



HAL
open science

Glycerol-plasticized agarose separator suppressing dendritic growth in Li metal battery

Pierre Blin, Bruno Boury, Aurélie Taguet, Justine Touja, Laure Monconduit, Snehangshu Patra

► **To cite this version:**

Pierre Blin, Bruno Boury, Aurélie Taguet, Justine Touja, Laure Monconduit, et al.. Glycerol-plasticized agarose separator suppressing dendritic growth in Li metal battery. *Carbohydrate Polymers*, 2020, 247, pp.116697. <10.1016/j.carbpol.2020.116697>. <hal-02900332>

HAL Id: hal-02900332

<https://imt-mines-ales.hal.science/hal-02900332v1>

Submitted on 20 Jul 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Glycerol-plasticized agarose separator suppressing dendritic growth in Li metal battery

Pierre Blin^{a,b}, Bruno Boury^a, Aurelie Taguet^c, Justine Touja^{a,b}, Laure Monconduit^{a,b,*}, Snehangshu Patra^{a,b,d,**}

^a ICGM, Université de Montpellier, CNRS, ENSCM, Montpellier, France

^b Réseau sur le Stockage Electrochimique de l'Energie (RS2E), CNRS FR3459, 33 Rue Saint Leu, 80039, Amiens Cedex, France

^c Polymers Composites and Hybrids (PCH), IMT Mines Ales, Ales, France

^d Laboratory of Electrochemistry for Energy and Environment (L3E), Centre of Excellence in Green Energy and Sensors Systems (CEGESS), Indian Institute of Engineering Science and Technology, (IIEST) Shibpur, Howrah, 711103, WB, India

ABSTRACT

The growth of dendrite is the major limitation to the development of the Li-metal battery. To solve it, we disclose the preparation and performances of separator (MAGly) with a complete “green” formulation using biosourced and sustainable compounds: agarose as biopolymer along with glycerol as plasticizing agent. The natural biopolymer films are non-porous in nature and possess high elasticity with high stiffness along a wide temperature range (−35 to 180 °C), able to prevent the perpendicular dendritic Li growth. Moreover, they provide high Li⁺ ionic conductivity, which was evident from electrochemical symmetrical battery tests resulted in efficient plating/stripping of Li metal, without dendrite formation. Preliminary tests in Li battery, with LiFePO₄ as positive electrode show very satisfying performance regarding the same test with the commercial Celgard® separator. Furthermore, the application of this new sustainable separator can be extended to post Li-metal system as demonstrated by the electrochemical tests realized with K⁺/K.

Keywords:

Carbohydrates

Agarose

Glycerol

Dendritic growth suppression

Li-metal batteries

1. Introduction

Renewed interest in Li-metal battery is at present driven by its exceptional high energy density that can satisfy the huge demand for long term autonomy of mobile devices (Xiang et al., 2019). Li-metal possesses high theoretical specific capacity of 3860 mA h g^{−1} and lowest-redox potential of -3.04 V (vs. SHE) motivating its use as anode instead of presently commercialized graphite (theoretical specific capacity: 374 mA h g^{−1}). Thus researches and developments of Li-metal batteries, Li-O₂, Li-S/Se are on the rise (Abouimrane et al., 2012; Bruce, Freunberger, Hardwick, & Tarascon, 2012; Yang, Yin, & Guo, 2015; Yin, Xin, Guo, & Wan, 2013). Growth of vertical lithium dendrites piercing the separator which cause short circuit and even fire, is the principal bottleneck for commercial application of such batteries (Lu et al., 2015; Tarascon & Armand, 2001; Wu et al., 2018). Additionally, the formation of dendrites produces “dead Li” and a specific solid–electrolyte interphase (SEI) (Cheng, Yan, Zhang, Liu, & Zhang, 2018) implying a decrease in Coulombic efficiency and affecting cycling efficiency. Various and numerous strategies (Xu et al., 2014), compatible with the use

of classical separator were adopted to suppress, regulate or eliminate the dendrites (Zhang, Wang, Liu, & Luo, 2019): mixing of ionic additives to solvent (Chen et al., 2018; Fang et al., 2017; Jiao et al., 2018; Liu et al., 2018; Ma et al., 2016; Qian et al., 2015; Suo, Hu, Li, Armand, & Chen, 2013; Zhang, Wang et al., 2019), coating of inorganic/metal/hybrid layer on Li surface (Yan et al., 2014; Zheng et al., 2014) or 3D micro-structuration of Li metal (Yang, Yin, Zhang, Li, & Guo, 2015). Well designed and with the desired physicochemical characteristics, a separator also can be a simple and cheap tool to fight the dendritic menace. Separator being an important part of the battery which essentially separates the positive and negative electrodes, it has to be efficient in the ion transport from side to side in the electrolyte. For such purpose, ideally a separator must exhibit electrochemical stability up to at least 5 V, thermal shrinkage < 5 % at 100 °C for 1 h, high mechanical strength (≥98 MPa), shear modulus 1.8 times higher than that of Li metal and a thickness in the 20–25 μm range (Kim & Pol, 2018; Wu et al., 2018; Waqas et al., 2019). Usually separator present a high macro-porosity filled with solvent or ionic liquids to achieve the required high ionic conductivity but macropores are unable to avoid the

* Corresponding author at: ICGM, Université de Montpellier, CNRS, ENSCM, Montpellier, France

** Corresponding author at: L3E, CEGESS, IIEST-Shibpur, Howrah, 711103, WB, India

E-mail addresses: laure.monconduit@umontpellier.fr (L. Monconduit), snehangshu.patra@cegess.iiests.ac.in (S. Patra).

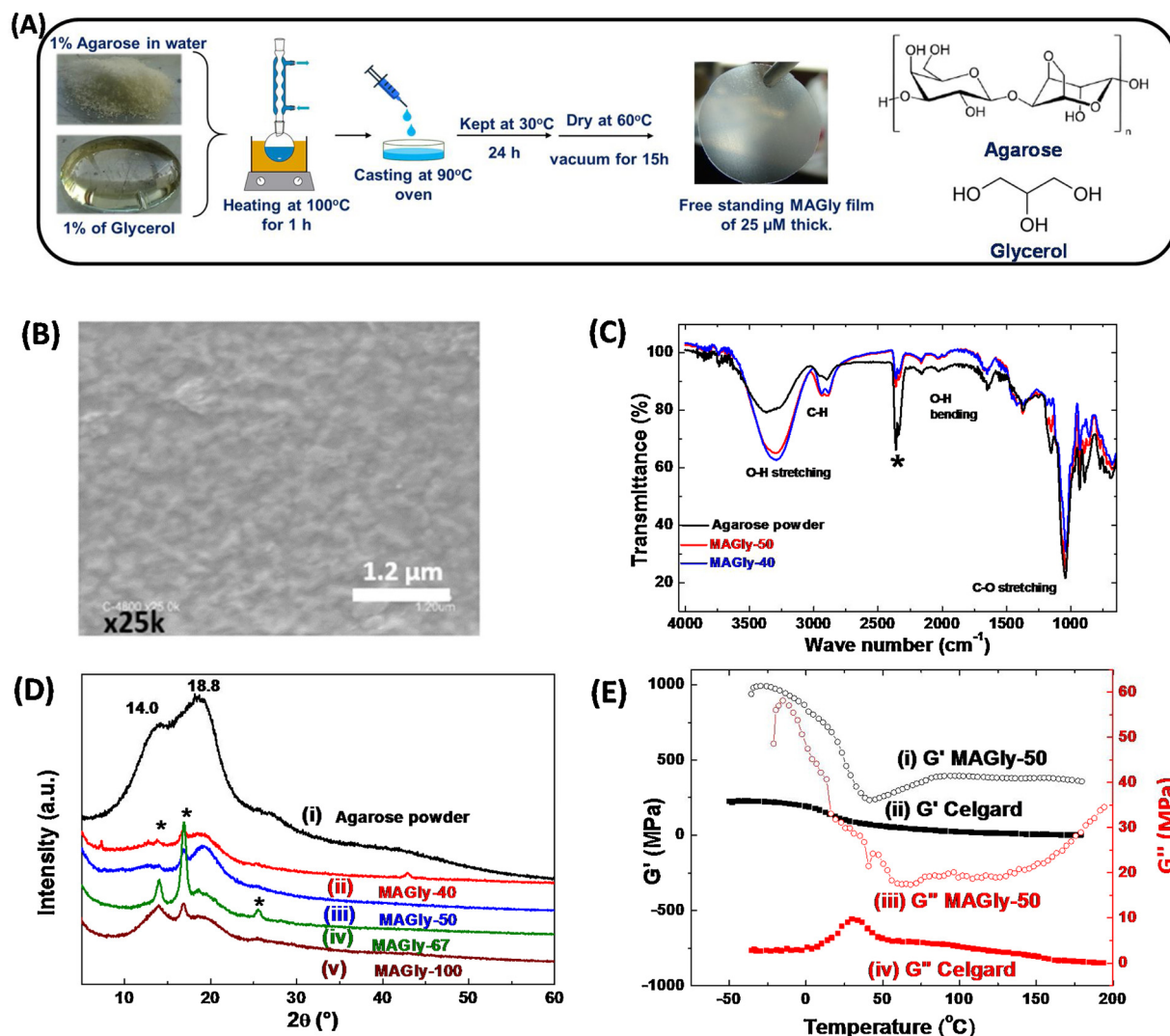


Fig. 1. (A) General overview of the MAGly synthesis protocol, (B) Scanning electron microscope of MAGly-50, (C) Infrared spectroscopy (* signal due to CO₂.) (D) Powder X-ray diffraction pattern of different membrane formulated with different aragose:glycerol mass ratio (* signals due to tape) (E) DMA analyses of MAGly-50 separator with respect to the Celgard® separator.

growth of the dendrites. Therefore, only dense free-standing film, with eventually nano-porosity are acceptable, containing a very limited quantity of liquid for safety reasons. Additionally, the development of such material must be in line with the sustainability of their preparation and use. Thus, we observed increase interest in alternative separators, especially those from cheap and renewable, non-toxic, easily disposable or recyclable biopolymers (Jabbour, Bongiovanni, Chaussy, Gerbaldi, & Beneventi, 2013; Zhang, Tian, Shen, Song, & Yao, 2019). Among these, water-soluble polysaccharides have additional properties like a chemical structure and functions compatible with ionic conduction, hydrophilicity and easy to process as film, satisfactory thermal stability and wide electrochemical stability. They have already shown their great potential in the electrode formulation, as binder or as precursor of carbon additives (Chen & Hu, 2018; Spirk, 2018), and also to control the synthesis of active minerals of the electrodes (Boury & Plumejeau, 2015). However their ionic conductivity remains still questionable in view of their use in separators (Iwaki, Escalona, Briones, & Pawlicka, 2012; Mattos, Raphael, Majid, Arof, & Pawlicka, 2012). Among recent examples, anionically-modified ethylcellulose was reported to present ionic conductivity value of $\sim 10^{-4}$ S. cm⁻¹ at 80 °C (Youcef et al., 2020). Starch chemically modified by γ -(2,3-epoxypropoxy)propyl-trimethoxysilane (GPTMS) presents ionic conductivity of 3.4×10^{-4} S cm⁻¹ at RT (Lin et al., 2016). However, all these chemical

modifications bear an additional cost while both limited number of synthesis steps and cost are desirable.

Besides, different biopolymers have been tested for the elaboration of solid state polymer electrolyte (starch (Pang, Tay, & Chin, 2014; Pawlicka, Sabadini, Raphael, & Dragunski, 2008), pectine (Andrade, Raphael, & Pawlicka, 2009), amylopectine (Marcondes et al., 2010), chitosan, carrageenan (Ghani, Othaman, Ahmad, Anuar, & Hassan, 2019; Jumaah, Mobarak, Ahmad, Ghani, & Rahman, 2015; Torres et al., 2019) and carboxycarrageenan (Mobarak, Ramli, Ahmad, & Rahman, 2012), hydroxyethylcellulose (Machado, Ferreira, & Pawlicka, 2005)), natural rubber (Ali et al., 2008; Mohamed, Johari, Ali, Harun, & Yahya, 2008), polyamide (gelatin) and even DNA (Firmino, Grote, Kajzar, M'Peko, & Pawlicka, 2011). The ionic conductivity of these biopolymers is extremely low when pure and, to raise a good level of conductivity (10^4 S cm⁻¹ or above) chemical modification or swelling with salts and solvent is generally necessary. To the best of author's knowledge, here is the first report on a separator made of only two biosourced and unmodified components: agarose and glycerol as plasticizer. In previous studies, Ion conduction in polysaccharides were already used in the gel state, but not in the bulk. Besides, ion conduction is often a bottleneck for many applications (fuel cells, batteries, membranes purification). Through this study, we wish to show the strong potential of polysaccharides, especially agarose, in terms of bulk

ionic conduction and thus allow a wider consideration of their use in applications that are different from already widely described. The next step will be to evidence the precise mechanism of ionic conduction at the molecular level.

We selected agarose due to its linear structure bearing intramolecular ether group limiting the number of hydroxyl group compared to other polysaccharides. Moreover, different studies assumed for agarose a helical structure (single or double) apparently as a result of the β -(1-4) glucose linkage found in other polysaccharides with helical forming structure like in amylose, carrageenan, schizophyllan or curdlane (Arnott et al., 1974; Kouwijzer & Pérez, 1998; Numata & Shinkai, 2011). We also noted that gel of agarose are intensively used for electrophoresis of biomolecule, suggesting a high ability for ion conduction, at least in the gel form. Since Li^+ conduction implies cooperative processes, whatever is the media, a helical structure could also be advantageous due to cooperative mechanism.

In batteries, agarose has already been introduced in the different parts of batteries, it was reported as an efficient binder for electrodes material as well as a precursor of highly functionalized carbon resulting from its pyrolysis (Hwang et al., 2016; Iwaki et al., 2012; Kim et al., 2015; Shin et al., 2019). Here we prepared an agarose membrane, denoted MAGly, as separator for Li-metal batteries, demonstrating an additional opportunity for the use of polysaccharide in batteries. MAGly was fabricated by a simple drop casting method consisting of a fully "bio-based" formulation with various ratio of agarose biopolymer and glycerol (see Fig. 1). Although glycerol ($\approx 10^{-7} \text{ S. cm}^{-1}$ at RT) (Choudhary & Sengwa, 2012) and agarose ($\approx 10^{-10} \text{ S cm S cm}^{-1}$ at RT) present a low conductivity (Alves et al., 2013). We found that plasticizing agarose with glycerol not only improves its flexibility and processability but also results in a high ionic conductivity. Glycerol is obtained from bio-resources and often used to improve mechanically properties and ion-conduction of biopolymer membranes (Vieira, da Silva, dos Santos, & Beppu, 2011). As reported by Awadhiya, Tyeb, Rathore, and Verma (2017), glycerol acts as an efficient plasticizer of agarose that, otherwise forms rigid and too brittle films. The agarose/glycerol was optimized to 50/50 W/W ratio. The as prepared non-porous separator exhibits a high ionic conductivity. Symmetrical Li/Li electrochemical tests demonstrated its robustness face to the Li dendrite formation, higher than the commercial Celgard based on synthetic polymer. Preliminary test of the MAGly separator in a Li/LiFePO₄ battery show very promising results, as it outperforms Celgard®.

2. Experimental

2.1. Materials

Demineralized 18.2 M Ω cm water is obtained by the PURELAB® Chorus system. Agarose (white powder, reference J66501, electrophoresis grade) and glycerol (viscous liquid, reference 36646, 99.5 % purity) were obtained from Alfa Aesar. The electrolytes 1 M LiPF₆ in EC/PC/3DMC (volume ratio 1/1/3) and 1 M LiPF₆ in EC/DMC (volume ratio 1/1, LP30) were supplied by Solvionic (bottles packaged in argon bags, directly placed in argon glove boxes before opening). Lithium metal (lithium block reference 265993, 99 %) was purchased from Sigma-Aldrich. The commercial Celgard 2325 was utilized through the work is a combination of PP-PE-PP assembly with an opaque white appearance, 25 μm thick, a pore size of $0.21 \times 0.05 \mu\text{m}$ and a porosity of 39 %.

2.2. Preparation of biopolymer films

The MAGly film was obtained by a simple solvent cast technique. Typically, 0.3 mg of agarose powder was added in a glass container (e.g. a flask) containing 30 mL (30 mg) of distilled water which then was heated at 100 °C under stirring for 30 min. Various amounts of Glycerol (typically 0.3 mg) were added to the solution up to the total dissolution

of agarose (the solution changed from turbid to transparent). The solution was then stirred for one hour at 100 °C and then 10 mL of the solution was then poured into a petri dish (inner diameter of 9.7 cm). The syringe and petri dish were stored in advance at 90 °C to avoid premature gelation (it immediately gelled if it was casted at room temperature). Film was dried in an oven at 30 °C for 24 h, then punched to 16 mm and finally dried at 60 °C under dynamic vacuum (Buchi furnace) for 15 h. The film thickness was measured by a Digimatic IP65 0 – 25 mm (Mitutoyo) micrometer (uncertainty of $\pm 1 \mu\text{m}$).

2.3. Characterization

Infrared analyses (ATR) of the powders and films were carried out by the Horiba Jobin Yvon – LabRAM ARAMIS apparatus, whose spectral range is 650 to 4000 cm^{-1} , with a MCT detector (Mercury Cadmium Tellurium with liquid nitrogen tank) and whose ATR objective is diamond. TGA analyses coupled with the mass spectrum of base powders, glycerol and MAGly films as obtained were performed by the STA 449 F1 Jupiter® apparatus (for TGA) and the QMS 403 D Aëolos apparatus (for mass spectrum), both products of the Netzsch Company. The structure of MAGly and Celgard films were studied by the FEG HITACHI s-4800 scanning electron microscope. The films were metallized with platinum by sputtering before the analysis.

2.4. Cathodes

For LiFePO₄ electrodes, 75 % LiFePO₄ powder, 20 % carbon black and 5% polyvinylidene fluoride (PVDF, binder) were thoroughly mixed and 1 mL N-methyl-2-pyrrolidone (NMP, solvent) per 300 mg of powder was added. After grinding (ball-milling, 500 rpm for 1 h), the ink was spread by a doctor blade at 150 μm on an aluminum foil, and dried in a fume hood for one day. The discs, after punching to 9.5 mm, were dried under dynamic vacuum at 100 °C for 15 h.

2.5. CR2032 coin cells

The CR2032 (SS 316 L type) coin cells were assembled in a MBraun LABstar glovebox, equipped with an MB-10-G atmosphere purifier. The coin cells were assembled and were sealed with a MTI sealer. The liquid electrolyte consists of 100 μL of LP30. The separators (Celgard and MAGly) were immersed in the electrolyte for at least 24 h to ensure that they are properly soaked. The cells include a stainless steel current collector on each side to ensure sufficient contact.

2.6. Electrochemical test

Electrochemical tests were performed in a Bio-Logic (MPG-2) and Neware instruments. Before each test, the open circuit voltage (OCV) was measured over 2 h as a function of time to check the voltage stabilization. In addition, tests were performed twice to ensure repeatability. Cyclic voltammetry were performed from -0.5 V to +5 V at sweep rate of 1 $\text{mV}\cdot\text{s}^{-1}$ for 10 cycles continuously. Galvanostatic cycling of Li//LiFePO₄ batteries was performed between 4.2 and 2.4 V at C/10 rate. The impedance analyses of the membranes were performed by assembling a coin cell in a configuration of SS/MAGly or Celgard/SS in the frequency range of 100 kHz to 10 mHz.

3. Results and discussion

Fig. 1A demonstrates the synthetic protocol of a self-standing MAGly film, which consists of simply solubilizing agarose in water (for example 1% by wt.) at 100 °C with various percentages of glycerol, the one prepared with a mass ratio of agarose:glycerol = 50:50 is called MAGly-50 Then a drop casting at 90 °C was realized on glass surface or on Cu or Al thin foil. After drying the average thickness of the membrane was in the $20 \pm 5 \mu\text{m}$ range, close to the commercially available

separator Celgard® ± 25 μm). The dried MAGly-50 membrane analyzed by scanning electron microscopy (SEM) exhibits a uniform surface at low magnification (X 100, Fig. S11(A)), and an amorphous-like polymeric aspect with uneven/shrinking surface and no visible porosity even at high magnification (X 5000, Figs. 1B, S11(B)). This morphology appears hugely different than that of Celgard® (see Fig. S12). A high degree of unevenness was observed with increasing percentage of glycerol in the formulation, as shown in Fig. S13.

The infrared spectra of MAGly-50 films were compared with the agarose powder. From Fig. 1C, the signals obtained in the range 1000–4000 cm⁻¹ correspond to the typical bonds of alcohols and ethers (Hu et al., 2016), and those in the 650–1000 cm⁻¹ area are typical signals of polysaccharides: anomeric carbons (930 and 890 cm⁻¹) and deformation of the pyranose ring (770, 740 and 690 cm⁻¹) (Matsuhiro & Rivas, 1993). Due to their structures, glycerol and agarose are too close to be precisely differentiated but at present, however no chemical modification occurring during the synthesis process of MAGly-type membrane can be evidenced.

The thermal stability of MAGly-50 membrane was determined by TGA and compared to those of agarose and glycerol, as given in Fig. S14. After water loss below 130 °C for both compounds, agarose powder started to degrade at 260 °C whereas glycerol degrades at 170 °C. For MAGly-50 in the same conditions, the thermal degradation consists of initial degassing of embedded species identified by mass spectrometry as mainly: H₂O, Ar, N₂, O₂, CO₂, which corresponds to mass loss of 6% at 60 °C and 8% at 100 °C. As the temperature increases, the degradation of MAGly-50 is consistent with the degradation of glycerol (170 °C) and of agarose (260 °C).

The crystallinity in MAGly-50 membrane is extremely important issue especially from the point of view of the ion conduction. It is believed that the crystallinity of the polymer is a hurdle for the ions to transport through the membrane. By wide angle X-ray diffraction (WAXRD), the agarose powder essentially showed two broad peaks at 18.8° and 14° as a result of the short-range order of the single or double helix structuration of the agarose macromolecules (Arnott et al., 1974; Foord & Atkins, 1989; Kanmani & Rhim, 2014; Kouwijzer & Pérez, 1998). The broadness of the peaks suggests that agarose powder is mostly nanocrystalline. These peaks are present in MAGly-50 although modified in shape and intensity. The peak intensity was observed to be lowered while increasing the glycerol percentage in the MAGly. However, complete disappearance was never observed even at high glycerol concentration, suggesting the plasticizing effect of the latter preserve the helical structure of agarose. The mechanical strength of the MAGly-50 is evidenced by dynamic mechanical analyses (DMA). It shows, as given in Fig. 1E, a much higher stiffness (G') for MAGly-50 membrane compared to Celgard®, on "dried" states. Moreover, MAGly-50 maintains its stiffness all along the temperature range (from 50 to 180 °C) whereas the G' of Celgard® gradually decreases up to the studied temperature range. MAGly-50 exhibits a glassy state up to 15 °C with G' close to 1 GPa as measured by DMA analysis. A gradual decrease in G' from -35 to 40 °C was observed as similar to the plasticized amylose membrane (Stading, 1998). The decrease of G' can be ascribed to the

expansion of MAGly-50 separator. In addition, decrease after 15 °C reveals that the glass transition temperature range is reached. The Tg of MAGly-50, considered to be the maximum of G''/G', is 38 °C which is quite low compared to reported literature (129 °C) (Mitsuiki, Mizuno, & Motoki, 1999). Mitsuiki et al. explain that the Tg of agarose depends on the molecular weight and water content. For example, the Tg decreased with increased water content (from Tg = 160 °C at 10 % water content to Tg = 40 °C at 30 % water content). In our case, as the membrane was dried before DMA experiments, the low Tg = 38 °C of MAGly-50 separator can thus be attributed to the presence of glycerol that is a plasticizer for agarose and of trace amount of water content. Finally on the rubbery state, at higher temperature (> 50 up to 85 °C), slow increase in G' was observed probably due to achieving some kind of order or crystallinity from random distribution of polymer chain at low temperature and also due to release of water. Further increase in temperature, the stiffness value of 0.38 GPa remains almost constant up to 180 °C whereas the stiffness of Celgard® reached close to 5 MPa at 160 °C and reaches less than zero with further increase in temperature. We also observed variations in the proportion of glycerol tend to produce changes in the mechanical strength of the film. Formulations with 67 % (MAGly-67), 50 % (MAGly-50) and 40 % (MAGly-40) agarose are suitable for handling and also can be bent up to θ = 180° without any observable cracking; 33 % (MAGly-33) agarose or less leads to too much elastic films. Finally, it can be concluded that the MAGly-50 film exhibits substantially high stiffness which can prevent dendritic growth and simultaneously adapt the volume expansion of electrode materials during electrochemical lithiation.

We tested the contact angle in the electrolyte in order to conclude whether the MAGly-50 is wettable and can further be utilized to perform electrochemistry. The contact angle for MAGly-50 separator in LP30 electrolyte is 17° in comparison to 12° on Celgard®, as given in Fig. S15. This implies that the MAGly-50 separator is wetted by the electrolyte almost similarly to Celgard®. To compare the stability of MAGly-50 and Celgard® membranes, both were dipped separately in LP30. No evidence of any dissolution in both the cases even after 70 days of dipping suggests a long-term stability of the separator in said electrolyte (Fig. S16). However, if the electrolyte is changed from LP30 to 1 M LiPF₆ in EC/PC/3DMC + 5% FEC + 1% VC, both membranes exhibited substantial degradation during the same period (see Fig. S17). Thus, these observations strongly suggested that MAGly-50 membrane possesses physicochemical properties of a suitable separator in LP30 electrolyte and further electrochemical tests were performed in order to understand its suitability to battery testing.

One of the most essential parameters that can be achieved from simple electrochemical experiments is the ionic conductivity just by performing the impedance spectroscopy. Thus, the Li⁺ conductivity in LP30 was measured in the range of 100 kHz to 10 mHz at an AC amplitude of 10 mV at 30 °C. The Nyquist plot (Fig. 2A) exhibits intercepts of the inclined spikes on the real axis corresponding to the resistance of the membranes. The ionic conductivity values (σ) can be calculated from the equation below;

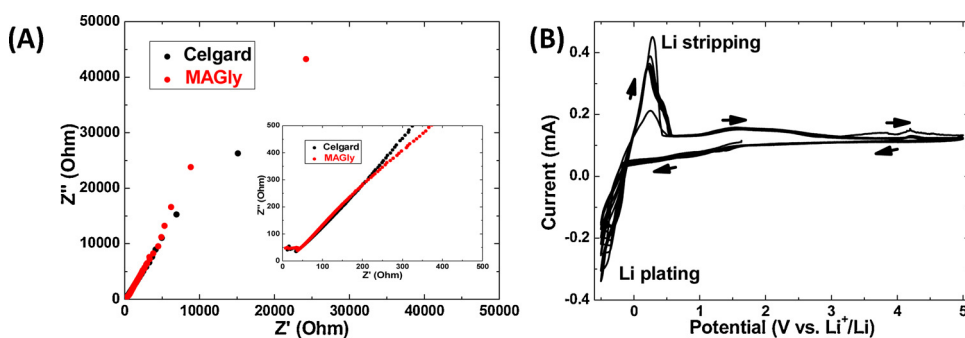


Fig. 2. (A) Impedance spectra of both the MAGly-50 and Celgard at an AC amplitude of 10 mV in the frequency range of 100 kHz to 10 mHz in Nyquist presentation. (B) Cyclic voltammetry of MAGly-50 sandwiched between a Lithium and SS electrode at a slow scan rate of 1 mV s⁻¹ in the potential range of -0.5 to 5 V in LP30 electrolyte.

$$\sigma = \frac{t}{RA} \quad (1)$$

where σ is the ionic conductivity, R is the bulk resistance, t and A are the thickness and area of the separator, respectively. The ionic conductivity was calculated to be $1.3 \times 10^{-4} \text{ S cm}^{-1}$ which is close to the value $1.7 \times 10^{-4} \text{ S cm}^{-1}$ for the Celgard separator at 30°C . At 80°C the conductivity is similar, $1.2 \times 10^{-4} \text{ S cm}^{-1}$ suggesting its intactness and suitability to high temperature batteries if needed. These experiments suggest that the ionic conductivity of the MAGly-50 separator is comparable to the Celgard's one. Then cyclic voltammetry (CV) was performed at sweep rate of 1 mV.s^{-1} from -0.1 V to 5 V , by assembling MAGly-50 between a Li foil and a stainless-steel (SS) plate in a coin cell setup, to check the Li plating/stripping as well as the stability of MAGly-50 in the harsh potential range (Fig. 2B). A sudden increase in cathodic current from -0.1 V indicates Li metal plating on the SS which is then stripped at a potential of 0.2 V on reverse cycle. The similar behavior is observed in case of battery assembled with a Celgard[®] membrane that clearly suggests the existence of a similar electrochemical environment at micro scale. It is also interesting that the MAGly-50 separator is stable in the potential range up to 5 V similar to that of Celgard[®] membrane. Plating/stripping tests were extended to the commonly used $1 \text{ M LiTFSI-EC/DEC}$ electrolyte. Even though the cathodic and anodic peaks of plating/stripping of Li are visible (Fig. S18), one clearly shows an "irreversible" redox process much more pronounced than with the LP30 electrolyte. The choice of electrolyte appears crucial for the reversible plating/stripping behavior as previously observed by Xiao, McCulloch, and Wu (2017) Li plating/stripping was further performed at current density of 1 mA.cm^{-2} for both symmetric cell (SS/Li/MAGly/Li/SS) and (SS/Li/ Celgard[®] /Li/SS) (Fig. 3).

The symmetric cell based on Celgard separator displayed a gradual increase in voltage hysteresis during Li plating/stripping processes. The polarization at 240 mV after 100 h increases chaotically after 150 h due to the formation of dendrites (Wood, Noked, & Dasgupta, 2017). In contrast, the symmetric cell with MAGly exhibited low voltage polarization during cycling, limited to 14 mV after 250 cycles. The SS/Li/MAGly-50/Li/SS battery exhibits a long term stability up to 450 h with low hysteresis below 25 mV (Zhang et al., 2018). This experiment clearly suggests that the MAGly-50 separator is helpful in suppressing the dendritic growth in the battery. The absence of any porosity (macro/micro porosity) in MAGly-50 and its stiffness have likely helped blocking the dendrites growth mechanically.

To verify the effectiveness of this new biopolymer as possible separator in Li free dendrite batteries, preliminary tests were realized with LiFePO_4 (LFP) (Theoretical specific capacity = 170 mAh.g^{-1}) as cathode. Same battery was tested with Celgard as separator. Both separators were soaked in electrolyte at least for 24 h before assembling them for the battery. Fig. 4 gathers the galvanostatic curve and cycling performance of the batteries (LFP/MAGly-50/Li and LFP/Celgard/Li) at

0.1C rate (0.017 A.g^{-1}). The initial charge capacities were 126 mA h.g^{-1} and 120 mA h.g^{-1} for the MAGly-50 and Celgard[®] batteries respectively. The polarization of the battery using MAGly-50 separator, although higher than that using Celgard ($0.20 \text{ vs. } 0.13 \text{ V}$) stays quite low. The coulombic efficiency in cycling are quite similar with an average rate of 99.5% (Fig. 4B) for both batteries. We observed comparable capacity retention over 50 cycles indicating that the MAGly-50 separator can perform with similar efficiency than that of Celgard[®] membrane. We observed no modification of the MAGly-50 separator when it was recovered from the battery after 50 cycles (Fig. S19).

These results show that MAGly-50 separator presents an efficiency comparable to that of Celgard[®], which is a reference separator. Interestingly, this later is a layer of polyethylene between two layers of polypropylene (average pore diameter of $0.21 \mu\text{m}$) with macroporosity, when MAGly-50 presents no porosity (neither macro- nor mesoporosity being evidenced, however microporosity not measured in this work cannot be excluded). Since the good performance of Celgard[®] is related to its adapted porosity filled by the electrolyte, allowing a good mobility of the Li^+ ions, the non-porous MAGly-50 presents obviously a different Li^+ conductivity mechanism. In first approach we propose that the Li^+ conductivity originates from a partial swelling of the MAGly-50 by LP30. Besides, the possible helical structure of the agarose is an additional element to take into account. Simulation of the crystal structure agrees with a large free volume ($30\text{--}45 \%$) (Arnott et al., 1974), possibly occupied by water in undried or aqueous gel of agarose and by the constituents of the LP30 in the present case. Moreover, the proposed macromolecular packing suggests inter- and intra-helical channels. Therefore, high mobility of the Li^+ -cations may result from both the free volume of the polymer, an important and favorable parameter for ionic conduction in solid polymer electrolyte and from its helical structure (Bresser, Lyonard, Iojoiu, Picard, & Passerini, 2019).

Herein, we show that the natural biopolymer, agarose, plasticized with glycerol can act as ionically conducting robust separator with exceptional stiffness all along the accepted temperature range indicating high thermal stability, adapted for low as well as high temperature Li metal batteries. The MAGly separator is also useful in preventing growth of lithium dendrite, as demonstrated by symmetric cells tests. Preliminary electrochemical Li/LFP battery tests are encouraging since well competing the commercial separator Celgard[®]. Such biopolymer could be promising separator especially for Li metal batteries. It could also represent a good base of solid electrolyte for efficient all-solid-state-battery. We further examined its potential use in post Li metal batteries such as K metal batteries (KB). KB are currently emerging due to their beneficial low standard potential of K^+/K , low desolvation energy and small solvated ionic radius of K^+ which are expected to greatly favor both the energy and power density compared to Na-ion batteries (Madec et al., 2018; Okoshi, Yamada, Komaba, Yamada, & Nakai, 2016). As preliminary tests we have measured the plating/stripping behavior of K metal in 5 M KFSI electrolyte in DME, as

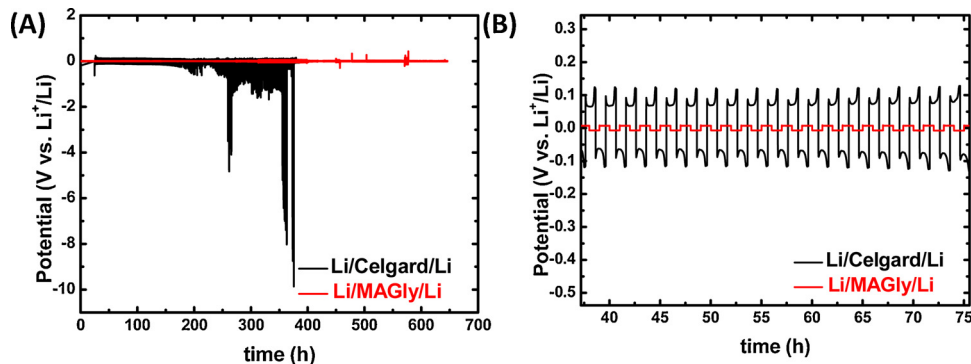


Fig. 3. (A) Voltage profiles of the symmetric cells Li/Li with MAGly-50 or Celgard[®] as a separator a current density of 1 mA cm^{-2} . The enlarged cycling version is given in (B).

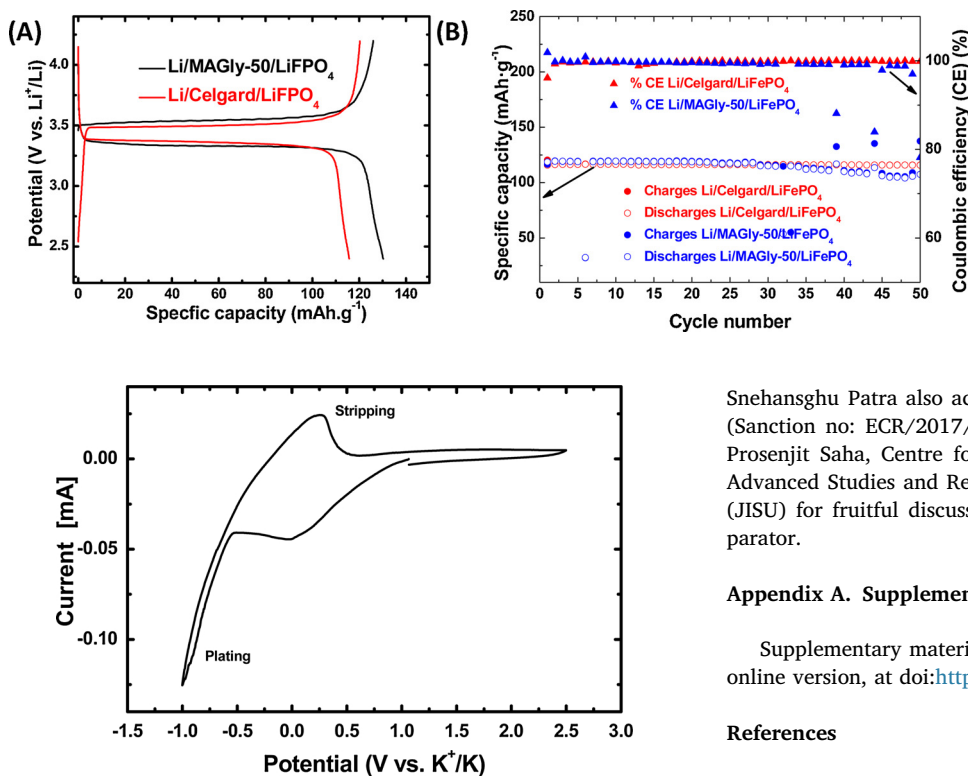


Fig. 4. Galvanostatic charge discharge curve (A) and cycling performance (B) of Li/MAGly-50/LiFePO₄ and Li/Celgard®/LiFePO₄ at rate of 0.1C. ▲ and △ in Figure B represents % CE of Li/Celgard/LiFePO₄ and % CE of Li/MAGly-50/LiFePO₄, respectively.

Fig. 5. The Cyclic voltammetry K plating/stripping in 5 M KFSI/DME.

given in Fig. 5 (Madec et al., 2018). K plating/stripping was observed suggesting that the conduction of K⁺ ion through MAGly-50 is possible and may be utilized as separator to other contemporary and alternative K batteries. The K plating/stripping behavior was worsen when CV was performed in 1 M KTFSI-EC-DEC (1:1 by V) (Fig. S110), similarly to that of Li battery (LiTFSI-EC-DEC) (Xiao et al., 2017). Nevertheless, K plating/stripping was observed suggesting that the conduction of K⁺ ion through MAGly-50 is possible and may be utilized as separator to other contemporary and alternative K batteries.

In conclusion we demonstrated that glycerol-plasticized agarose is an attractive candidate as separators preventing efficiently from the dendritic Li growth in Li batteries. Besides the simplicity of the processing, the high elasticity and stiffness this separator also has an appropriated thermal and electrochemical stability. More interestingly, this work demonstrates that, although the ionic conductivity of the two starting components is very low, their mixture result in a high ionic conductivity and showed equivalent performance than that of classical Celgard separator in preliminary tests with LiFePO₄. Furthermore, the application of this new sustainable separator can be extended to post Li-based battery as demonstrated by the electrochemical tests realized with K⁺/K.

CRedit authorship contribution statement

Pierre Blin: Methodology, Validation. **Bruno Boury:** Writing - review & editing. **Aurelie Taguet:** Methodology, Validation, Writing - review & editing. **Justine Touja:** Methodology, Validation. **Laure Monconduit:** Writing - review & editing, Supervision. **Snehangshu Patra:** Conceptualization, Methodology, Validation, Writing - review & editing, Supervision.

Acknowledgements

Dr. Snehangshu Patra would like to acknowledge DST-Inspire Faculty Award, Ministry of Science & Technology, India. Dr.

Snehangshu Patra also acknowledge the funding of SERB-ECR Award (Sanction no: ECR/2017/000044, Dated: 06.02.2018). We thank Dr. Prosenjit Saha, Centre for Interdisciplinary Sciences, JIS Institute of Advanced Studies and Research (JISIASR), affiliated to JIS University (JISU) for fruitful discussion on mechanical properties of MAGly separator.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.carbpol.2020.116697>.

References

- Abouimrane, A., Dambournet, D., Chapman, K. W., Chupas, P. J., Weng, W., & Amine, K. (2012). A new class of lithium and sodium rechargeable batteries based on selenium and selenium-sulfur as a positive electrode. *Journal of the American Chemical Society*, *134*(10), 4505–4508.
- Ali, A. M. M., Subban, R. H. Y., Bahron, H., Winie, T., Latif, F., & Yahya, M. Z. A. (2008). Grafted natural rubber-based polymer electrolytes: ATR-FTIR and conductivity studies. *Ionics*, *14*(6), 491–500.
- Alves, R. D., Rodrigues, L. C., Andrade, J. R., Pawlicka, A., Pereira, L., Martins, R., & Silva, M. M. (2013). Study and characterization of a novel polymer electrolyte based on agar doped with magnesium triflate. *Molecular Crystals and Liquid Crystals*, *570*(1), 1–11.
- Andrade, J. R., Raphael, E., & Pawlicka, A. (2009). Plasticized pectin-based gel electrolytes. *Electrochimica Acta*, *54*(26), 6479–6483.
- Arnott, S., Fulmer, A., Scott, W. E., Dea, I. C. M., Moorhouse, R., & Rees, D. A. (1974). The agarose double helix and its function in agarose gel structure. *Journal of Molecular Biology*, *90*(2), 269–284.
- Awadhiya, A., Tye, S., Rathore, K., & Verma, V. (2017). Agarose bioplastic-based drug delivery system for surgical and wound dressings. *Engineering in Life Sciences*, *17*(2), 204–214.
- Boury, B., & Plumejeau, S. (2015). Metal oxides and polysaccharides: An efficient hybrid association for materials chemistry. *Green Chemistry*, *17*(1), 72–88.
- Bresser, D., Lyonnard, S., Iojoiu, C., Picard, L., & Passerini, S. (2019). Decoupling segmental relaxation and ionic conductivity for lithium-ion polymer electrolytes. *Molecular Systems Design & Engineering*, *4*(4), 779–792.
- Bruce, P. G., Freunberger, S. A., Hardwick, L. J., & Tarascon, J.-M. (2012). Li-O₂ and Li-S batteries with high energy storage. *Nature Materials*, *11*(1), 19–29.
- Chen, C., & Hu, L. (2018). Nanocellulose toward advanced energy storage devices: Structure and electrochemistry. *Accounts of Chemical Research*, *51*(12), 3154–3165.
- Chen, S., Zheng, J., Mei, D., Han, K. S., Engelhard, M. H., Zhao, W., & Zhang, J.-G. (2018). High-voltage lithium-metal batteries enabled by localized high-concentration electrolytes. *Advanced Materials*, *30*(21), Article 1706102.
- Cheng, X.-B., Yan, C., Zhang, X.-Q., Liu, H., & Zhang, Q. (2018). Electronic and ionic channels in working interfaces of lithium metal anodes. *ACS Energy Letters*, *3*(7), 1564–1570.
- Choudhary, S., & Sengwa, R. J. (2012). Investigations on ionic conduction in amides + glycerol binary mixtures. *Journal of Molecular Liquids*, *167*, 99–102.
- Fang, Z., Ma, Q., Liu, P., Ma, J., Hu, Y.-S., Zhou, Z., & Chen, L. (2017). Novel concentrated Li[(FSO)₂(n-C₄F₉SO₂)N]-based ether electrolyte for superior stability of metallic lithium anode. *ACS Applied Materials & Interfaces*, *9*(5), 4282–4289.
- Firmino, A., Grote, J. G., Kajzar, F., M'Peko, J. C., & Pawlicka, A. (2011). DNA-based ionic conducting membranes. *Journal of Applied Physics*, *110*(3), Article 033704.
- Foord, S. A., & Atkins, E. D. Y. (1989). New x-ray diffraction results from agarose: Extended single helix structures and implications for gelation mechanism. *Biopolymers*, *28*(8), 1345–1365.
- Ghani, N. A. A., Othaman, R., Ahmad, A., Anuar, F. H., & Hassan, N. H. (2019). Impact of purification on iota carrageenan as solid polymer electrolyte. *Arabian Journal of Chemistry*, *12*(3), 370–376.
- Hu, Z., Hong, P., Liao, M., Kong, S., Huang, N., Ou, C., ... Li, S. (2016). Preparation and characterization of chitosan-Agarose composite films. *Materials*, *9*(10), 816.
- Hwang, G., Kim, J.-M., Hong, D., Kim, C.-K., Choi, N.-S., Lee, S.-Y., ... Park, S. (2016).

- Multifunctional natural agarose as an alternative material for high-performance rechargeable lithium-ion batteries. *Green Chemistry*, 18(9), 2710–2716.
- Iwaki, Y. O., Escalona, M. H., Briones, J. R., & Pawlicka, A. (2012). Sodium alginate-based ionic conducting membranes. *Molecular Crystals and Liquid Crystals*, 554(1), 221–231.
- Jabbour, L., Bongiovanni, R., Chaussy, D., Gerbaldi, C., & Beneventi, D. (2013). Cellulose-based Li-ion batteries: A review. *Cellulose*, 20(4), 1523–1545.
- Jiao, S., Ren, X., Cao, R., Engelhard, M. H., Liu, Y., Hu, D., & Xu, W. (2018). Stable cycling of high-voltage lithium metal batteries in ether electrolytes. *Nature Energy*, 3(9), 739–746.
- Jumaah, F. N., Mobarak, N. N., Ahmad, A., Ghani, M. A., & Rahman, M. Y. A. (2015). Derivative of iota-carrageenan as solid polymer electrolyte. *Ionics*, 21(5), 1311–1320.
- Kanmani, P., & Rhim, J.-W. (2014). Antimicrobial and physical-mechanical properties of agar-based films incorporated with grapefruit seed extract. *Carbohydrate Polymers*, 102, 708–716.
- Kim, P. J., & Pol, V. G. (2018). High performance lithium metal batteries enabled by surface tailoring of polypropylene separator with a polydopamine/graphene layer. *Advanced Energy Materials*, 8(36), Article 1802665.
- Kim, J.-M., Kim, C., Yoo, S., Kim, J.-H., Kim, J.-H., Lim, J.-M., & Lee, S.-Y. (2015). Agarose-biofunctionalized, dual-electrospun heteronano-fiber mats: toward metal-ion chelating battery separator membranes. *Journal of Materials Chemistry A*, 3(20), 10687–10692.
- Kouwijzer, M., & Pérez, S. (1998). Molecular modeling of agarose helices, leading to the prediction of crystalline allomorphs. *Biopolymers*, 46(1), 11–29.
- Lin, Y., Li, J., Liu, K., Liu, Y., Liu, J., & Wang, X. (2016). Unique starch polymer electrolyte for high capacity all-solid-state lithium sulfur battery. *Green Chemistry*, 18(13), 3796–3803.
- Liu, X., Shen, C., Gao, N., Hou, Q., Song, F., Tian, X., ... Xie, K. (2018). Concentrated electrolytes based on dual salts of LiFSI and LiODFB for lithium-metal battery. *Electrochimica Acta*, 289, 422–427.
- Lu, D., Shao, Y., Lozano, T., Bennett, W. D., Graff, G. L., Polzin, B., & Xiao, J. (2015). Failure mechanism for fast-charged lithium metal batteries with liquid electrolytes. *Advanced Energy Materials*, 5(3), Article 1400993.
- Ma, Q., Fang, Z., Liu, P., Ma, J., Qi, X., Feng, W., & Zhou, Z. (2016). Improved cycling stability of lithium-metal anode with concentrated electrolytes based on lithium (fluorosulfonyl)(trifluoromethanesulfonyl)imide. *ChemElectroChem*, 3(4), 531–536.
- Machado, G. O., Ferreira, H. C. A., & Pawlicka, A. (2005). Influence of plasticizer contents on the properties of HEC-based solid polymeric electrolytes. *Electrochimica Acta*, 50(19), 3827–3831.
- Maded, L., Gabaudan, V., Gachot, G., Stievano, L., Monconduit, L., & Martinez, H. (2018). Paving the way for K-ion batteries: Role of electrolyte reactivity through the example of Sb-based electrodes. *ACS Applied Materials & Interfaces*, 10(40), 34116–34122.
- Marcondes, R. F. M. S., D'Agostini, P. S., Ferreira, J., Girotto, E. M., Pawlicka, A., & Dragunski, D. C. (2010). Amylopectin-rich starch plasticized with glycerol for polymer electrolyte application. *Solid State Ionics*, 181(13), 586–591.
- Matsuhiro, B., & Rivas, P. (1993). Second-derivative Fourier transform infrared spectra of seaweed galactans. *Journal of Applied Phycology*, 5(1), 45–51.
- Mattos, R. I., Raphael, E., Majid, S. R., Arof, A. K., & Pawlicka, A. (2012). Enhancement of electrical conductivity in plasticized chitosan based membranes. *Molecular Crystals and Liquid Crystals*, 554(1), 150–159.
- Mitsuiki, M., Mizuno, A., & Motoki, M. (1999). Determination of molecular weight of agars and effect of the molecular weight on the glass transition. *Journal of Agricultural and Food Chemistry*, 47(2), 473–478.
- Mobarak, N. N., Ramli, N., Ahmad, A., & Rahman, M. Y. A. (2012). Chemical interaction and conductivity of carboxymethyl κ -carrageenan based green polymer electrolyte. *Solid State Ionics*, 224, 51–57.
- Mohamed, S. N., Johari, N. A., Ali, A. M. M., Harun, M. K., & Yahya, M. Z. A. (2008). Electrochemical studies on epoxidised natural rubber-based gel polymer electrolytes for lithium-air cells. *Journal of Power Sources*, 183(1), 351–354.
- Numata, M., & Shinkai, S. (2011). "Supramolecular wrapping chemistry" by helix-forming polysaccharides: A powerful strategy for generating diverse polymeric nano-architectures. *Chemical Communications*, 47(7), 1961–1975.
- Okoshi, M., Yamada, Y., Komaba, S., Yamada, A., & Nakai, H. (2016). Theoretical analysis of interactions between potassium ions and organic electrolyte solvents: A comparison with Lithium, sodium, and magnesium ions. *Journal of the Electrochemical Society*, 164(2), A54–A60.
- Pang, S. C., Tay, C. L., & Chin, S. F. (2014). Starch-based gel electrolyte thin films derived from native sago (Metroxylon sagu) starch. *Ionics*, 20(10), 1455–1462.
- Pawlicka, A., Sabadini, A. C., Raphael, E., & Dragunski, D. C. (2008). Ionic conductivity thermogravimetry measurements of starch-based polymeric electrolytes. *Molecular Crystals and Liquid Crystals*, 485(1), 804–816.
- Qian, J., Henderson, W. A., Xu, W., Bhattacharya, P., Engelhard, M., Borodin, O., ... Zhang, J.-S. (2015). High rate and stable cycling of lithium metal anode. *Nature Communications*, 6(1), 6362.
- Shin, M., Song, W.-J., Han, J.-G., Hwang, C., Lee, S., Yoo, S., & Park, S. (2019). Metamorphosis of seaweeds into multitalented materials for energy storage applications. *Advanced Energy Materials*, 9(19), Article 1900570.
- Spirk, S. (2018). *Polysaccharides in batteries. Polysaccharides as battery components. Springer briefs in molecular science*. Cham: Springer.
- Stading, M. (1998). Dynamic mechanical analysis of biopolymers films. *Annual Transaction of the Nordic Rheological Society*, 6, 147–150.
- Suo, L., Hu, Y.-S., Li, H., Armand, M., & Chen, L. (2013). A new class of Solvent-in-Salt electrolyte for high-energy rechargeable metallic lithium batteries. *Nature Communications*, 4(1), 1481.
- Tarascon, J. M., & Armand, M. (2001). Issues and challenges facing rechargeable lithium batteries. *Nature*, 414(6861), 359–367.
- Torres, F. G., Arroyo, J., Alvarez, R., Rodriguez, S., Troncoso, O., & López, D. (2019). Carboxymethyl κ /i-hybrid carrageenan doped with NH4I as a template for solid bio-electrolytes development. *Materials Chemistry and Physics*, 223, 659–665.
- Vieira, M. G. A., da Silva, M. A., dos Santos, L. O., & Beppu, M. M. (2011). Natural-based plasticizers and biopolymer films: A review. *European Polymer Journal*, 47(3), 254–263.
- Waqas, M., Ali, S., Feng, C., Chen, D., Han, J., & He, W. (2019). Recent development in separators for high-temperature lithium-ion batteries. *Small*, 15(33), Article 1901689.
- Wood, K. N., Noked, M., & Dasgupta, N. P. (2017). Lithium metal anodes: Toward an improved understanding of coupled morphological, electrochemical, and mechanical behavior. *ACS Energy Letters*, 2(3), 664–672.
- Wu, F., Yuan, Y.-X., Cheng, X.-B., Bai, Y., Li, Y., Wu, C., ... Zhang, Q. (2018). Perspectives for restraining harsh lithium dendrite growth: Towards robust lithium metal anodes. *Energy Storage Materials*, 15, 148–170.
- Xiang, J., Yang, L., Yuan, L., Yuan, K., Zhang, Y., Huang, Y., ... Huang, Y. (2019). Alkali-metal anodes: From lab to market. *Joule*, 3(10), 2334–2363.
- Xiao, N., McCulloch, W. D., & Wu, Y. (2017). Reversible dendrite-free potassium plating and stripping electrochemistry for potassium secondary batteries. *Journal of the American Chemical Society*, 139(28), 9475–9478.
- Xu, W., Wang, J., Ding, F., Chen, X., Nasybulin, E., Zhang, Y., ... Zhang, J.-G. (2014). Lithium metal anodes for rechargeable batteries. *Energy & Environmental Science*, 7(2), 513–537.
- Yan, K., Lee, H.-W., Gao, T., Zheng, G., Yao, H., Wang, H., & Cui, Y. (2014). Ultrathin two-dimensional atomic crystals as stable interfacial layer for improvement of lithium metal anode. *Nano Letters*, 14(10), 6016–6022.
- Yang, C.-P., Yin, Y.-X., & Guo, Y.-G. (2015). Elemental selenium for electrochemical energy storage. *The Journal of Physical Chemistry Letters*, 6(2), 256–266.
- Yang, C.-P., Yin, Y.-X., Zhang, S.-F., Li, N.-W., & Guo, Y.-G. (2015). Accommodating lithium into 3D current collectors with a submicron skeleton towards long-life lithium metal anodes. *Nature Communications*, 6(1), 8058.
- Yin, Y.-X., Xin, S., Guo, Y.-G., & Wan, L.-J. (2013). Lithium-sulfur batteries: Electrochemistry, materials, and prospects. *Angewandte Chemie International Edition*, 52(50), 13186–13200.
- Youcef, H. B., Orayech, B., Del Amo, J. M. L., Bonilla, F., Shanmukaraj, D., & Armand, M. (2020). Functionalized cellulose as quasi single-ion conductors in polymer electrolyte for all-solid-state Li/Na and LiS batteries. *Solid State Ionics*, 345, Article 115168.
- Zhang, S.-J., Gao, Z.-G., Wang, W.-W., Lu, Y.-Q., Deng, Y.-P., You, J.-H., & Sun, S.-G. (2018). A natural biopolymer film as a robust protective layer to effectively stabilize lithium-metal anodes. *Small*, 14(31), Article 1801054.
- Zhang, T.-W., Tian, T., Shen, B., Song, Y.-H., & Yao, H.-B. (2019). Recent advances on biopolymer fiber based membranes for lithium-ion battery separators. *Composites Communications*, 14, 7–14.
- Zhang, X., Wang, A., Liu, X., & Luo, J. (2019). Dendrites in lithium metal anodes: Suppression, regulation, and elimination. *Accounts of Chemical Research*, 52(11), 3223–3232.
- Zheng, G., Lee, S. W., Liang, Z., Lee, H.-W., Yan, K., Yao, H., & Cui, Y. (2014). Interconnected hollow carbon nanospheres for stable lithium metal anodes. *Nature Nanotechnology*, 9(8), 618–623.