Hybrid Organic-Inorganic Materials and Interfaces With Mixed Ionic-Electronic Transport Properties: Advances in Experimental and Theoretical Approaches

Mariano Romero*, Dominique Mombrú, Fernando Pignanelli, Ricardo Faccio* and Alvaro W. Mombrú*

Centro NanoMat & Área Física, Departamento de Experimentación y Teoría de la Estructura de la Materia y Sus Aplicaciones (DETEMA), Facultad de Química, Universidad de la República, Montevideo, Uruguay

The main goal of this mini-review is to provide an updated state-of-the-art of the hybrid organic-inorganic materials focusing mainly on interface phenomena involving ionic and electronic transport properties. First, we review the most relevant preparation techniques and the structural features of hybrid organic-inorganic materials prepared by solution-phase reaction of inorganic/organic precursor into organic/inorganic hosts and vapor-phase infiltration of the inorganic precursor into organic hosts and molecular layer deposition of organic precursor onto the inorganic surface. Particular emphasis is given to the advances in joint experimental and theoretical studies discussing diverse types of computational simulations for hybrid-organic materials and interfaces. We make a specific revision on the separately ionic, and electronic transport properties of these hybrid organic-inorganic materials focusing mostly on interface phenomena. Finally, we deepen into mixed ionic-electronic transport properties and provide our concluding remarks and give some perspectives about this growing field of research.

Keywords: organic-inorganic hybrid, mixed ionic and electronic conducting, sol-gel—alkoxide route, computational modeling, polymer nano composite

TAXONOMY AND DEFINITIONS

Hybrid materials were previously defined by the IUPAC (International Union of Pure and Applied Chemistry) as materials composed of an intimate mixture of inorganic components, organic components, or both types, which usually interpenetrate on scales of less than 1 μm (Alemán et al., 2007). This definition excludes large-sized components for which the term composite is usually used in the literature, but does not exclude those named as nano-composites (with at least one component exhibiting at least one of its dimensions in the nanoscale) which, in practice, is also considered in the previous hybrid material definition. Then, the term hybrid organic-inorganic (hOI) materials refer to multi-component compounds having at least one of their organic or inorganic component in the sub-micrometric and, more usually, in the nano-metric size domain (Judeinstein and Sanchez, 1996). hOI materials can be classified into two classes named Class I (when organic and inorganic phases interact weakly via Van der Waals, hydrogen bonding, or electrostatic interactions)
and Class II (when organic and inorganic phases interact strongly via chemical bonding interactions), without excluding those interacting simultaneously via both types of interactions (Class I and II) (Judeinstein and Sanchez, 1996). Although the previous definitions are more general, in the vast literature hOI materials refer mostly to polymers as organic material and metal oxide compounds as inorganic materials. The term hybrid organic-inorganic polymers has also been used in the literature mostly referring to organic polymers and inorganic materials blended by mutual dispersion at molecular dimensions (Schmidt, 1992; Saegusa, 1995). This terminology can be useful as it excludes the inorganic materials in the form of inorganic particles or nanoparticles and refers mostly to inorganic clusters on the molecular or macromolecular scale. However, other authors simply refer to the later by using the hOI materials terminology as it still fits perfectly to its definition which does not specify a lower limit for inorganic components size (Sanchez and In, 1992; Sanchez and Ribot, 1993; Judeinstein and Sanchez, 1996). Our major focus in this mini-review will be given to organic-inorganic interface phenomena for hOI materials belonging to both Class I and Class II but only those involving organic polymers and metal oxide nanomaterials.

PREPARATION, CHARACTERIZATION AND COMPUTATIONAL SIMULATION OF hOI MATERIALS AND INTERFACES

Solution-Phase Reaction of Inorganic/ Organic Precursor Using Organic/Inorganic Hosts

The solution-phase reaction of inorganic precursors into organic hosts such as organic polymers was first reported in the early nineties (Sanchez and In, 1992; Schmidt, 1992; Sanchez and ribot, 1993; Saegusa, 1995). The mechanism for metal alkoxides hydrolysis-condensation towards metal oxide clusters or particles (widely known as the sol-gel method) has been thoroughly studied since the late sixties and it is quite well-understood (Livage et al., 1988; Brinker and Scherrer, 1989). Furthermore, the solution-phase reaction of inorganic precursors (metal alkyl or alkoxide) in the presence of organic polymers essentially follows the ordinary hydrolysis-condensation mechanism. However, the presence of certain functional groups in the polymer structure can interact via non-chemical (Class I) and chemical (Class II) bonding interactions with the metal alkoxide hydrolysis-condensation.
products at different stages such as the case depicted in Figure 1A—left panel.

On the other hand, the solution-phase reaction of organic precursor (organic monomer or oligomer) in the presence of inorganic hosts is a quite different process as the organic polymerization is the main reaction taking place. In this case, the inorganic hosts are usually nanoparticles or well-defined clusters interacting via non-chemical interactions during the organic polymerization (Class I) but these nanoparticles or well-defined clusters can be also pre- or post-functionalized with the organic monomer or oligomer to act as an initiator for organic polymerization (Class II) such as the case depicted in Figure 1A—right panel (Ohno et al., 2006). The mechanism behind hOI materials preparation is much more complex and will not be discussed further in this mini-review but the reader can refer to some outstanding reviews on this topic in the literature (Saegusa, 1995; Judeinstein and Sanchez, 1996; Sanchez et al., 2001; Krasia-Christoforou, 2015; Zhang et al., 2016a; Gon et al., 2017).

Vapor-Phase Infiltration of the Inorganic Precursor Into Organic Hosts and Molecular Layer Deposition of Organic Precursor Onto the Inorganic Surface

Over the past decade, a new approach to obtain hOI materials has emerged in which organic polymers are exposed to metalorganic vapors using different approaches such as multiple pulsed infiltration, (Lee et al., 2009; Lee et al., 2010), sequential infiltration synthesis (Peng et al., 2011; Tseng et al., 2011; Segal-Peretz et al., 2015) and sequential vapor infiltration (Gong et al., 2011; Dandley et al., 2014; Akyildiz et al., 2014; Obuchovsky et al., 2014). These approaches essentially respond to the same general mechanism involving the infiltration of inorganic precursor (metal alkyl or alkoxide) molecules into a “dried” organic polymer yielding to Class I and Class II hOI materials and, thus, the unifying term vapor-phase infiltration (VPI) processes and their corresponding reaction mechanisms have been recently proposed to describe all of them (Leng and Losego, 2017). VPI into different kinds of organic polymers [e.g. silk, collagen, polymethyl methacrylate (PMMA), polystyrene (PS), polybutylene terephthalate (PBT), polyethylene terephthalate (PET), polyactic acid (PLA) and polyethylene naphthalate (PEN)] using trimethylaluminum, diethylzinc and titanium isopropoxide precursors have proven to be successful routes toward hybrid polymers with Al2O3, TiO2 and ZnO interesting nanostructures such as the case depicted in Figure 1B—left panel (Lee et al., 2009; Lee et al., 2010; Gong et al., 2011; Peng et al., 2011; Tseng et al., 2011; Akyildiz et al., 2014; Dandley et al., 2014; Obuchovsky et al., 2014; Segal-Peretz et al., 2015; Leng and Losego, 2017).

On the other hand, the vapor-phase infiltration of organic precursors (organic monomer or oligomer) into “dried” inorganic hosts is not referred to as such in the literature as it is mostly limited to surface phenomena and the term molecular layer deposition (MLD) of organic precursor onto the inorganic surface is defined instead (Gregorczyk and Knez, 2016; Meng, 2017). MLD of organic precursors onto inorganic surfaces is a sister of the atomic layer deposition (ALD) technique but still much less explored due to the complexity of its mechanism (Gregorczyk and Knez, 2016; Meng, 2017). However, the successful advances using MLD for obtaining nanoscale films of organic polymers (Yoshimura et al., 1991; Yoshimura et al., 1992; Kim et al., 2005; Zhou et al., 2013; Atanasov et al., 2014; Kim et al., 2015) have also encouraged the preparation of hOI materials such as metal-based hybrid polymers named as alucones, zincones, titanicones among others (Dameron et al., 2008; Lee et al., 2007; Peng et al., 2009; Abdulagatov et al., 2013; Yoon et al., 2012; Park et al., 2016; Van de Kerckhove et al., 2016; Nisula and Karppinen, 2016). In the latter case, the host inorganic surface reacts with the metal-organic precursor vapor and once it is grafted to the surface it allows further organic oligomerization processes and, that is probably why most cases refer to Class II hOI materials such as the case depicted in Figure 1B—right panel (Yoshimura et al., 1991; Yoshimura et al., 1992; Kim et al., 2005; Lee et al., 2007; Dameron et al., 2008; Peng et al., 2009; Yoon et al., 2012; Abdulagatov et al., 2013; Zhou et al., 2013; Atanasov et al., 2014; Kim et al., 2015; Nisula and Karppinen, 2016; Park et al., 2016; Van de Kerckhove et al., 2016; Meng, 2017).

Computational Simulation Insights on Structural Features of hOI Materials and Interfaces

Computational simulation is quite relevant to predict or explain structural features of hOI materials and interfaces. For instance, classical Montecarlo (MC) and molecular dynamics (MD) are one of the best (non-atomistic and atomistic, respectively) approaches to model up to several nanometer large crystalline or amorphous organic and inorganic materials allowing obtaining rich information about molecular and nuclear position-related properties (Zeng et al., 2003; Heinz and Ramezani-Dakhel, 2016; Ramakrishnan et al., 2017; Eckert et al., 2020). To compute electronic-related properties, we must perform first-principles calculations such as Density Functional Theory (DFT) and ab-initio MD (AIMD) to access static and dynamic information, respectively (Zeng et al., 2003; Heinz and Ramezani-Dakhel, 2016; Ramakrishnan et al., 2017; Eckert et al., 2020). When performing first-principles calculations, due to the complexity of the hOI interface, one of the organic or inorganic phases is usually oversimplified to systems comprising organic monomer/inorganic surface (Alexandre et al., 2010; Semoto et al., 2011; Hofmann et al., 2013; Motta et al., 2015; Wang et al., 2017a; Pourrahimi et al., 2017; Liao et al., 2019) or organic oligomers/inorganic small clusters (Mombrú et al., 2017a; Ullah et al., 2017; Wang et al., 2020a). The rational simplification of the hOI interface model is a key to computing these calculations using an appropriate level of theory at a reasonable computational cost (Hofmann et al., 2021).

There are a lot of experimental characterization techniques to study hOI materials and interfaces such as nuclear magnetic resonance, X-ray photoemission, vibrational and optical spectroscopies to access chemical features and high-resolution electron, atomic force and tunneling microscopies, in addition to...
small/wide-angle X-ray scattering, to access structural features of hOI interfaces. Probably because of their popularity, infrared and Raman spectroscopies are the most commonly observed in the literature to study the organic-inorganic interactions mainly for Class II hOI materials (Atanasov et al., 2014; Yoon et al., 2012; Mombbrü et al., 2017a; Wang et al., 2020a; Schöttner et al., 2020). Moreover, surface-enhanced Raman scattering (SERS) effect without using noble metals but inorganic (e.g. TiO₂, MoO₃, WO₃, NiO, ZnO and Cu₂O) (Sun et al., 2007; Alessandri, 2013; Bontempi et al., 2014; Qi et al., 2014; Shin et al., 2014; Wang et al., 2014; Cong et al., 2015; Bontempi et al., 2016; Wang et al., 2017b; Lin et al., 2017; Wu et al., 2017; Zhang et al., 2017; Demirel et al., 2018) or organic (e.g. graphene, thiophene oligomers) (Ling and Zhang, 2010; Yu et al., 2011; Ling et al., 2012; Ling et al., 2013; Huang et al., 2015; Kang et al., 2015; Zhang et al., 2016b; Lombardi, 2017; Yilmaz et al., 2017; Liu et al., 2018) semiconductors is rising and appears to be a very promising technique to study hOI interfaces. Not only there is a vast experimental database that can be useful for vibrational modes assignment but also infrared and, to a lesser extent, Raman spectra can be easily computed using first-principles calculations (Mombbrü et al., 2017a; Wang et al., 2020a; Schöttner et al., 2020; Fernández-Werner et al., 2017; Pignanelli et al., 2017). Undoubtedly, nuclear magnetic resonance and X-ray photoelectron spectroscopies are other powerful tools to obtain chemical information about hOI interfaces but are less accessible than vibrational spectroscopies and computational calculations demand a high computational cost. High-resolution electron, atomic force and tunneling microscopies can give direct local information about hOI materials and interfaces but it is almost impossible to access a large amount of sample as in the case of using X-ray scattering techniques, thus both techniques should be complemented. Furthermore, the modeling of X-ray scattering data by using Rietveld (for crystalline) or Debye (for both crystalline and amorphous) methodologies are quite simple to perform and can be also assisted by classical molecular dynamics calculations (Scardi and Gelsio, 2016; Fernández-Werner et al., 2017; Pignanelli et al., 2017; Bokuniaeva and Vorokh, 2019; Bertolotti et al., 2020).

**MIXED IONIC-ELECTRONIC TRANSPORT OF hOI MATERIALS AND INTERFACES**

**Ionic Transport**

Since the early nineties, it has been evidenced that the presence of inorganic nanomaterials into polymer matrices increases the ionic conductivity and improves the mechanical properties of solid polymer electrolytes (Croce et al., 1998; Appetecchi et al., 1998; Croce et al., 2000; Serra Moreno et al., 2014). Although most of these cases involve no chemical bonding between inorganic nanomaterials and polymers, there is a vast variety of inorganic nanomaterials morphologies such as nanoparticles, nanorods and nanotubes acting as both passive and active fillers that have yielded an enhancement on the ionic conductivities (Romero et al., 2015; Liu et al., 2015; Pignanelli et al., 2018a; Pignanelli et al., 2018b). The enhancement of ionic conduction due to the presence of inorganic nanostructures is mostly related to the ionic-pair dissociation of ordinary salts mediated by the interaction with the inorganic surface, thus favoring the fixation of anionic species and favoring the cationic conduction as evidenced by Raman microscopy and schematically depicted in Figure 2A (Romero et al., 2015; Pignanelli et al., 2018a; Pignanelli et al., 2018b). There are other hOI materials involving chemical bonding between organic and inorganic oligomers that have shown an enhancement in the ionic conductivity with respect to their organic counterparts (Saikia et al., 2012; Vélez et al., 2013; Saikia et al., 2014). Other approaches using borate and carbonate salts as precursors where the “undesired” mobile anionic species are eliminated or chemically bonded to the polymer have been also reported favoring single ionic conduction of the “desired” mobile cation (Zhu et al., 2013; Zhang et al., 2014; Pignanelli et al., 2019). However, the advances on single lithium-ion conductors based on Class II hOI materials comprising well-defined inorganic clusters chemically bonded to organic polymers represent a more rational and promising approach (Onishi et al., 1996; Fujinami et al., 1997; Onishi et al., 1998; Fujinami et al., 2000; Villaluenga et al., 2013; Meyer et al., 2014; Zhao et al., 2015a; Zhao et al., 2015b; Lago et al., 2015).

Regarding computational simulation studies, there is a relatively easy and low-cost DFT approach that provides insights on the interactions between ions and organic molecules/inorganic surfaces that can be used to explain dissociation processes but only represents a static picture without giving direct information about transport (Romero et al., 2016; Kwon et al., 2018; Pignanelli et al., 2019; Xie et al., 2019). To have direct insight on ionic transport for hOI materials and interfaces, larger-scale approaches using non-atomistic or atomistic calculations including organic oligomers and inorganic clusters or surfaces are necessary. MD can provide rich information about ion diffusion and transport directly from the trajectories but these calculations need to be conducted over sufficiently long time scales (Webb et al., 2015; Deng et al., 2016; Sun et al., 2016; Mogurampelly et al., 2017; Pignanelli et al., 2017; Xue et al., 2017; Patra et al., 2019; Pignanelli et al., 2021). However, such long-time scales are highly demanding for AIMD and this first-principle approach is rare in large systems (such as amorphous solids) and it is more usually performed for relatively small crystalline systems (Jalem et al., 2013; Meier et al., 2014; Mo et al., 2014). Furthermore, other first-principles calculations based on the nudged elastic band (NEB) method are also commonly used to determine the barrier of the ionic migration but it is also particularly useful for inorganic crystalline systems (Ong et al., 2011; Shi et al., 2012; Mo et al., 2014; Bachman et al., 2015; Moriwake et al., 2015; Zhang et al., 2018). Nonetheless, the vast majority of lithium-ion transport calculations are solely within the bulk of organic (Webb et al., 2015; Sun et al., 2016; Mogurampelly et al., 2017; Pignanelli et al., 2017; Xue et al., 2017; Patra et al., 2019; Pignanelli et al., 2021) or inorganic (Ong et al., 2011; Shi et al., 2012; Mo et al., 2014; Bachman et al., 2015; Moriwake et al., 2015; Deng et al., 2016; Zhang et al., 2018) phases, but still rarely for hOI materials and interfaces (Li et al., 2016; Pignanelli et al., 2018a; Li et al., 2020). Recently, there have been interesting approaches based on AIMD and NEB calculations studying the solid
electrolyte interface (SEI) comprising organic oligomers and metallic lithium electrodes (Yildirim et al., 2017; Merinov et al., 2019; Ramasubramanian et al., 2019; Merinov et al., 2020).

Electrochemical Transport

The electronic interactions in hOI materials have been extensively studied particularly for sensing, energy storage and energy conversion applications (Kumar et al., 2018; Singh et al., 2019; Duan et al., 2020; Niederhausen et al., 2021; Rathnayake et al., 2021; Zhang et al., 2021). The electronic interactions in these hOI materials and interfaces are mostly via proximity of the n-cloud of the organic phase with the inorganic surface, and thus Class I hOI materials are the most studied for these purposes. However, there have been recent advances in Class I and II hOI materials comprising well-defined inorganic clusters with promising properties in a broad range of applications (Horn et al., 2021). One of the major challenges of hOI materials for polymer solar cells applications is the substitution of the fullerene electronic acceptors for inorganic metal oxides nanostructures counterparts in the active layer and also the enhancement of electronic transport at the hOI interface in the electrodes (Moet et al., 2007; Boucle et al., 2008; Dridi et al., 2008; Lin et al., 2009; Chandrasekaran et al., 2011; Aashish et al., 2016; Ikram et al., 2016). The later reports comprise hOI materials based on different electronic conducting polymers with ZnO, TiO2 and In-doped SnO2 (ITO) inorganic nanostructures or surfaces (Moet et al., 2007; Boucle et al., 2008; Dridi et al., 2008; Lin et al., 2009; Chandrasekaran et al., 2011; Aashish et al., 2016; Ikram et al., 2016). However, only a few studies have provided more fundamental insights on the electronic interactions and correlations with structural features for hOI materials and interfaces (Schlesinger et al., 2013; Whittaker-Brooks et al., 2014; Mombrú et al., 2017b; Mombrú et al., 2018; Singh et al., 2019).

As we mentioned earlier, it is quite challenging to perform computational simulation of hOI interfaces using first-principles level of theory and most calculations usually refer to organic molecules or oligomers interacting with inorganic surfaces. For instance, DFT studies on the electronic interactions of tetrafluoro-tetracyanoquinodimethane (F4-TCNQ)/ZnO surfaces (Xu et al., 2013), hexafluoro-tetracyano-naphthoquinodimethane (F6-TCNNQ)/ZnO surfaces (Schöttner et al., 2020), oligothiophenes and ZnO (and In-doped SnO2) surfaces (Timpel et al., 2020) has shed some light on the work function and other relevant electronic properties of these hOI interfaces. Other DFT studies on the electronic interactions between larger and more complex systems such as polyaniline oligomer/graphene oxide quantum dots (GQD) including edge functionalization (Mombrú et al., 2017c) and vinyl carbazole monomer/TiO2 surfaces including oxygen and titanium vacancy defects (Mombrú et al., 2019a; Mombrú et al., 2019b) has shown interesting features on the electronic properties evidencing the relevance of using more realistic models as depicted in Figure 2B. For instance, the difference between the LUMO level of vinyl carbazole and the conduction band of TiO2 surface with oxygen vacancies decreases thus favoring the energy barrier associated with the charge injection at this hOI interface (Mombrú et al., 2019b).

Mixed Ionic-Electronic Transport

There are a lot of recent examples of hOI materials with promising mixed ionic-electronic transport properties in different applications such as lithium and sodium-ion battery

FIGURE 2 | (A) AIMD calculations showing the Li⁺ - ClO₄⁻ ionic-pair dissociation for an hOI interface based on polyacrylonitrile (PAN) and titanate surface (HTNT) [Portion of figure adapted/alterd minimally with permission from American Chemical Society] (Mombrú et al., 2019b). (B) DFT calculations showing the electronic charge transfer interactions between vinyl carbazole monomer (PVK) and TiO2 surface including oxygen vacancies (TiO2-x) [Portion of figure adapted/alterd minimally with permission from Elsevier] (Mombrú et al., 2019b). (C) AIMD calculations showing the probability density of Li⁺ spatial occupancy and the elongation feature of probability density along the migration channel with the corresponding isosurfaces for LLZO and LATP [Portion of figure adapted/altered minimally with permission from American Chemical Society] (Mombrú et al., 2022).

- **A** ionic transport (hOI interface)  
- **B** electronic transport (hOI interface)  
- **C** mixed ionic-electronic transport (I)  
- **D** mixed ionic-electronic transport (O)
Grif et al. simultaneously into their nearest sites within a few picoseconds as depicted in Figure 2C (He et al., 2017). Griffith et al. have just evidenced by DFT calculations that, Li⁺ in TiNb₂O₇ with high states of lithiation exhibits a transition from interstitial-mediated to a vacancy-mediated diffusion mechanism, and the vacancy formation energetics may become rate-determining (Griffith et al., 2019). Within the same framework, the diffusion of Na⁺, K⁺, and Mg²⁺ was also examined in these inorganic structures and these cations exhibit very high diffusion barriers suggesting minimal ionic conduction at room temperature (Griffith et al., 2019). However, in the later report authors remark that they have used standard DFT to capture the mechanisms associated with ionic diffusion without the presence of simultaneous additional electron transfer processes and that it would be also important to further consider the full compositional range, not only the host structure and/or end point (Griffith et al., 2019).

For organic materials, due to their typical amorphous and/or crystalline nature, larger systems including the evaluation of these structural features are usually studied by MD calculations, at least to evaluate their effects on the isolated ionic or (indirectly) electronic transport (Dong et al., 2019; Mombrú et al., 2020; Dong et al., 2021; Onorato et al., 2021). Furthermore, MD simulations have been useful to evidence that, upon swelling cations interact with the polymer side chains while upon doping the excess anions penetrating the polymer microstructure are expected to be more closely interacting with the polymer backbone, stabilizing polarons (Matta et al., 2020; Cendra et al., 2019; Flagg et al., 2018; Inal et al., 2016; Savva et al., 2019). A quite challenging simultaneous access to ionic and electronic transport by AIMD calculations has been reported just recently for a system comprising crystalline P3HT polymer using explicit LiTFSI dopant and glycol molecules depicted in Figure 2D (Mombrú et al., 2022). In the later report, both ionic and electronic transport simultaneous calculations showed a good correlation with the experimental reports of similar mixed ionic–electronic conductors. Furthermore, these AIMD calculations have also allowed introducing the role of the explicit dopant in the interchain, intrachain, “effective” doping, and charge-transfer complex bonding distances, and their associated static and dynamic disorder effects on electronic transport (Mombrú et al., 2022).

**FINAL REMARKS AND PERSPECTIVES**

To make some final comments and define some perspectives, we conclude that, although quite computationally expensive, AIMD seems to be the best choice for modeling hO1 interfaces as the mixed ionic-electronic transport of both organic and inorganic phases can be adequately modeled simultaneously and be compared with the available literature on their isolated counterparts. However, only a few of the computational simulation from those described above comprises mixed ionic-electronic transport using AIMD calculations (He et al., 2017; Taylor et al., 2017; Wind et al., 2018; Mombrú et al., 2022) so more efforts are definitely still needed in this field. It is also important to mention that the mixed ionic-electronic transport of hO1 materials is much more complex as it includes crystalline and amorphous regions well above the nm scale that be no longer accessed through atomistic models. Furthermore, relevant processes in experimental devices occurring on the μm scale are out of reach for quantum chemistry and molecular dynamics, and thus continuum models also play an important role here to provide understanding at this level (Zozoulenko et al., 2021).

**AUTHOR CONTRIBUTIONS**

MR, RF, and AM contributed to the conception and design of the study. DM and FP selected, compiled, and organized the literature references database. MR created the schematizations, adaptation of figure artwork, and wrote the first draft of the manuscript. DM, FP, RF, and AM wrote sections of the manuscript. All authors contributed to manuscript revision, read, and approved the submitted version.

**ACKNOWLEDGMENTS**

The authors wish to thank the support of Uruguayan CSIC, ANII, and PEDECIBA institutions.
Wang, X., Esfarjani, K., and Zebarjadi, M. (2017). First-Principles Calculation of
Yoshimura, T., Tatsuura, S., and Sotoyama, W. (1991). Polymer Films Formed with
Monolayer Growth Steps by Molecular Layer Deposition. Appl. Phys. Lett. 59 (4), 482–484. doi:10.1063/1.105415
Yu, X., Cai, H., Zhang, W., Li, X., Pan, N., Luo, Y., et al. (2011). Tuning Chemical
Enhancement of SERS by Controlling the Chemical Reduction of Graphene
Oxide Nanosheets. ACS Nano 5, 952–958. doi:10.1021/nn102291J
Zeng, Q. H., Yu, A. B., Lu, G. Q., and Standish, R. K. (2003). Molecular Dynamics
Simulation of Organic–Inorganic Nanocomposites: Layering Behavior and
Interlayer Structure of Organoclay. Chem. Mater. 15 (25), 4732–4738. doi:10.1021/cm0342952
Zhang, B., Tan, R., Yang, L., Zheng, J., Zhang, K., Mo, S., et al. (2018). Mechanisms
and Properties of Ion-Transport in Inorganic Solid Electrolytes. Energ. Storage
Mater. 10, 139–159. doi:10.1016/j.ensm.2017.08.015
Zhang, N., Tong, L., and Zhang, J. (2016). Graphene-Based Enhanced Raman
Scattering toward Analytical Applications. Chem. Mater. 28, 6426–6435. doi:10.1021/acs.chemmaterial.6b02925
Zhang, Q., Li, X., Ma, Q., Zhang, Q., Bai, H., Yi, W., et al. (2017). A Metallic
Molybdenum Dioxide with High Stability for Surface Enhanced Raman
Spectroscopy. Nat. Commun. 8, 14903. doi:10.1038/ncomms14903
Zhang, Y., Rohan, R., Sun, Y., Cai, W., Xu, G., Lin, A., et al. (2014). A Gel Single
Polymer Electrolyte Membrane for Lithium-Ion Batteries with Wide-Range
Temperature Range Operability. RSC Adv. 4, 2116–21170. doi:10.1039/
C3ra02729a
Zhang, Zhou, Han, Faming., Fang, Jie., Zhuo, Chaowei., Li, Shuai., Wu, Yonggang.,
et al. (2021). An Organic–Inorganic Hybrid Material Based on Benzog[hl]
perylene-imide and Cyclic Titanium-Oxo Cluster for Efficient Perovskite and
Organic Solar Cells. CCS Chem. 3, 1217–1225. doi:10.1038/s43585-021-
0208825
Zhang, Z., Zhang, P., Wang, Y., and Zhang, W. (2016). Recent Advances in
Organic-Inorganic Well-Defined Hybrid Polymers Using Controlled Living
Radical Polymerization Techniques. Polym. Chem. 7, 3950–3976. doi:10.1039/
cp800675b
Zhao, H., Asfour, F., Fu, Y., Jia, Z., Yuan, W., Bai, Y., et al. (2015). Pulsed Silica-
Based Single-Ion Nanocomposite Electrolyte for Lithium Batteries. ACS Appl.
Mater. Inter. 7, 19494–19499. doi:10.1021/acsami.5b06096
Zhao, H., Jia, Z., Yuan, W., Hu, F., Yu, B., Baker, G. L., et al. (2015). Fumed Silica-
Based Single-Ion Nanocomposite Electrolyte for Lithium Batteries. ACS Appl.
Mater. Inter. 7, 19335–19341. doi:10.1021/acsami.5b05419
Zhou, H., Toney, M. F., and Bent, S. F. (2013). Cross-Linked Ultrathin Polyurea
Films via Molecular Layer Deposition. Macromolecules 46 (14), 5638–5643.
doi:10.1021/ma400998m
Zhu, Y. S., Wang, X. J., Hou, Y. Y., Gao, X. W., Liu, L. L., Wu, Y. P., et al. (2013).
A New Single-Ion Polymer Electrolyte Based on Polyvinyl Alcohol for Lithium
Ion Batteries. Electrochimica Acta 87, 113–118. doi:10.1016/j.electacta.2012.
08.114
Zozoulenko, I., Franco-Gonzalez, J. F., Gueskine, V., Mehndizhiyski, A.,
Modaresi, M., Rolland, N., et al. (2021). Electronic, Optical, Morphological,
Transport, and Electrochemical Properties of PEDOT: A Theoretical
Perspective. Macromolecules 54 (13), 5915–5934. doi:10.1021/acs.macro.
1c00444

Conflict of Interest: The authors declare that the research was conducted in the
absence of any commercial or financial relationships that could be construed as a
potential conflict of interest.

Publisher’s Note: All claims expressed in this article are solely those of the authors
and do not necessarily represent those of their affiliated organizations, or those of
the publisher, the editors and the reviewers. Any product that may be evaluated in
this article, or claim that may be made by its manufacturer, is not guaranteed or
endorsed by the publisher.

Copyright © 2022 Romero, Mombrà, Pignanello, Faccio and Mombrà. This is an
open-access article distributed under the terms of the Creative Commons Attribution
License (CC BY). The use, distribution or reproduction in other forums is permitted,
provided the original author(s) and the copyright owner(s) are credited and that
the original publication in this journal is cited, in accordance with accepted
academic practice. No use, distribution or reproduction is permitted which does not comply
with these terms.