement in Relation to Glass Transition Temperature of Crosslinked Polymer Electrolyte Membranes". *Macromolecules* **49**(15), 5637–5648. DOI: [10.1021/acs.macromol.6b00918](https://doi.org/10.1021/acs.macromol.6b00918).
- Higa, M., Yaguchi, K., and Kitani, R. (2010). "All solid-state polymer electrolytes prepared from a graft copolymer consisting of a polyimide main chain and poly(ethylene oxide) based side chains". *Electrochimica Acta* **55**(4), 1380–1384. DOI: [10.1016/j.electacta.2009.07.046](https://doi.org/10.1016/j.electacta.2009.07.046).
- Immergut, E. H. and Mark, H. F. (1965). "Principles of Plasticization". In: *Plasticization and Plasticizer Processes*. Ed. by N. A. J. Platzer. Vol. 48. Advances in Chemistry. American Chemical Society. Chap. 1, pp. 1–26. DOI: [10.1021/ba-1965-0048.ch001](https://doi.org/10.1021/ba-1965-0048.ch001).
- Jauhari, H., Grover, R., Gupta, N., Nanda, O., Mehta, D. S., and Saxena, K. (2018). "Solid state dye sensitized solar cells with polyaniline-thiourea based polymer electrolyte composition". *Journal of Renewable and Sustainable Energy* **10**(3), 033502. DOI: [10.1063/1.5019293](https://doi.org/10.1063/1.5019293).
- Li, H., Ma, X.-T., Shi, J.-L., Yao, Z.-K., Zhu, B.-K., and Zhu, L.-P. (2011). "Preparation and properties of poly(ethylene oxide) gel filled polypropylene separators and their corresponding gel polymer electrolytes for Li-ion batteries". *Electrochimica Acta* **56**(6), 2641–2647. DOI: [10.1016/j.electacta.2010.12.010](https://doi.org/10.1016/j.electacta.2010.12.010).
- Li, Y.-J., Fan, C.-Y., Zhang, J.-P., and Wu, X.-L. (2018). "A promising PMHS/PEO blend polymer electrolyte for all-solid-state lithium ion batteries". *Dalton Transactions* **47** (42), 14932–14937. DOI: [10.1039/C8DT02904K](https://doi.org/10.1039/C8DT02904K).
- McConnell, I., Li, G., and Brudvig, G. W. (2010). "Energy Conversion in Natural and Artificial Photosynthesis". *Chemistry & Biology* **17**(5), 434–447. DOI: [10.1016/j.chembiol.2010.05.005](https://doi.org/10.1016/j.chembiol.2010.05.005).
- Park, S.-H., Choi, H.-J., Lee, S.-B., Lee, S.-M., Cho, S.-E., Kim, K.-H., Kim, Y.-K., Kim, M.-R., and Lee, J.-K. (2011). "Fabrications and photovoltaic properties of dye-sensitized solar cells with electrospun poly(vinyl alcohol) nanofibers containing Ag nanoparticles". *Macromolecular Research* **19**(2), 142–146. DOI: [10.1007/s13233-011-0212-6](https://doi.org/10.1007/s13233-011-0212-6).
- Rokesh, K., Sambandam, A., and Jothivnkatachalam, K. (2015). "Polymer Electrolytes in Dye Sensitized Solar Cells". *Materials Focus* **4**(4), 262–271. URL: <https://www.ingentaconnect.com/contentone/asp/mf/2015/00000004/00000004/art00002>.
- Sinopoli, A., Citro, I., Calogero, G., and Bartolotta, A. (2017). "Combined experimental and DFT-TDDFT investigation on anthocyanidins for application in dye-sensitized solar cells". *Dyes and Pigments* **143**, 291–300. DOI: [10.1016/j.dyepig.2017.04.018](https://doi.org/10.1016/j.dyepig.2017.04.018).
- Starkweather, H. W. (1990). "Distribution of activation enthalpies in viscoelastic relaxations". *Macromolecules* **23**(1), 328–332. DOI: [10.1021/ma00203a056](https://doi.org/10.1021/ma00203a056).
- Tehare, K. K., Navale, S. T., Stadler, F. J., He, Z., Yang, H., Xiong, X., Liu, X., and Mane, R. S. (2018). "Enhanced DSSCs performance of TiO₂ nanostructure by surface passivation layers". *Materials Research Bulletin* **99**, 491–495. DOI: [10.1016/j.materresbull.2017.11.046](https://doi.org/10.1016/j.materresbull.2017.11.046).
- Vashishta, P., Mundy, J. N., and Shenoy, G. K., eds. (1979). *Fast ion transport in solids, electrodes and electrolytes. Proceedings of the International Conference on Fast Ion Transport in Solids*,

- Electrodes, and Electrolytes, Lake Geneva, Wisconsin, U.S.A., May 21-25, 1979.* New York: North-Holland.
- Villamagua, L., Rivera, R., Castillo, D., and Carini, M. (2017). “A quantum chemical analysis of Zn and Sb doping and co-doping in SnO₂”. *AIP Advances* **7**(10), 105010. DOI: [10.1063/1.4999014](https://doi.org/10.1063/1.4999014). eprint: <https://doi.org/10.1063/1.4999014>.
- Villamagua, L., Stashans, A., Lee, P.-M., Liu, Y.-S., Liu, C.-Y., and Carini, M. (2015). “Change in the electrical conductivity of SnO₂ crystal from n-type to p-type conductivity”. *Chemical Physics* **452**, 71–77. DOI: [10.1016/j.chemphys.2015.03.002](https://doi.org/10.1016/j.chemphys.2015.03.002).
- Wright, P. V. (1975). “Electrical conductivity in ionic complexes of poly(ethylene oxide)”. *British Polymer Journal* **7**(5), 319–327. DOI: [10.1002/pi.4980070505](https://doi.org/10.1002/pi.4980070505).
- Yang, H., Huang, M., Wu, J., Lan, Z., Hao, S., and Lin, J. (2008). “The polymer gel electrolyte based on poly(methyl methacrylate) and its application in quasi-solid-state dye-sensitized solar cells”. *Materials Chemistry and Physics* **110**(1), 38–42. DOI: [10.1016/j.matchemphys.2008.01.010](https://doi.org/10.1016/j.matchemphys.2008.01.010).
- Zhang, F., Dong, G., Liu, J., Ye, S., and Diao, X. (2017). “Polyvinyl butyral-based gel polymer electrolyte films for solid-state laminated electrochromic devices”. *Ionics* **23**(7), 1879–1888. DOI: [10.1007/s11581-017-1996-y](https://doi.org/10.1007/s11581-017-1996-y).
- Zhang, H. P., Zhang, P., Li, Z. H., Sun, M., Wu, Y. P., and Wu, H. Q. (2007). “A novel sandwiched membrane as polymer electrolyte for lithium ion battery”. *Electrochemistry Communications* **9**(7), 1700–1703. DOI: [10.1016/j.elecom.2007.03.021](https://doi.org/10.1016/j.elecom.2007.03.021).
- Zhang, H., Ma, X., Lin, C.-E., and Zhu, B. (2014). “Gel polymer electrolyte-based on PVDF/fluorinated amphiphilic copolymer blends for high performance lithium-ion batteries”. *RSC Advances* **4**, 33713–33719. DOI: [10.1039/C4RA04443F](https://doi.org/10.1039/C4RA04443F).

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