

Agarose-based Gel Electrolytes for Sustainable Primary and Secondary Zinc-Air Batteries

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Agarose-based Gel Electrolytes for Sustainable Primary and Secondary Zinc-Air Batteries / García-Gaitán, Estibaliz; Carmen Morant-Miñana, María; Frattini, Domenico; Maddalena, Lorenza; Fina, Alberto; Gerbaldi, Claudio; Cantero, Igor; Ortiz-Vitoriano, Nagore. - In: CHEMICAL ENGINEERING JOURNAL. - ISSN 1385-8947. - STAMPA. - 472:(2023), pp. 1-17. [10.1016/j.cej.2023.144870]

*Availability:*

This version is available at: 11583/2981932 since: 2023-09-11T10:50:45Z

*Publisher:*

Elsevier

*Published*

DOI:10.1016/j.cej.2023.144870

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<http://doi.org/10.1016/j.cej.2023.144870>

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# 1 **Agarose-Based Gel Electrolytes for Sustainable Primary and Secondary Zinc-Air** 2 **Batteries**

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22  
23 **Abstract** Present Zn-air batteries (ZABs) are based on concentrated alkaline liquid electrolytes,  
24 with high ionic conductivity, but suffer from leakage, evaporation, and carbonate precipitation  
25 due to the semi-open characteristic of these systems. To overcome these issues, gel polymer  
26 electrolytes (GPE), based on naturally occurring biopolymers, arise as a green option to  
27 overcome the above-mentioned limitations. In this work, a novel GPE based on pure agarose  
28 from seaweed is presented as a smart alternative to liquid (adsorbed on a separator) and gel  
29 electrolytes (based on synthetic polymers). The innovative synthesis method described can  
30 directly encapsulate concentrated KOH liquid electrolytes into an agarose matrix in one-pot;  
31 the process requiring approx. 10 min. The unique gel developed in this work, with 2 wt.%  
32 agarose and 8 M KOH electrolyte, presents the best compromise between physicochemical and  
33 electrochemical properties, at lab scale. The characterization results revealed an outstanding  
34 ionic conductivity of  $0.45 \pm 0.05 \text{ S cm}^{-1}$ ,  $\approx 100\%$  water retention up to 200-250 h, retarded Zn

35 self-corrosion up to 30 days (symmetric cell under open circuit), average Zn utilization >70-  
36 80% in primary ZABs in the range 1-20 mA cm<sup>-2</sup> with peaks of ≈96%. In secondary ZABs the  
37 gel electrolyte presents high round-trip efficiency and improved cyclability at high areal  
38 capacities, under soft and severe cycling conditions, never tested before. This agarose gel  
39 represents a potential benchmark for future development of GPE-based ZABs for stationary  
40 applications.

41

42 **Keywords:** gel polymer electrolyte, agarose, natural biopolymer, solid-state, zinc-air battery

43

## 44 **1. Introduction**

45 In the development of batteries with high energy density, safety, sustainability, and  
46 rechargeability at very low cost, rechargeable zinc-air batteries (ZABs) [1] arise as a great  
47 opportunity due to their semi-open character, the use of inexhaustible oxygen from air,  
48 providing a high theoretical energy density ( $1350 \text{ Wh kg}^{-1}$ , theoretical cell voltage of 1.66 V  
49 [2]), so that are regarded as one of the best candidates to complement standard lithium-ion  
50 batteries (LIBs). In recent reports [3,4] environmental and economical assessment conclude that  
51 the costs and impacts of ZABs are potentially lower than other technologies like lead acid, Na-  
52 S, Ni-Cd, LIBs, and redox flow if the cyclability is improved, and have attracted therefore the  
53 utmost attention due to the cheap materials involved, environmental friendliness, and safe  
54 operation [5,6] that can be used in hybrid storage solutions to exploit the high energy density  
55 and low cost of ZAB in synergy with the durability and rate capability of LIB. For their practical  
56 use, challenges such as low Zn utilization and lifetime for primary, short cycle life and low  
57 power density for secondary ZABs have not been solved yet. These issues involve all the  
58 components, and particularly the electrolyte system plays an essential role in the performance  
59 because it is the medium for the bidirectional ionic migration [7].

60 In ZABs, KOH 6-8 M concentrated solutions are the most commonly used liquid electrolytes  
61 due to their optimal viscosity, conductivity, and possibility to dissolve Zn salts (e.g., zinc  
62 acetate) to pre-saturate the electrolyte with zinc ion, however, they present several challenges  
63 such as the precipitation of zinc-based compounds (e.g., ZnO,  $\text{Zn(OH)}_2$ ) [8], vulnerability to  
64  $\text{CO}_2/\text{O}_2$  crossover, susceptibility to evaporation or leakages, and hydrogen evolution reaction  
65 (HER) [9,10]. Carbonate precipitation caused by atmospheric  $\text{CO}_2$  and leakage and/or  
66 evaporation of the liquid electrolyte are the two main drawbacks and ZABs' barriers to  
67 challenge LIBs [6]. To alleviate these disadvantages, the substitution of the liquid electrolyte  
68 by a soft gel polymer electrolyte (GPE) [11–14], is particularly useful for flexible applications  
69 [15,16]. The use of GPEs minimizes the flooding of the electrodes, evaporation, leakage, and  
70 corrosion problems, while possessing sufficiently high ionic conductivity, demonstrated  
71 adaptability to extreme temperatures [17,18], but often weak mechanical strength [19,20].  
72 Currently, GPEs with high ionic conductivities and good mechanical properties are obtained  
73 from (crosslinked) synthetic polymers, like poly(vinyl alcohol) (PVA), poly(acrylic acid)  
74 (PAA), poly(acryl amide) (PAM), and poly(ethylene oxide) (PEO). However, the use of  
75 naturally occurring biopolymers (e.g., cellulose, agars, gelatins, starch-based, chitosan, etc.) is  
76 rapidly gaining importance [21] to avoid petroleum-based plastics in electrochemical storage  
77 devices [22] and in ZABs [23–26]. Many reports [27,28] have already established the benefits

78 of naturally occurring biopolymers as substitutes of petrochemical plastics in terms of  
79 greenhouse gas and fossil fuel savings, lower environmental impacts, and non-competitive  
80 nature to food and land-use, especially if algal-derived [29,30].

81 Among others, red seaweeds (Rhodophyceae) contain sulphated galactans as the main structural  
82 materials of cell walls and intercellular matrices, known as Agar, a mix of agaropectin  
83 (containing the sulphated groups), and agarose (the main component giving jellification) [31].  
84 This extraordinary jellification is due to the 1,3-linked  $\beta$ -d-galactopyranose and 1,4-linked 3,6-  
85 anhydro- $\alpha$ -l-galactopyranose blocks constituting the agarose biopolymer chain, including  $\approx$ 400  
86 repeating units. Agarose gels are considered reversible physical gels forming a 3D structure of  
87 channels commonly employed for proteins' separation.

88 So far, previous examples of the specific use of agarose and/or agar in energy storage devices  
89 can be found in the literature. Agar has been employed as electrolyte mixed with PVA [32],  
90 water soluble graphene oxide [33] or sorbitol [34], as a component of electrochromic devices  
91 [35], as anode additive [36,37], and electrode binder [19,38,39]. Agarose has been used as gel  
92 electrolyte with NaCl for supercapacitors and the mechanical and conductivity properties of  
93 agarose matrices in the presence of KOH (1 M) have been described by Moon et al. [40], and  
94 Ueno et al. [41], respectively. Further examples of agarose as solid-state electrolyte (SSE) have  
95 been reported in other technologies such as Mg-air [33], Li-ion [42], Al-air [43], supercapacitor  
96 [44], or zinc-ion batteries [45]. In ZABs, agarose has been often reported as binder for  
97 electrodes. Mohamad et al. [46] reported agar as binder for the anodes, prepared by mixing Zn  
98 powder and agar paste with 0.2, 0.4 and 0.6 M KOH. Han et al. [47] reported a Fe-N/C catalyst  
99 derived from the pyrolysis of agarose in the presence of urea and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles as  
100 cathode. Similarly, Zhang et al. [48] reported the use of an agarose gel to prepare bimetallic  
101 (iron and cobalt) nitrogen doped carbon composites (FeCo-NC). Jose et al. [49] reported the  
102 use of an agarose-based gel as binder, mixed with Mn(NO<sub>3</sub>)<sub>2</sub> and NaNO<sub>3</sub>, for a gelled cathode.  
103 Kim et al. [50] reported agarose as a binder for electrode to form a gel for the electrodeposition  
104 of MnO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> onto 3D porous nickel foam as support.

105 The scenario is that many of the agarose-based gel electrolytes and applications reported in  
106 previous literature are used in different intercalation-based storage devices. In this work we  
107 focus on ZAB that is a conversion-based device, relying on the chemical reduction and  
108 evolution reactions of oxygen (ORR/OER). Hence, although agarose is used as the polymer  
109 matrix material, the conduction mechanism is different, and less examples of sustainable GPEs  
110 for this technology are reported. Agarose gel electrolytes are an excellent choice for zinc-air  
111 batteries due to their enhanced stability, safety, mechanical integrity, controlled ion transport,

112 longer shelf life, and adequate ionic conductivity. The solid or semi-solid consistency of gel  
113 electrolytes reduces the risk of leakage and evaporation, ensuring the battery's safety and  
114 longevity by providing mechanical support, preserving the battery's structural integrity. Unlike  
115 liquid electrolytes, gels are less prone to leakage, minimizing spills, hazardous chemical  
116 exposure, and preventing short circuits. Additionally, gel electrolytes can be designed with  
117 specific pore sizes or structures to regulate ion movement, enabling better control over ion  
118 diffusion; thus, improving efficiency. They also present an extended life because the solid or  
119 semi-solid nature preserves the electrolyte composition and reduces degradation during storage.  
120 Although gel electrolytes may exhibit slightly lower ionic conductivity compared to liquid  
121 electrolytes, the numerous advantages make them highly preferable in various applications,  
122 where the benefits outweigh the lower ionic conductivity.

123 In this work, we report a novel and comprehensive study about the encapsulation of  
124 concentrated KOH solutions in the agarose biopolymer matrix that avoids the direct contact  
125 with the Zn anode, and therefore retarding Zn corrosion in presence of high KOH concentration  
126 because the larger time needed for electrolyte release avoids the surface corrosion of the anode  
127 and allows for % of Zn utilization close to 100% which are rarely reported in the literature.

128 In addition, the synthesis method and the liquid electrolyte embedding strategy are extremely  
129 important to determine the final properties of the gel [51]. In ZAB technology, several  
130 biopolymer-based electrolytes such as starch, PVA, PAA, cellulose, sago, and agarose/agar  
131 have been prepared by not direct (e.g., not one-pot) methods, requiring multi-steps, hence time  
132 consuming, potentially not industrially scalable [51]. A new approach for the use of agarose as  
133 GPE in ZABs is therefore required to improve properties and performance.

134 Unlike the actual state-of-the-art, in this work, agarose is directly dissolved in a KOH solution  
135 (6 or 8 M), and the total process for obtaining a ready-to-use gel is less than 10 minutes. The  
136 agarose matrix does not form granules during the gelation process, providing homogeneous  
137 smooth interfaces between the gel electrolyte and both electrodes. The successful encapsulation  
138 of concentrated KOH solutions reported here is embodied by a new GPE with excellent balance  
139 between flexibility, stiffness, compression resistance, and ionic conductivity, obtaining  
140 unprecedented properties for excellent electrolyte retention, electrochemical stability, and  
141 therefore excellent performance in ZABs, with a zinc utilization >96% in primary batteries and,  
142 remarkably, secondary batteries based on GPE with longer operating time and cyclability,  
143 demonstrated at high areal capacities never investigated before [52].

144

## 145 **2. Materials and Methods**

## 146 **2.1. Materials and electrolyte/electrodes**

147 For gel electrolyte preparation, agarose (Low EEO, electrophoresis grade, Scharlab, Spain),  
148 agar-agar (Agar for microbiology, Sigma-Aldrich, Germany), xanthan (Xanthan gum from  
149 *Xanthomonas campestris*, Sigma-Aldrich, Germany) powders, and  $\kappa$ -carrageenan (Kappa-  
150 Carrageenan; Acros Organics, Belgium), potassium hydroxide (KOH, pellets, extra pure grade,  
151 Scharlab, Spain), and distilled water (type II analytical grade,  $<1 \mu\text{S cm}^{-1}$ , ECOMATIC,  
152 Wasserlab, Spain) were used. All chemicals were used as received without further purification.  
153 For full cells, anode is obtained by mixing zinc powder (Zn  $>98\%$ , CEGASA Energía SLU,  
154 Spain) and a 45 wt.% KOH solution to form a paste (Zn mass loading approx. 65%). The  
155 cathode for primary cells is a mixture of  $\text{MnO}_2$ , carbon conductive additive, and  
156 poly(tetrafluoroethylene) (PTFE) binder, kindly provided by CEGASA, Spain. For secondary  
157 cells, this primary catalyst is purposefully mixed with nickel cobalt oxide (NCO,  $\text{NiCo}_2\text{O}_4$ ,  
158  $>99\%$ , Sigma-Aldrich, Germany), and ethanol in a 1:1:1 mass ratio to obtain a paste.

159

## 160 **2.2. Ionic conductivity and FTIR measurements**

161 The ionic conductivity was measured by electrochemical impedance spectroscopy (EIS), using  
162 a Solartron 1260A Impedance/Gain-Phase Analyzer (Ametek Inc., Berwyn, PA, United States).  
163 The materials were tested in a frequency range from 10 MHz to 100 Hz applying 50 mV as  
164 polarization amplitude. The gel electrolytes were punched with a 3 mm diameter punch tool  
165 and assembled inside a coin cell (type CR2032) with a Teflon sheet spacer, where a 3 mm  
166 diameter hole is used to place the sample. For ionic conductivity measurements as function of  
167 temperature, a temperature-controlled incubator (KB-23, Binder Inc., Bohemia, NY, United  
168 States) was used. The average of, at least, three replicated measures is reported. The value for  
169 the electrolyte resistance is obtained from the intercept of the Nyquist plot with the X axis. The  
170 ionic conductivity ( $\sigma$ ) of the membrane is then calculated using the following equation:

$$171 \quad \sigma = \frac{t}{A} \cdot \frac{1}{R} \quad (1)$$

172 where  $t$ ,  $A$ , and  $R$  are the thickness, area, and resistance of the membrane, respectively. The  
173 thickness of the membrane was measured after performing the EIS measurements. The ionic  
174 conductivity has been used for the estimation of the activation energy ( $E_a$ ) – related to the  
175 energy required by the ion to release from its bond and migrate to another coordinating site  
176 through the conduction process – employing Arrhenius plot of  $\ln \sigma$  against  $1000/T$ . Arrhenius  
177 plot is obtained using the following equation:

$$178 \quad \ln \sigma = \left(-\frac{E_a}{R}\right) \frac{1}{T} + \ln A \quad (2)$$

179 being  $E_a$  the activation energy in  $\text{J mol}^{-1}$ ,  $R$  ideal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the  
180 temperature in K,  $A$  the Arrhenius constant.

181 FTIR measurements were carried out running a Vertex 70 Microscope from Bruker (Billerica,  
182 MA, United States). All the sample spectra of materials were recorded under argon flow,  
183 corrected for the background, and collected in the wavelength range  $4000\text{--}400 \text{ cm}^{-1}$  as average  
184 of 64 repeated scans.

185

### 186 **2.3. Relative weight losses and flexibility test**

187 The materials' weight losses were measured by using a precision scale and a temperature-  
188 controlled incubator (KB-23, Binder Inc., Bohemia, NY, United States) at  $30\pm 1^\circ\text{C}$  and  
189 environmental relative humidity  $40\pm 5\%$ . Three replicated samples for each electrolyte were  
190 poured into a vial tapped by an aluminum foil with tiny holes and weighted at the initial time.  
191 The weight of each vial was checked daily for a total of 21 days (approx. 500 h), and average  
192 relative weights,  $R_w$  were calculated using the following equation:

$$193 \quad R_w = \frac{m_f \cdot 100}{m_i} \quad (3)$$

194 where  $m_f$ , and  $m_i$  are final mass of each day and initial mass, respectively.

195 The bending angle of material (2 wt.% agarose in 8 M KOH) was simply measured by placing  
196 specimen on lab beakers/stirrers with different radii, from 5 cm to 0.5 cm. The arc angles were  
197 measured with a manual goniometer.

198

### 199 **2.4. Compression tests (till failure and hysteresis)**

200 Stress [kPa] vs Compression strain [%] curves were collected by means of Instron 5966 (Instron  
201 engineering Corp., Norwood, MA, United States) equipped with a 2kN cell applying a  $5 \text{ mm}$   
202  $\text{min}^{-1}$  compression strain rate. The hydrogel samples (cylindrical, diameter 24 mm and heights  
203  $2.4 \pm 0.1 \text{ mm}$  for 6 M KOH and  $2.7 \pm 0.3 \text{ mm}$  for 8 M KOH) were placed between the self-  
204 leveling plates, with protective polyethylene sheets to avoid plates corrosion, and tested until  
205 failure occurred. For the hysteresis test, the loading and unloading cycles (5 cycles) were  
206 performed at a constant compression/decompression rate ( $5 \text{ mm min}^{-1}$ ) and up to a compression  
207 strain of 15%. The elastic modulus was calculated as the slope of the tangent line to compression  
208 stress/strain curve in the range 0-2% of strain. For each sample, a minimum of three  
209 measurements is conducted and the most representative curves are reported.

210

### 211 **2.5. Cell assembly and electrochemical measurements**



212 Full cells were assembled using an in-house design, consisting of a circular Teflon body with  
 213 compartments for components. Anode paste is dripped in a circular cavity of 13 mm. Upon it,  
 214 an agarose gel disk of 24 mm in diameter is placed. Then, for primary cells, approx. 250 mg of  
 215 cathode powder covered it, whereas for secondary cells the MnO<sub>2</sub>/NCO paste was pressed on a  
 216 Ni mesh and dried in oven at 60 °C overnight. The assembly is completed by Ni-based current  
 217 collectors as electrical contacts. A Teflon cap, with two aeration holes, closes the cell. Sealing  
 218 is ensured by pression thanks to an O-ring and two bolts. For symmetric cells, the same in-  
 219 house design was used but the Teflon cap had no aeration holes and presents a circular cavity  
 220 of 13 mm designed to place approx. the same amount of Zn paste on both sides of the gel  
 221 electrolyte. Both sides are thus not exposed to air.

222 The anode area (1.33 cm<sup>2</sup>) is used to calculate current densities in all experiments; Zn  
 223 extractions, specific capacities, and all the other metrics [53], are normalized by using the  
 224 theoretical capacity of Zn (819.73 mAh g<sup>-1</sup>), and the masses indicated for each cell. For primary  
 225 cells, metrics were calculated according to the following equations:

$$226 \quad Z_{n_{utilization}} = \frac{C_{cell}}{m_{Zn} \cdot 819.73} \cdot 100 \quad (4)$$

$$227 \quad f_{Zn} = \frac{m_{Zn}}{m_{anode} + m_{gel} + m_{cathode}} \quad (5)$$

$$228 \quad E_{density} = \frac{Z_{n_{utilization}}}{100} \cdot 819.73 \cdot f_{Zn} \cdot V_{avg} \quad (6)$$

229 Where  $Z_{n_{utilization}}$  is the percentage of discharged zinc vs. available zinc in the primary cell,  $C_{cell}$   
 230 is the total capacity delivered by the primary cell,  $m_{Zn}$  is the mass of active zinc,  $f_{Zn}$  is the zinc  
 231 weight fraction in the cell,  $E_{density}$  is the gravimetric energy density of the cell,  $m_{anode}$ ,  $m_{gel}$ , and  
 232  $m_{cathode}$  are the total mass of anode, gel, and cathode used in the cell, and  $V_{avg}$  is the average  
 233 discharge voltage of the cell. For secondary cells, metrics were calculated according to the  
 234 following equations:

$$235 \quad DoD_c = \frac{1.33 \cdot j \cdot t_{dis}}{m_{Zn} \cdot 819.73} \cdot 100 \quad (7)$$

$$236 \quad DoD_{tot} = n_c \cdot DoD_c \quad (8)$$

$$237 \quad RTE = \frac{V_{avg}}{V_{ch}} \cdot 100 \quad (9)$$

$$238 \quad E_{density} = \frac{DoD_{tot}}{100} \cdot 819.73 \cdot f_{Zn} \cdot V_{avg} \quad (10)$$

239 Where 1.33 cm<sup>2</sup> is the anode area in this work used for normalization,  $DoD_c$  and  $DoD_{tot}$  are the  
 240 depth of discharge per cycle and total (cumulative), respectively,  $j$  is the current density,  $t_{dis}$  is  
 241 the discharge time per cycle,  $n_c$  is the number of cycles, RTE is the round-trip efficiency  
 242 (voltaic), and  $V_{ch}$  is the average charge voltage.

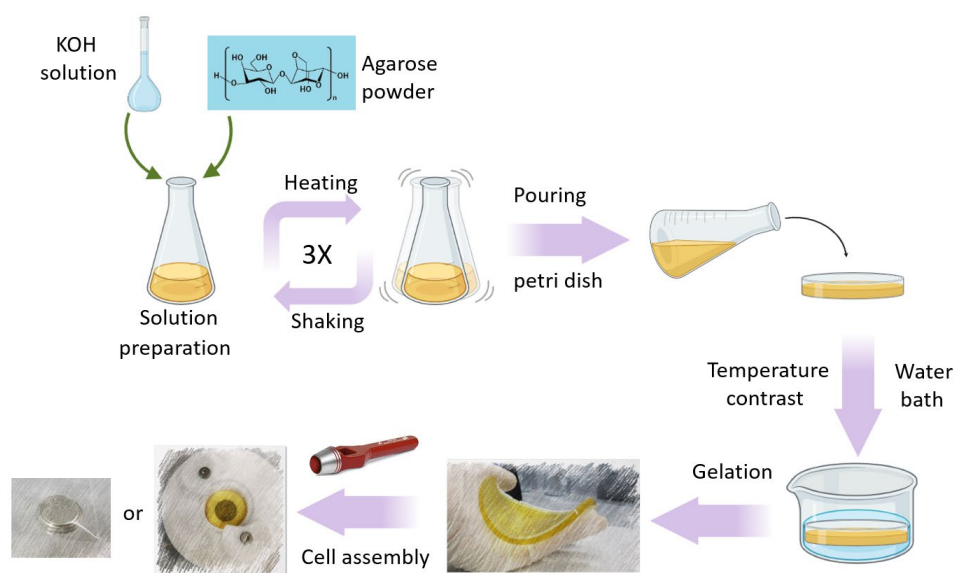
243 Galvanostatic experiments were performed on a BCS 815 potentiostat (BioLogic, Seyssinet-  
 244 Pariset, France) to determine the electrochemical behavior of agarose biopolymer gel  
 245 electrolyte jellified in KOH solutions. Tests were conducted in constant current (CC) mode. For  
 246 primary cells, the current density applied was from 1 to 30 mA cm<sup>-2</sup>, limiting the cutoff voltage  
 247 to 0.8 V. For secondary cells, symmetric cycles (i.e., same discharge/charge time) and current  
 248 densities ranging between 1, 2, 5, and 10 mA cm<sup>-2</sup> were applied at various cycling times, to  
 249 span different areal capacities, from 1.67 to 60 mAh cm<sup>-2</sup> [54]. Cutoff voltages for discharge  
 250 and charge were 0.6 V and 2.2 V, respectively. For symmetric cells, open circuit voltage (OCV)  
 251 was monitored over time up to 1400 h (approx. 60 days), and impedance response (EIS) was  
 252 checked every 8 h in a frequency range of 300 kHz to 100 mHz, and 10 mV as polarization  
 253 amplitude using a VMP3 potentiostat (BioLogic, Seyssinet-Pariset, France). Symmetric cells  
 254 cycling was carried out at 2 mA cm<sup>-2</sup> for 12 h per cycle.

255

### 256 3. Results and Discussion

#### 257 3.1. Preparation of the biopolymer gel electrolytes

258 The biopolymer gel electrolyte was obtained by mixing the desired amount of biopolymer in  
 259 25 mL of KOH solution at different molar concentrations to achieve the desired weight  
 260 percentage of agarose. After reaching a homogeneous dispersion, the mixture was uniformly  
 261 and rapidly heated up to 100-120 °C for few minutes, under continuous shaking as it is shown  
 262 in **Figure 1**.



263

264 **Figure 1.** Schematic diagram of the synthesis of the agarose and KOH gel electrolyte.

265

266 Subsequently, the mixture was quickly poured into a petri dish and quenched by immersion in  
 267 a water bath until the complete jellification. The gel time formation depended on the KOH  
 268 concentration. The jellifying process of the gels containing a KOH concentration lower than 8  
 269 M, started at room temperature, and finished requiring one hour of curing in the oven. The  
 270 selected temperature, 36 °C, is the jelling point of the agarose. On the contrary, samples  
 271 containing 8 or 10 M KOH solutions formed a gel after a few seconds. A summary with the  
 272 experimental conditions for the obtention of the 2 wt.% of agarose gels is listed in **Table 1**.

273 **Table 1.** Synthesis conditions of agarose-based biopolymer gels.

KOH concentration [M]	Heating time [min]	Water cooling [Yes/No]	Curing Temperature [°C]	Curing time [h]	Jellifying time [h]
2	4	Yes	36	1	24
4	4	Yes	36	1	15
6	5	Yes	36	1	5.5
8	5.5	Yes	(a)	0	0.01
10	4	No	(a)	0	0.01

274 (a) Not needed

275  
 276 Indeed, gels with 2 wt.% agarose present a jellification time (**Table 1**) inversely proportional  
 277 to the KOH molar concentration, being 1 day for 2 M KOH and requiring in some cases a curing  
 278 step, down to few minutes for 10 M KOH, without any curing. A very short, quite instant,  
 279 jellification limits the processability of the gels, hence the gels at 2 wt.% agarose, KOH 6 M  
 280 and 8 M, have been selected for further study. As it is shown in **Table 1**, the higher the  
 281 concentration of KOH solution, the faster the jellifying process and the curing step is no longer  
 282 required. The gelation mechanism of agarose still remains a matter of controversy and it is not  
 283 clear yet if the mechanism is spinodal decomposition or nucleation and growth [55]. However,  
 284 according to the most accredited theory, the gelation mechanism is explained for the formation  
 285 of intramolecular and intermolecular hydrogen bonding occurring between the D-galactose and  
 286 3,6-anhydro-alpha-L-galactopyranose molecules. This association results in a cage effect,  
 287 which leads to the lowest energy state of electrons of the lone pairs of ring oxygen atoms of the  
 288 anhydro-L-galactopuranosyl residues. The conformation adopts a tetrahedral distribution and,  
 289 therefore, attracts not only each other but also water molecules due to hydrogen bonding [56].  
 290 In presence of NaOH (ca. 2.5 M, 50-60 °C and 0.5-1 h of treatment), it is described by some  
 291 authors a reinforcement of the gel strength, and this is correlated with a decrease in the yield of

292 sulfate molecules, the increase of the 3,6-anhydrogalactose, and a negligible change in the O-  
 293 methyl and pyruvic acid contents [57]. Based on this, we hypothesize that the mechanism  
 294 behind the rapid gelation with increasing KOH concentration is due to the higher hydrolysis of  
 295 the sulfate content and simultaneous formation of numerous bonds within the 3,6-  
 296 anhydrogalactose blocks, thereby improving the gelling properties [58].

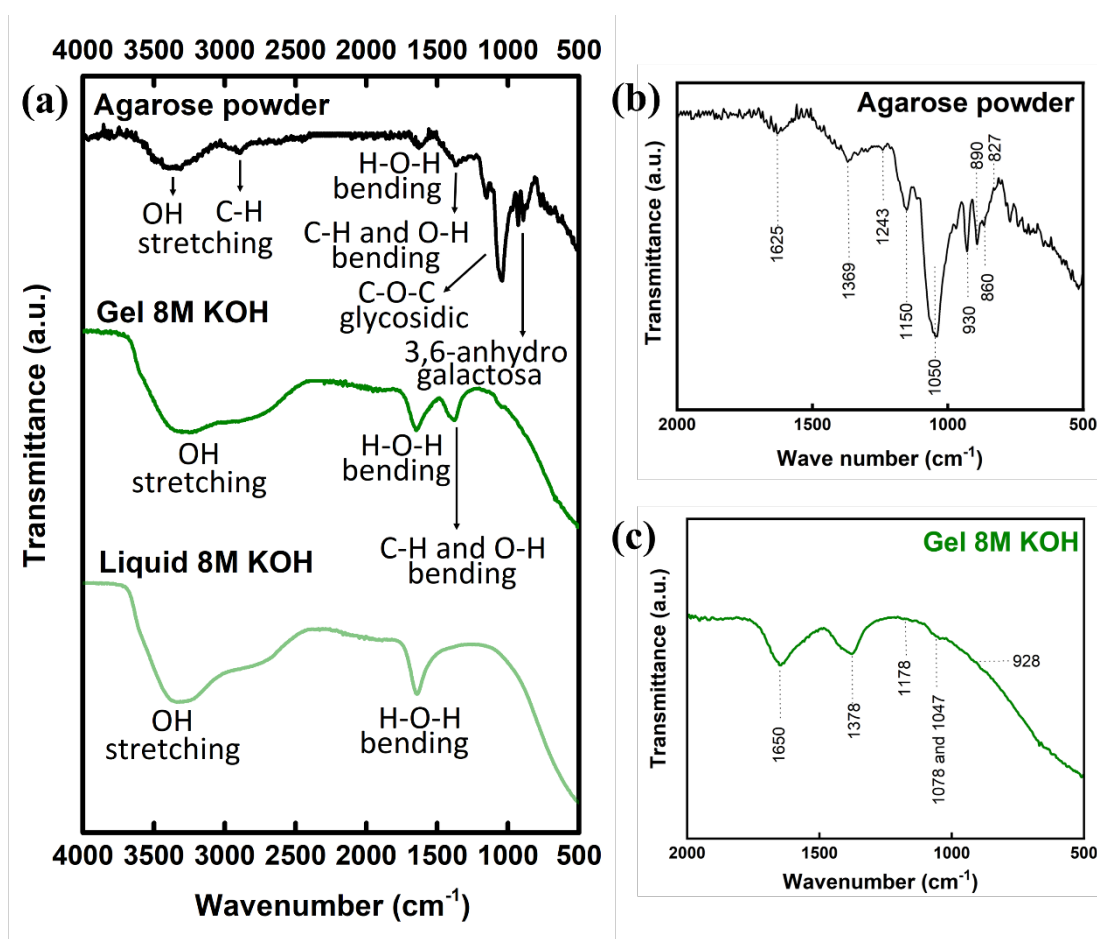
297

## 298 3.2. Characterization results

### 299 3.2.1. FTIR

300 In order to verify the synthesis procedure, and that the electrolyte is embedded in the  
 301 biopolymer matrix, the molecular structure of the 8 M KOH gel was checked and compared to  
 302 agarose powder precursors and 8 M KOH liquid electrolyte (**Figure 2**). FTIR spectra of gel 6  
 303 M KOH are reported in **Figure S1**.

304



305

306

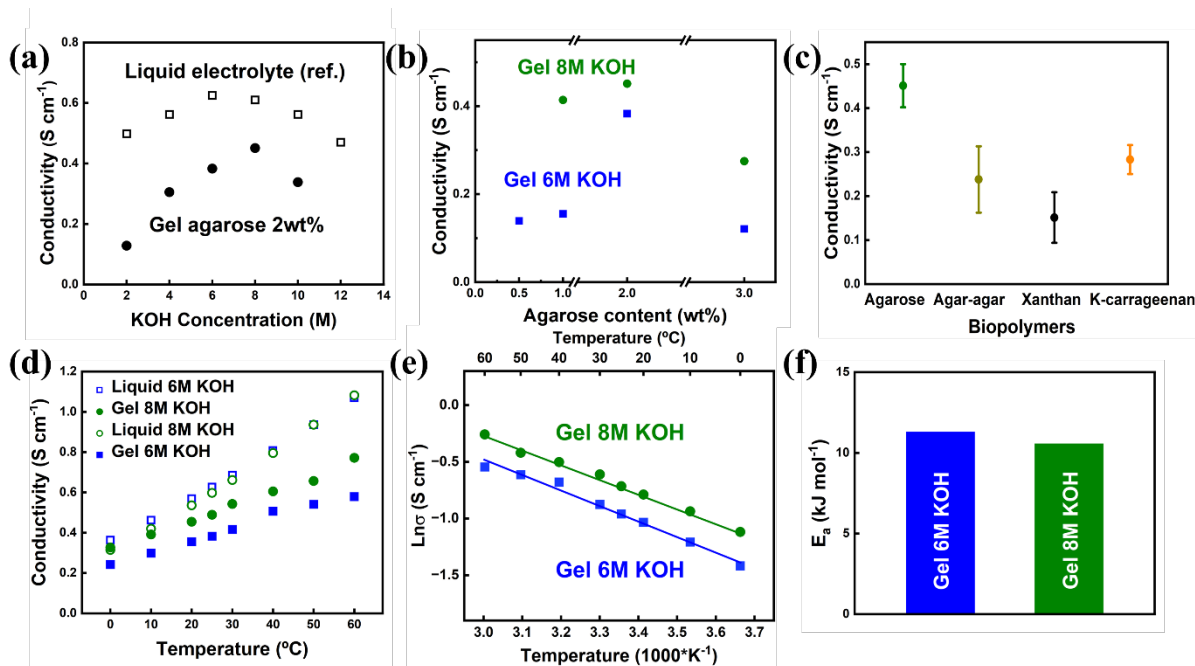
307 **Figure 2.** a) FTIR spectra of agarose powder, agarose gel with 8 M KOH electrolyte, and liquid  
 308 electrolyte 8 M KOH; b) Inset of FTIR spectrum of agarose powder; c) Inset of FTIR spectrum  
 309 of agarose gel 6 M KOH.

310

311 In **Figure 2a** the characteristic absorption bands of the spectra, with the corresponding  
312 functional groups are reported, and together with literature references for the three samples in  
313 **Table S1**. The agarose powder spectrum shows a broad and relatively weak absorption band  
314 between 3680-3050  $\text{cm}^{-1}$  and centered approx. at 3365  $\text{cm}^{-1}$  that is ascribed to stretching mode  
315 of the hydroxyl group of water molecules (agarose powder is hygroscopic) [59,60]; the sharp  
316 and medium intensity band at 1045  $\text{cm}^{-1}$  coupled with a weak band at 1156  $\text{cm}^{-1}$ , are both  
317 assigned to the vibration mode of C–O–C bridge of glycosidic linkage [59,60], while the band  
318 at 932  $\text{cm}^{-1}$  reflects the vibration mode of the C–O–C bridge of the 3,6-anhydrogalactose unit  
319 [61,62]. The other secondary bands for agarose powder (see **Figure 2b**) are listed in **Table S1**.  
320 For the gel 8 M KOH, three characteristic adsorption bands are visible. The first two, at 3272  
321 and 1645  $\text{cm}^{-1}$  are the same as the liquid 8 M KOH [60,63,64]. Comparing the values of the O-  
322 H stretching vibration bands in **Table S1**, it is possible to interpret the small shift toward lower  
323 wavenumbers, from 3320  $\text{cm}^{-1}$  of the liquid to the 3272  $\text{cm}^{-1}$  of the gel as an effect of the  
324 formation of strong hydrogen bonds between the water molecules and the biopolymer matrix,  
325 especially if the polymer is hydrophilic [65], as in the case of agarose. The third one at 1378  
326  $\text{cm}^{-1}$  is new, absent in the liquid 8 M KOH and not clearly visible, or very weak, in agarose  
327 powder, and represents the overlapped bending modes of C-H and O-H (hydroxyl groups not  
328 related to water) bonds [61,62]. The appearance of this peak could be ascribed to the strong  
329 hydrogen bonds formed inside the gel due to the reaction between water, KOH, and agarose  
330 functional groups [58,61,62]. Finally, a residual signal around 1000-1180  $\text{cm}^{-1}$  can be noted in  
331 the spectrum of gel (**Figure 2c**) that is ascribed to the strong C-O-C glycosidic band from  
332 agarose powder. For liquid 8 M KOH, the spectrum is almost identical to that of water, with  
333 only two absorption bands detected. The first band at 3320  $\text{cm}^{-1}$  corresponds to the O-H  
334 stretching band [59,60], and the band at 1645  $\text{cm}^{-1}$  is ascribed to bending mode of H-O-H  
335 [60,63,64].

### 336 3.2.2. Ionic conductivity

337 Among the different parameters to be considered for developing GPEs, ionic conductivity is  
338 crucial because it influences the ohmic resistance of the battery and determines the ion mobility  
339 inside the gel [7]. Hence, the effect of the KOH molar concentration in the range between 2 and  
340 10 M and the amount of biopolymer (from 0.5 wt.% to 3 wt.%) on the GPE ionic conductivity  
341 was measured and the results are summarized in **Figure 3a and 3b**, respectively.



342  
 343 **Figure 3.** Ionic conductivity of alkaline biopolymer gels as a function of: (a) KOH  
 344 concentration, (b) agarose content, (c) biopolymer type, (all measures are at room temperature)  
 345 and (d) temperature; (e) Arrhenius plot showing ionic conductivity vs. temperature for liquid  
 346 and gel electrolytes at KOH 6 M and 8 M, and (f) activation energy of gel 6 M KOH and gel 8  
 347 M KOH. Data for liquid electrolytes in Figure 3a and 3d are taken from Gilliam et al. [66].

348  
 349 In **Figure 3a**, the ionic behavior of agarose gel electrolytes was determined and compared to  
 350 reference KOH liquid electrolyte conductivities at different KOH concentrations as from  
 351 Gilliam et al. [66]. The agarose gel possesses a very high ionic conductivity, just slightly lower  
 352 than KOH liquid electrolytes and in the same order of magnitude. The gels with 6 M and 8 M  
 353 KOH present the highest ionic conductivity and therefore were selected for further studies. In  
 354 **Figure 3b**, the initial 2 wt.% agarose content, for the 6 M and 8 M KOH concentrations, was  
 355 varied to check the effect on ionic conductivity. The gels at 2 wt.% possess the highest ionic  
 356 conductivity for both KOH concentrations. An interesting comparison is proposed in **Figure**  
 357 **3c**, where, by using the 8 M KOH solution, 2 wt.% of biopolymer content, and the same  
 358 jellification protocol used for agarose, the ionic conductivity of gels with other natural  
 359 biopolymers is compared. Although being in the same order of magnitude, the conductivity  
 360 values of gels using agar-agar, xanthan, and  $\kappa$ -carrageenan are lower than agarose, thus proving  
 361 the benefits of agarose. This result also demonstrates that this synthesis method can be applied  
 362 with no substantial modifications also to other biopolymers, such as Xanthan (0.151 S cm<sup>-1</sup>) or  
 363  $\kappa$ -carrageenan (0.283 S cm<sup>-1</sup>) (**Figure 3c**) achieving higher ionic capacities than those reported  
 364 in the literature for similar Xanthan/8 M KOH and  $\kappa$ -carrageenan/8 M KOH gels [33].

365 A useful information for prospective industrial development toward market, is related to gel  
 366 ionic conductivity behavior as function of temperature. In **Figure 3d** the ionic conductivity  
 367 trends are shown in the 0 – 60 °C range and compared to data for liquid electrolytes as available  
 368 from Gilliam et al. [66], viz. the common operational temperature range for a commercial  
 369 battery. To complement this information, a brief thermal characterization of pristine and an  
 370 aged gel 8 M KOH is reported and discussed in the supplementary information (see **Figure S2**).  
 371 Ionic conductivity values of both liquid and gel electrolytes increase with the temperature as  
 372 expected [66]. However, in an alkaline gel, the conduction mechanism is different because,  
 373 dissimilarly to proton hopping mechanism, hydroxyl anions are conducted via hyper-  
 374 coordinated and per-solvated complexes of OH<sup>-</sup> by four H<sub>2</sub>O molecules. When this  
 375 [OH(H<sub>2</sub>O)<sub>4</sub>]<sup>-</sup> complex gets close to a new water molecule, the coordinated OH<sup>-</sup> establishes a H-  
 376 bond with the water molecule and takes over an H<sup>+</sup> to form a new OH<sup>-</sup> that carries the negative  
 377 charge, and pass it again to other solvent molecule [67]. A temperature increment expands the  
 378 pores of the biopolymer matrix, redistributing the liquid electrolyte in the gel, hence increasing  
 379 ionic conductivity without causing evaporation [68].

380 The Arrhenius plot and activation energies of the gels at 2 wt.% agarose with 6 M and 8 M  
 381 KOH are shown in **Figure 3e and f**, respectively. The linear fits of conductivity data are  
 382 reported in **Figure 3e**, showing a good regression for both gels ( $R^2$  is 0.985 for gel 6 M KOH,  
 383 while is 0.995 for gel 8 M KOH). The activation energy values calculated are compared in  
 384 **Figure 3f**, showing  $E_a$  11.32 kJ mol<sup>-1</sup> for the gel 6 M KOH whereas for the gel 8 M KOH is  
 385 10.57 kJ mol<sup>-1</sup>. This lower value of  $E_a$  for the gel 8 M KOH, and the superior ionic conductivity,  
 386 further supports that the involved ions could transport/diffuse easier because less energy is  
 387 required, compared to the gel 6 M KOH. For instance, **Table 2** compares the  $E_a$  reported for  
 388 other gel electrolytes based on natural/synthetic polymers.

389 **Table 2.** Comparison of  $E_a$  ranges for GPEs based on synthetic or natural polymers.

Gel type	$E_a$ [kJ mol <sup>-1</sup> ]	Refs.
Agarose 8 M KOH	10.57	This work
Agarose 6 M KOH	11.32	This work
QAFC with/without GO	8.40-16.30	[69]
Chitosan with NH <sub>4</sub> SCN	13.40-14.30	[70]
κ-carrageenan with NH <sub>4</sub> NO <sub>3</sub>	6.07-10.13	[71]
PVA-KOH	22.00-28.00	[72]

PVA-KOH	13.50-14.00	[73]
PVA-KOH	15.44-20.26	[74]
PVA-KOH	3.00-15.00	[75,76]

---

390  
391 Zhang et al. [69] reported  $E_a$  in the range of 8.4 to 16.3 kJ mol<sup>-1</sup> for a quaternary ammonium  
392 functionalized cellulose (QAFC) with/without graphene oxide; Shukur et al. [70] further  
393 reported values of  $E_a$  between 13.4 and 14.3 kJ mol<sup>-1</sup> for chitosan-based solid biopolymer  
394 electrolytes containing ammonium thiocyanate (NH<sub>4</sub>SCN) with glycerol as plasticizer, and  
395 Rudhziah et al. [71] reported values of approx. 6.07 and 10.13 kJ mol<sup>-1</sup> for a gel electrolyte  
396 based on seaweed  $\kappa$ -carrageenan with NH<sub>4</sub>NO<sub>3</sub>. In all cases the ionic conductivities were in the  
397 range of few mS cm<sup>-1</sup>. Similarly, for gel electrolytes based on synthetic polymers, different  
398 activation energy values are available for PVA-based gel. For a PVA-KOH polymer electrolyte  
399 with a ionic conductivity of 10<sup>-3</sup> S cm<sup>-1</sup> at room temperature, Lewandowski et al. [72] reported  
400  $E_a$  in the range of 28 and 22 kJ mol<sup>-1</sup> whereas Mohamad et al. [73] reported an  $E_a$  of approx.  
401 14-13.5 kJ mol<sup>-1</sup>; Santos et al. [74] described  $E_a$  in the range of approx. 15.44 to 20.26 kJ mol<sup>-1</sup>  
402 for PVA-KOH electrolyte with a high ionic conductivity of 0.34 S cm<sup>-1</sup> and Yang et al. [75,76]  
403 disclosed  $E_a$  in the range of 3–15 kJ mol<sup>-1</sup> for PVA-KOH gel electrolyte with ionic conductivity  
404 ranging between 47-61 mS cm<sup>-1</sup>. Therefore, the gels developed in this work present both  
405 favorable ionic conductivity (0.383 and 0.451 S cm<sup>-1</sup> for 6 M KOH and 8 M KOH gels) and  
406 lower activation energy (13.29 kJ mol<sup>-1</sup> for the gel 6 M KOH and 10.57 kJ mol<sup>-1</sup> for the gel 8  
407 M KOH.) compared to gel based on synthetic (from 10<sup>-3</sup> S cm<sup>-1</sup> to 0.34 S cm<sup>-1</sup>; and from 3 to  
408 28 kJ mol<sup>-1</sup>) and/or natural (from 0.141·10<sup>-4</sup> S cm<sup>-1</sup> to 0.042 S cm<sup>-1</sup>; from 8.4 to 16.3 kJ mol<sup>-1</sup>)  
409 biopolymers in the literature.  
410 Moreover, the synthesis method is also important to evaluate the overall benefits of the agarose  
411 gel developed in this work. For instance, some of the methods reported to synthesize  
412 agarose/agar gels for ZABs [37,77,78] consist of first dissolving the agarose powder in water  
413 at high temperature (90 °C), requiring at least 30 minutes, and then further soaking of the  
414 obtained neutral gel in an alkaline media (KOH or KOH/ZnCl<sub>2</sub>) for several hours. Very recently,  
415 Yang et al. [77], the reported method for agar-PVA/GO gel is more complex and longer, as agar  
416 is dissolved in a PVA/GO solution at 95 °C, but the gelation requires two freezing/thawing (-  
417 20 °C/RT) cycles. This method requires approx. 9 h for obtaining the final gel. Additional steps  
418 prolong and complicate the synthesis. In another recent work [78], before the jellification of  
419 agar, the biopolymer dissolution is injected into a melamine foam and cooled down to RT for  
420 1 h and then soaked for 12 h in the liquid electrolyte. In this case, the discharge capacity reported



421 was given by area instead of Zn mass, and the applied current density was  $2 \text{ mA cm}^{-2}$ , but the  
422 performances were not good enough. The synthesis method developed here is one-pot and can  
423 synthesize a highly performing gel in few minutes instead of hours, thus being very convenient,  
424 time saving, and providing superior gel properties.

### 425 3.2.3. Electrolyte retention and weight losses

426 One of the key considerations to replace liquid electrolytes soaked in standard separators in  
427 ZABs is due to their low stability and durability once exposed to air [79]. Indeed, liquid  
428 electrolytes in technologies open to air tend to evaporate and if added in excessive amounts,  
429 could cause a leakage instead. This leads to safety concerns due to the release of corrosive  
430 media. To quantify this aspect, the 8 M and 6 M KOH gels have been tested for liquid retention  
431 against a glass fiber separator soaked with 8 M KOH. The relative weight vs. time measurement  
432 is presented in the supporting **Figure S3**. The agarose biopolymer matrix can retain electrolyte  
433 for longer time when using a KOH concentration of 8 M: it is observed that the gel can retain  
434 water without substantial weight change up to 240 h (i.e., 10 days) and, after 528 hours (22  
435 days), only loses 26% of its initial weight. On the contrary, the gel 6 M KOH shows poorer  
436 retention, and a noticeable weight loss ( $\approx 10\%$ ) after few days, which remains stable until  
437 approximately 240 h (10 days). At this point, the material is not capable of retaining the liquid,  
438 causing a strong drop in weight, almost 40% of weight loss (22 days). This effect is directly  
439 related to the microstructure of the agarose gel since the higher the KOH concentration the  
440 higher the density of the network and the lower the water release observed due to the decreased  
441 pore size [58].

442 Nonetheless, the results obtained with the glass fiber separator show the importance of  
443 embedding the liquid electrolyte in a polymer matrix to ensure a longer battery life. Indeed, the  
444 glass fiber cannot retain the liquid electrolyte, and after 24 h the relative weight loss is already  
445  $\approx 40\%$ . After 10 days (240 h), the weight loss is almost 55%, and then reaches a constant value.  
446 This is due to the precipitation of KOH crystals, when all the liquid is evaporated, and the  
447 residual weight represents the dried glass fiber. This means that the gel offers not only the  
448 possibility to avoid evaporation and leakage, but also to “immobilize” larger excesses of  
449 electrolyte by using just 2 wt.% of biopolymer matrix instead of around 40 wt.% of inactive  
450 separator. In **Table 3** a brief comparison with examples from the literature is reported.

451 **Table 3.** Comparison of weight losses for different GPEs.

Gel type	Time [h]	Weight loss [%]	Refs.
Agarose 8 M KOH	528	25.95	This work

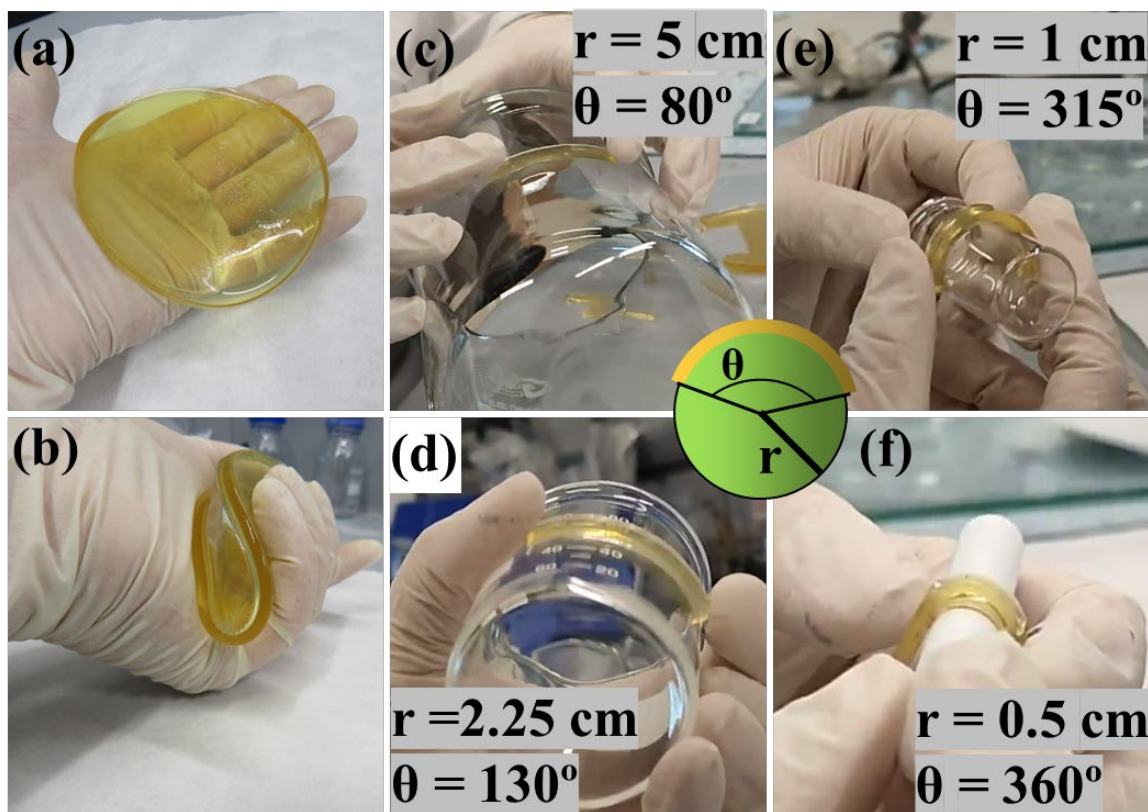
Agarose 6 M KOH	528	39.47	This work
Agar-PVA-GO	24	41.80	[77]
Agar-melamine foam	24	58.00	[78]
Starch 6 M KOH	18	16.00	[80]
PVA 1.7 M KOH	72	40.60	[81]
PVA-SiO <sub>2</sub> 5 wt.% 6 M KOH	40	37.60	[82]
PANa 6 M KOH	185	2.70	[83]

452

453 Comparing with the literature it should be considered that, for the data reported, humidity and  
454 temperature of tests may vary, however, embedding the liquid electrolyte in an agarose  
455 biopolymer matrix, as shown in this work, greatly retard the time needed for electrolyte  
456 evaporation. Other recently reported agar-based gels present liquid electrolyte retention of  
457 58.2% [77] and 42% [78] after 24 h; a starch-based gel, soaked in 6 M KOH for 12 h, showed  
458 a weight loss of 16% already after 18 h at room temperature (larger times not reported) [80]; a  
459 PVA-based gel embedding 1.7 M KOH presented a weight loss of  $\approx 40\%$  after 72 h [81] while  
460 a PVA-5 wt.% SiO<sub>2</sub> composite gel, soaked in 6 M KOH for 24 h and exposed to ambient  
461 conditions (25°C, 50% RH), gave a weight loss of 37.6% after 40 h [82]. Sodium polyacrylate  
462 (PANa) hydrogel, soaked in 6 M KOH for 24 h and then exposed to air at room temperature,  
463 was reported to have only 2.7% weight loss after 185 h [83]; Therefore, embedding the liquid  
464 electrolyte in an agarose biopolymer matrix, as shown in this work, greatly retard the time  
465 needed for electrolyte evaporation. Compared to other systems found in the literature (60-80%  
466 retention, in one case 97%, after few hours), superior electrolyte retention capacity (100-98%  
467 retention after 200 h for the gel 8 M KOH) within the agarose biopolymer matrix is here  
468 achieved, which also acts as an electrolyte reservoir.

#### 469 3.2.4. Flexibility tests

470 The flexibility of the gel based on 8 M KOH embedded in 2 wt.% agarose was determined first  
471 visually and then by calculating bending angle using different radii, as shown in **Figure 4**.



472  
 473 **Figure 4.** Gel bending test of agarose 2 wt.% biopolymer gel electrolyte with KOH 8 M: (a)  
 474 not bended; (b) fully banded; (c) 5 cm; (d) 2.25 cm; (e) 1 cm; (f) 0.5 cm ( $r$  = radius;  $\theta$  = arc  
 475 angle).

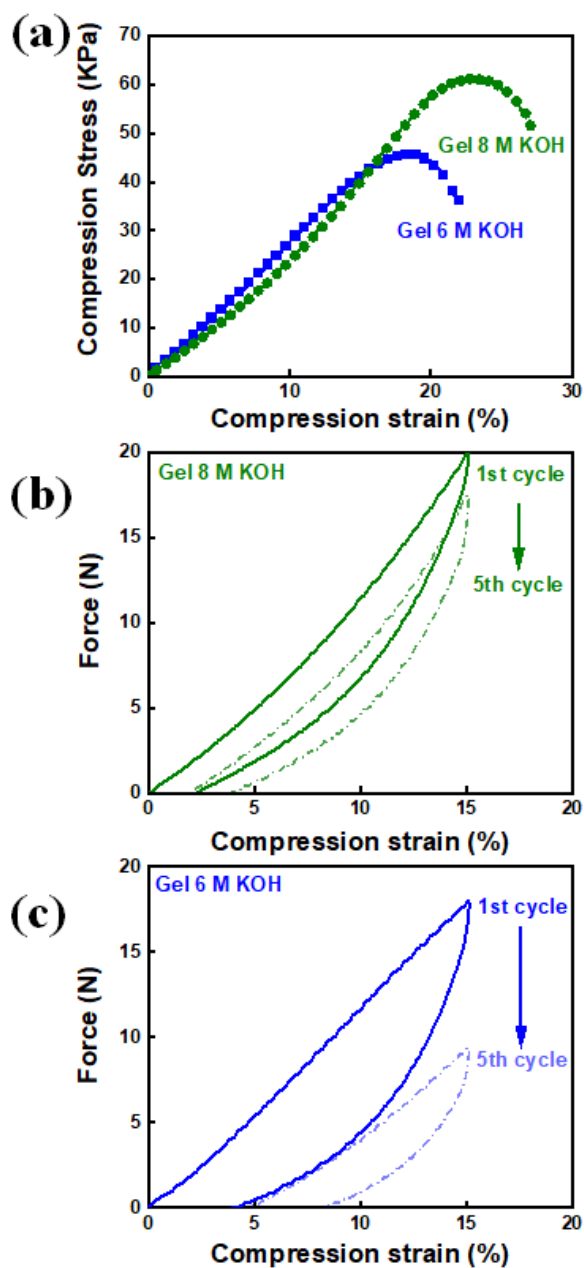
476  
 477 The pristine gel seems flexible and mechanically stable and can withstand bending both at small  
 478 and large angles (**Figure 4a-b**). The experiment was conducted by applying different radii, from  
 479 big to small radius (5 cm to 0.5 cm, **Figure 4c-f**) at bending, and the measured arc angles ( $^{\circ}$ )  
 480 are reported in **Figure 4c-f**, together with the radius used. Similar results for the gel 2 wt.%  
 481 agarose with 6 M KOH (here omitted for brevity, see **Figure S4**) have been achieved.

482 Overall, the gel shows notable visual flexibility, no water release upon squeezing, and  
 483 remarkable resistance to repeated bending. Each specimen was deposited onto different circular  
 484 objects to bend them to different angles, without breaking. The arc angles achieved ranged from  
 485  $80^{\circ}$  to  $360^{\circ}$ , i.e., completely wrapping the circular support of 0.5 cm radius, the smallest radius  
 486 tested, considering the size (i.e., 6.5 x 1.0 cm) of the specimen. Usual bending angles reported  
 487 in the related literature for flexible ZABs are in the range of 0 to  $120^{\circ}$ , rarely approaching full  
 488  $180^{\circ}$  bending (equivalent to an arc angle of  $360^{\circ}$ ), corresponding to a portion [84] of the arc  
 489 angles reported in **Figure 4**. The qualitative flexibility test above has shown the possibility to  
 490 fold the agarose gels up to completely wrapping (i.e.,  $360^{\circ}$  arc angle) a small cylinder,

491 demonstrating the very good flexibility achieved by present agarose-based gels, comparable to  
492 already reported synthetic and natural GPEs [69,85,86].

### 493 3.2.5. Compression-strain

494 The ZAB cells used in this work undergo moderate compression when sealed and during battery  
495 operation, to ensure component contact. Mechanical testing under uniaxial compression, till  
496 failure or cyclically, has been therefore carried out. Compressive strength, ultimate strength,  
497 and elastic modulus are determined to compare the elastic behavior of agarose gels 2 wt.% with  
498 6 M or 8 M KOH. The results are shown in **Figure 5**.



499 **Figure 5.** Compression-strain behavior of gels agarose 2 wt.% 6 M and 8 M KOH: (a) failure  
500 test under compression; (b) cyclic compression for the 8 M KOH gel; (c) cyclic compression  
501 for the 6 M KOH gel.  
502

503

504 In **Figure 5a**, the 6 M KOH gel showed approx. linear stress-strain until  $16\pm 1\%$  compression  
505 strain, followed by the failure of the sample after reaching maximum strain at  $22.0\pm 1.0\%$  and  
506 maximum stress at  $45.0\pm 2.0$  kPa. The shape of the curve resembles to what observed in  
507 literature for agarose hydrogels prepared in hot water, without any covalent crosslinking [87],  
508 and the elastic modulus (at low deformation, 0 to 2% strain) was calculated to be  $2.4\pm 0.1$  kPa.  
509 Differently, the gel 8 M KOH compression tests display a more remarkable progressive  
510 compression hardening, eventually leading to sample failure at  $27.0\pm 1.0\%$  (green curve in  
511 **Figure 5a**). Although the elastic modulus is  $2.1\pm 0.2$  kPa, very similar to the 6 M KOH gel, the  
512 maximum strength was  $62.0\pm 1.0$  kPa, at 25% compression strain, namely  $\approx 37\%$  higher as  
513 compared to 6 M KOH. A brief comparison with the literature is reported in **Table 4**.

514

**Table 4.** Comparison of selected mechanical properties for different GPEs.

Gel type	Max compressive strength [MPa]	Strain (at max compression) [%]	Compression modulus [MPa]	Refs.
Agarose 8 M KOH	$62.0\pm 1.0\cdot 10^{-3}$	$25.0\pm 1.0\%$	$2.1\pm 0.2\cdot 10^{-3}$	This work
Agarose 6 M KOH	$45.0\pm 2.0\cdot 10^{-3}$	$22.0\pm 1.0\%$	$2.4\pm 0.1\cdot 10^{-3}$	This work
Agarose/LiOH/Urea	0.09-0.33	$\approx 41$	-	[87]
Cellulose/NaOH	2.1-7.2	40-50	2-7	[88]
poly(2-acrylamido-2-methylpropanesulfonic acid potassium salt)/methyl cellulose	$170\cdot 10^{-3}$	-	-	[89]
PVA/nanocellulose (crosslinked)	$26.2\cdot 10^{-3}$	-	-	[90]

515

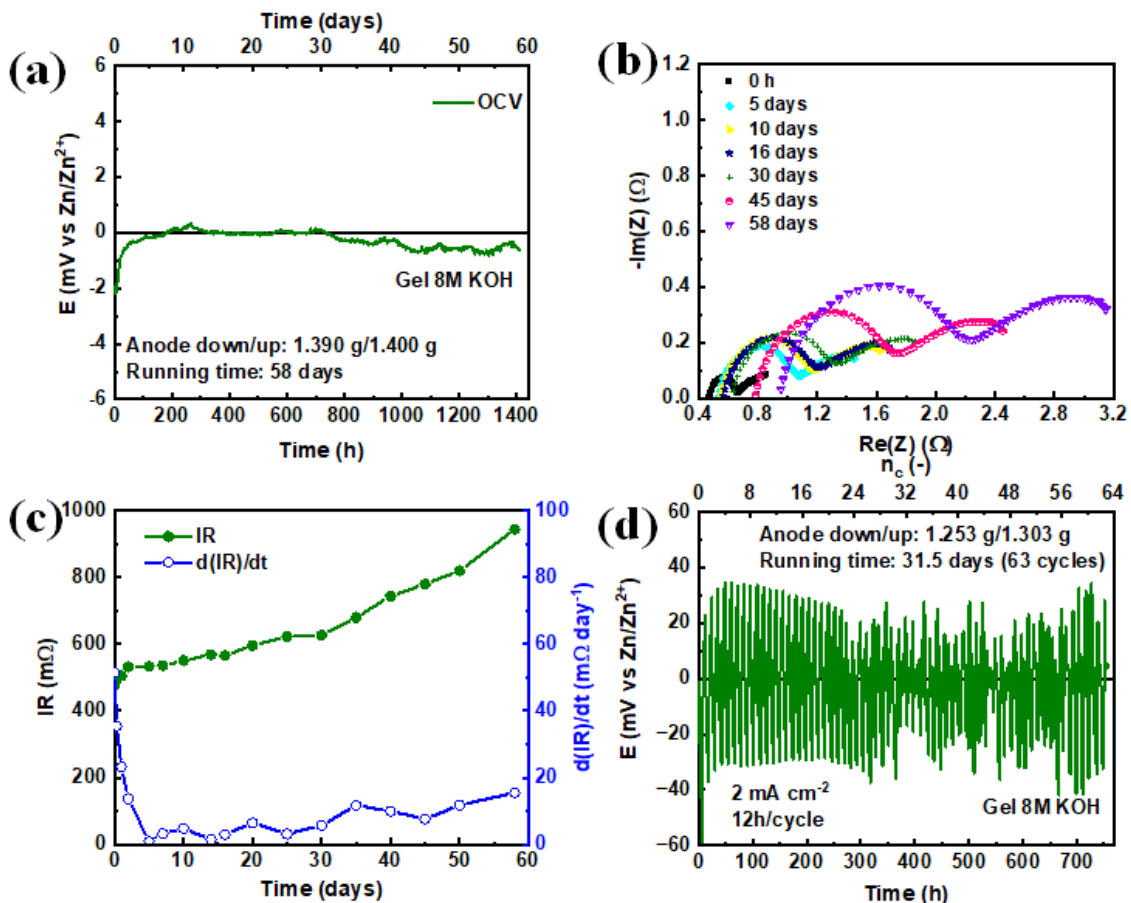
516 shows that Wang et al. [88] reported cellulose/NaOH hydrogels with max. compressive strength  
517 in the 2.1-7.2 MPa range (strain 40-50%, compression modulus from 2 to 7 MPa); in another  
518 work [87], agarose-based hydrogels showed max. compressive strength from 0.09 to 0.33 MPa  
519 (strain up to 41%), while for a poly(2-acrylamido-2-methylpropanesulfonic acid potassium  
520 salt)/methyl cellulose gel [89] a max. compressive strength of 170 kPa was reported, and for a  
521 borax crosslinked PVA/nanocellulose hydrogel the max. compressive strength was 26.2 kPa  
522 [90]. The agarose gels developed in this work show lower compressive strengths because no  
523 additional crosslinking or reinforcing additives have been considered in the formulation, to  
524 maximize ionic conductivity. Future work will be carried out to also improve the mechanical  
525 behavior of these gels.

526 Cyclic compression tests were conducted to determine the hydrogel properties regarding  
 527 repeated stress. In these tests, samples were placed between two plates and compressed 5 times  
 528 up to 15% compression strain to guarantee the sample integrity.

529 The results reported in **Figure 5b-c** show higher stiffness for 8 M KOH samples compared to  
 530 6 M KOH, as higher load is needed to reach 15% deformation, while a lower hysteresis area  
 531 between compression and decompression plots is observed. In addition to this, the deformation  
 532 recovery of 6 M KOH sample is lower compared to the 8 M KOH as evidenced by the initial  
 533 strain shift with increasing the number of compression cycles. The higher stiffness of the gel 8  
 534 M KOH with respect to the 6 M KOH might be ascribed to the role of the  $K^+$  cation as the  
 535 higher concentration in 8 M could lead to a higher propensity of agarose matrix to complex it  
 536 by hydrogen bonding, while increasing its ionic conductivity.

### 537 3.2.6. Preliminary stability study of 8 M KOH gel electrolyte

538 Finally, a preliminary characterization of gel 8 M KOH stability was carried out in a symmetric  
 539 cell configuration (i.e., Zn paste/gel biopolymer electrolyte/Zn paste). The evolution of the open  
 540 circuit voltage (OCV) and internal resistance (IR, taken as the intercept of EIS spectra with the  
 541 impedance real part axis in the Nyquist plot) are recorded over time. The results are shown in  
 542 **Figure 6**.



543

544 **Figure 6.** Zn paste/Gel 8 M KOH/Zn paste symmetric cell test of agarose biopolymer gel 8 M  
545 KOH: (a) OCV stability over time; (b) EIS spectra evolution; (c) IR evolution; (d) cycling at  
546 high areal capacity of 24 mAh cm<sup>-2</sup>.

547  
548 In **Figure 6a**, OCV was continuously recorded up to 1400 h (≈58 days), showing an initial  
549 stabilization period of approx. 100 h, reaching the equilibrium value of 0 mV as expected. A  
550 slight deviation from this value is noticed after 30 days (approx. 700 h) which might indicate  
551 the beginning of irreversible Zn corrosion. During the OCV experiment, the impedance  
552 response of the symmetric cell was also monitored, and the corresponding EIS spectra, in the  
553 frequency range 300 kHz-100 mHz, for selected time points, are shown in **Figure 6b**. Clearly  
554 shaped spectra were obtained, evolving with time. At the beginning and up to day 10-16, one  
555 close semicircle is visible, reflecting the hindrance of Zn ions and electron movements, as  
556 reported by Zhang et al. [91], showing a remarkable ability to maintain a compatible  
557 electrode/electrolyte interface under the 10 mV EIS polarization amplitude [92]. From day 30  
558 the tails of EIS spectra, at low frequency, start to exhibit a close shape thus possibly identifying  
559 a second semicircle due to a raising second contribution to impedance. Together with the  
560 increasing internal resistance and impedance, this could suggest the formation of another  
561 interface. We hypothesize that this is due to the formation of a Zn passivation layer due to the  
562 prolonged exposition to the alkaline environment. This effect of time on the EIS response of Zn  
563 symmetric cells highly depends on the assembly, wettability, and the adhesion between anode  
564 and the gel electrolyte [92–94], and would require a dedicated work. The evolution of the IR  
565 values is quantified in **Figure 6c**. The assembled symmetric cell presents an initial IR of approx.  
566 500 mΩ that slowly but constantly increases up to approx. 1000 mΩ after 58 days, thus doubling  
567 the internal resistance (i.e., the total conductivity is reduced by almost 50%) after 2 months. In  
568 **Figure 6c**, the IR increasing rate (i.e., the derivative d(IR)/dt) is also reported. It is observed  
569 that after an initial decrease, the rate is <10 mΩ day<sup>-1</sup> up to 30 days, and then it starts to increase  
570 significantly, possibly indicating degradation of the Zn/gel electrolyte interface. In **Figure 6d**,  
571 a symmetric cell was cycled at 2 mA cm<sup>-2</sup> per 12 h/cycle (i.e., 12 mAh cm<sup>-2</sup>) to explore long  
572 cycling conditions at high areal capacity. The results revealed a stable cycling up to approx.  
573 300 h and 24 cycles, and then irregular cycling profile with final failure at approx. 750 h and  
574 63 cycles (total operation 31.5 days). These timing reflects the compatibility and stability  
575 observed in **Figure 6a** under OCV and confirms the retard of degradation, mainly ascribed to  
576 the corrosion of the Zn paste itself in the high pH environment (**Figure 6b**) rather than to a  
577 decomposition of the gel. The overpotential and cycle shape are in line and very similar to those

578 reported in other works [91–93,95] based on gel electrolytes for zinc-ion batteries using Zn  
 579 metal anodes instead of Zn paste as per this work, demonstrating that the gel itself is suitable  
 580 for cycling and compatible with zinc. Although encouraging, as said above for EIS, the unique  
 581 assembly used for the tests, the KOH concentration, and the distribution of the anode, introduce  
 582 relevant differences with respect to the common standards in the literature, and ad hoc studies  
 583 of these aspects are needed. This is in accordance with the trend observed for the OCV and the  
 584 EIS spectra. The result is useful when considering conservation on shelf of assembled cells,  
 585 with proper protection from air infiltration, to retard degradation. Further work on these aspects  
 586 is ongoing, and dedicated studies will be done in the future.

587

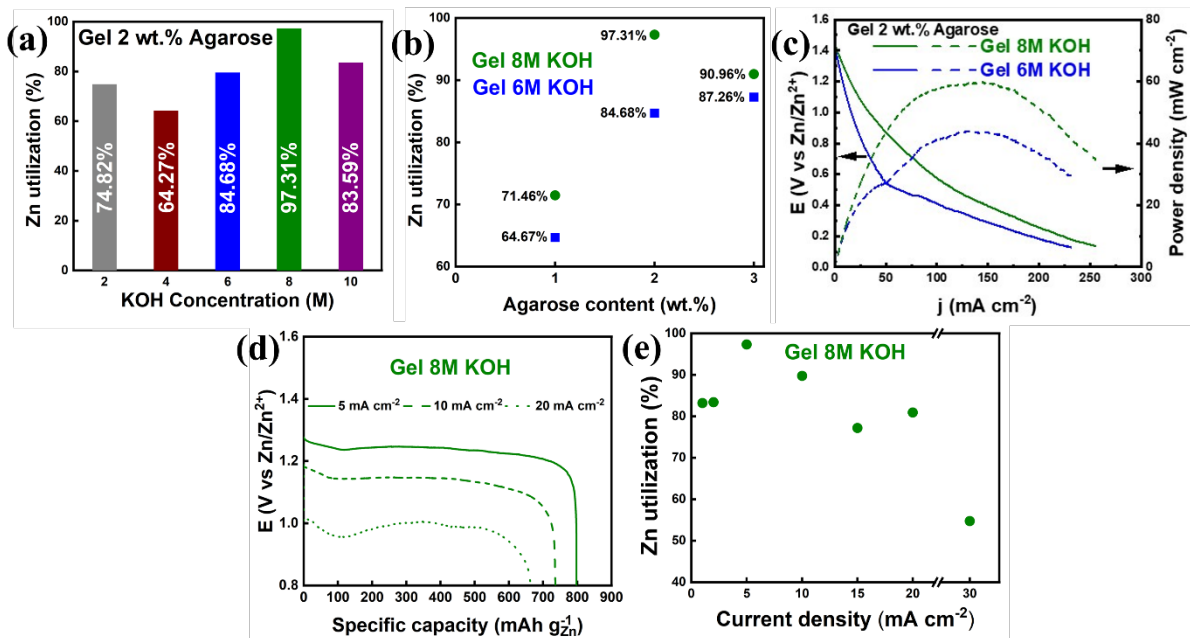
### 588 3.3. Electrochemical results

#### 589 3.3.1. Use of gel biopolymer electrolytes in primary ZABs

590 In primary ZABs, similarly, to the ionic conductivity data discussed in subsection 2.2.2, to  
 591 choose the optimal concentration of the liquid electrolyte and the solid percentage of the  
 592 biopolymer, galvanostatic discharges were conducted at  $5 \text{ mA cm}^{-2}$  varying these parameters.

593 The overall results are shown in **Figure 7**.

594



595

596 **Figure 7.** Zn utilization in primary ZABs: (a) 2 wt.% agarose biopolymer gels with different  
 597 KOH concentrations; (b) gels with 6 M and 8 M KOH at different agarose contents; (c) power  
 598 density at discharge of gels 6 M and 8M KOH; (d) galvanostatic discharge curves of primary  
 599 batteries with 8 M KOH (see also **Table 5**) and (e) calculated Zn utilization at different current  
 600 densities.



601  
602 In **Figure 7a**, the KOH concentration of the liquid electrolyte embedded in a matrix with 2  
603 wt.% agarose is varied. On average, using the gel 8 M KOH, a zinc extraction of almost 97%  
604 can be achieved upon full discharge at  $5 \text{ mA cm}^{-2}$ . By using 6 M and 10 M KOH gels, interesting  
605 Zn utilizations can be achieved, roughly 80% and 84% respectively, that are very close to each  
606 other, but far lower than gel 8 M KOH. In **Figure 7b**, 6 M and 8 M KOH liquid electrolytes are  
607 used for varying the concentration of the biopolymer within 1 and 3 wt.%. The gels containing  
608 1 wt.% agarose, regardless of the KOH concentration (**Figure 7b**), resulted in low Zn utilization,  
609  $<72\%$ , while increasing agarose to 3 wt.% sensibly increased the Zn utilization for both 6 M  
610 and 8 M KOH from 65 and 72% at 1 wt.% agarose to 87 and 91% at 3 wt.% agarose,  
611 respectively. These differences in Zn utilization between gel 8 M and 6 M KOH could be  
612 possibly related to factor other than ionic conductivity such as the lower weight losses measured  
613 for 8 M gels (**Figure S3**) that might slow down cathode flooding, zinc corrosion and passivation,  
614 and the better mechanical behavior that might allow more sealing pressure and better contact  
615 within the electrodes. However, the maximum utilization still lays in the gel 2 wt.% agarose 8  
616 M KOH. Moreover, in **Figure 7c**, the polarization curves at discharge and related power  
617 densities of full cells assembled with the two gels are shown. The cell with the gel 8 M KOH  
618 achieved a maximum power density of  $60 \text{ mW cm}^{-2}$  whereas the gel 6 M KOH reached  $44 \text{ mW}$   
619  $\text{cm}^{-2}$ , showing also in this case the better performance of the gel 8 M KOH. However, it must  
620 be noted that power density strongly depends on cell assembly, geometry, and cathode catalyst  
621 employed. Compared to the literature, as reported in [96], ZABs using various GPE and  
622 precious cathode catalysts (e.g., Pt, Ir, Co, etc.) have shown power densities in the range 40-  
623  $140 \text{ mW cm}^{-2}$ , hence the result obtained in this work for the gel 8 M KOH is very promising  
624 and can be upgraded by using a different cathode. In **Figure 7d**, some representative discharge  
625 profiles at increasing current densities are shown. For the selected current densities, all the  
626 discharge profiles show a flat plateau, typical of ZABs, and the voltage value of the plateau  
627 decreases due to the higher overpotential associated to the higher current densities applied. As  
628 a comparison, the discharge profile ( $5 \text{ mA cm}^{-2}$ ) of a primary ZAB using a glass fiber separator  
629 wetted with a 8 M KOH liquid electrolyte is reported in **Figure S5**, while the discharge profiles  
630 using the gel 6 M KOH at different current densities are reported in **Figure S6a**. Finally, **Figure**  
631 **7e** shows the rate capability of primary ZABs, fully discharged in a large range of current  
632 densities (between  $1\text{-}30 \text{ mA cm}^{-2}$ ), using the gel 2 wt.% agarose 8 M KOH (for gel with 6 M  
633 KOH see **Figure S6b**). The primary ZABs showed a Zn utilization  $>70\%$  in the  $2\text{-}15 \text{ mA cm}^{-2}$   
634 range for both gels, and notably  $>80\%$  Zn utilization in the  $2\text{-}20 \text{ mA cm}^{-2}$  range for the gel 8 M

635 KOH. Moreover, the contact between the gel and the electrodes, before and after discharge, did  
636 not show visible compatibility issues upon disassembling and inspection (**Figure S7**). A deeper  
637 post-mortem analysis was carried out at the interface between anode and gel to inspect the  
638 structure and morphology of discharge products. In **Figure S8**, SEM images of the gel 8 M and  
639 6 M KOH pristine surfaces are compared, showing a very flat and regular surface for the gel 8  
640 M KOH compared with the less regular one of gel 6 M KOH. The surfaces in contact with the  
641 Zn anode paste after discharge also show differences in the morphology of the ZnO discharge  
642 products where the particles on the 8 M KOH form a uniform veil of regularly shaped short  
643 “sticks” whereas for 6 M KOH the sticks appear more irregularly distributed, shaped, and longer.  
644 This is further confirmed in **Figure S9**, where the SEM images of the pristine Zn anode paste  
645 is compared with the discharged anode in contact with gel 8 M and 6 M KOH. It is clearly  
646 visible how the ZnO sticks deposited with the gel 8 M KOH have an average size of approx. 1  
647  $\mu\text{m}$  whereas for the 6 M KOH the size is  $> 3 \mu\text{m}$ , probably determining a slower deposition of  
648 Zn and formation of bulky irreversible products that could accelerate the growth of crystals and  
649 hence the formation of a thick passivation layer hindering capacity extraction. Finally, XRD  
650 spectra of Zn paste before and after discharging are shown and discussed in **Figure S10** to  
651 determine the chemical nature of the other secondary discharge products formed.

652 The performance of ZABs with different gel electrolytes are compared within the relevant  
653 literature in **Table 5** showing that the results achieved in this work are very notable and that  
654 other studies obtained lower ionic conductivity (up to one order of magnitude in some cases)  
655 and poorer discharge performance at high rates ( $> 1\text{-}2 \text{ mA cm}^{-2}$ ). **Table S2** compares our data  
656 normalizing discharged capacity by area (anode) for current density values of 2 and  $5 \text{ mA cm}^{-2}$   
657  $^2$  (see also **Figure S11**). The discharge capacity by area achieved in this work is almost 600  
658 times higher than that in Zuo et al. [78] at 2 and also  $5 \text{ mA cm}^{-2}$  specifically using an agar-based  
659 gel with a melamine foam.

660 **Table 5.** Literature comparison of ionic conductivity and primary discharge performances of  
661 GPEs for ZABs with those from this work.

Gel type	Current density [mA cm <sup>2</sup> ]	Discharge Capacity [mAh g <sup>-1</sup> ]	Zn utilization [%]	Discharge time [min]	Ionic conductivity [S cm <sup>-1</sup> ]	Refs.
Agarose 8 M KOH	5	797.701	97.31	11573	0.451	This work
Agarose 8 M KOH	10	735.46	89.72	5024	0.451	This work
Agarose 8 M KOH	20	663.12	80.89	2743	0.451	This work
Agarose 8 M KOH	30	468.49	57.15	959.00	0.451	This work
Agarose 6 M KOH	5	694.12	84.68	9447.42	0.383	This work

<b>Agarose 6 M KOH</b>	10	657.62	80.22	4238.59	0.383	<b>This work</b>
<b>Agarose 6 M KOH</b>	20	498.95	60.87	1669.50	0.383	<b>This work</b>
<b>Agarose 6 M KOH</b>	30	341.09	41.61	790.76	0.383	<b>This work</b>
Starch 6 M KOH	2	752.00	91.71	-	0.112	[80]
PVA:PAA (10:7.5) + 32 wt.% KOH	150 mA	1347 mAh	89.80	539	0.300	[97]
PVA/PECH + 32 wt.% KOH	150 mA	1338 mAh	89.00	-	-	[98]
PVA/5wt% SiO <sub>2</sub> + 6 M KOH	3	720.60	87.00	-	-	[99]
PAA 6 M KOH	5	684.00	83.44	-	-	[100]
Cellulose + 6 M KOH/Zn acetate	5	695.00	84.00	-	-	[101]
PEO-PVA-glass-fibre-mat + KOH	150 mA	1305 mAh	83.65	522	PEO:PVA (5:5) = 0.048 (7:3) = 0.020	[102]
PVA + 6 M KOH/Zn acetate	5	660.00	80.49	-	-	[103]
hydroponics gel + 6 M KOH	≈4	657.50	80.20	1578	-	[104]
CMC:PAA (1:2) + 8 M KOH	5	641.90	78.84	136	0.231	[51]
PVA + 0.1 M KOH /Zn acetate	5	623.40	76.02	960	-	[105]
PVA + 6 M KOH	2.5 mA cm <sup>-3</sup>	603.70	73.00	-	-	[106]
PVA + KOH	2	595.00	72.00	>180	-	[107]
PVA + 0.15 KOH	6 mA cm <sup>-3</sup>	≈550	67.00	-	-	[108]
acrylic acid + K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , + 4 M KOH	25	530.00	64.63	-	0.288	[109]
Sago + 6 M KOH	100 mA	505.00	61.58	-	0.445	[36]
Nanoporous cellulose + 1 M KOH	25 mA g <sup>-1</sup>	492.00	60.00	1200	0.0212	[110]
PVA + KOH	250 A L <sup>-1</sup> [50 A kg <sup>-1</sup> ]	460.00	56.00	-	-	[84]
Crosslinked PAA + 11.25 M KOH	25 mA cm <sup>-3</sup>	>387	>47	-	-	[111]
Agar-PVA/GO + 6 M KOH/ZnCl <sub>2</sub>	0.5	230.60	28.12	-	0.075	[112]
PVA + 8.3 wt.% KOH	-	-	-	-	0.153	[113]
PVAA-cellulose in 6 M KOH + 0.2 M Zn acetate	3	724.00	88.32	-	0.123	[96]
Liquid 6 M KOH + 0.2 M Zn acetate	10	797.80	97.32	-	-	[114]

662

663 Further quantitative information and calculated metrics for the cells in **Figure 7** (i.e., masses,  
664 Zn loading, Zn weight fraction, energy density etc.) are fully reported in **Table S3** that can be  
665 used for optimization of the single cell, especially for Zn weight fraction and energy density  
666 because these two parameters are dependent on the precise assembly, total mass of each  
667 component, and mass of active Zn material, that are not always reported in the literature.

668 The data in **Table 5** are useful for further comparison with literature of reported ionic  
669 conductivity, discharged capacity/time, and Zn utilization. For instance, Kwon et al. [100]  
670 reported a specific capacity of 684 mAh g<sup>-1</sup> at 5 mA cm<sup>-2</sup> using a 6 mol KOH PAA gel; Fu et  
671 al. [115] used a porous cellulose film gelled with 6 M KOH and extracted a capacity of 652.6  
672 mAh g<sup>-1</sup> applying a discharge current of 5 mA cm<sup>-2</sup>, comparable with the actual agarose gel 6  
673 M KOH while superior values are obtained by the agarose gel 8 M KOH (**Table 5**). Despite the  
674 current densities applied were lower, Zuo et al. [80] obtained 752 mAh g<sup>-1</sup> (at 2 mA cm<sup>-2</sup>) using  
675 a starch/KOH 6 M gel electrolyte, Jiang et al. [116] reported a DMSO-based organo-hydrogel  
676 delivering a high specific capacity (700 mAh g<sup>-1</sup>) always at 2 mA cm<sup>-2</sup>, while Sun et al. [89]  
677 reported a specific capacity of 764.7 mAh·g<sup>-1</sup> at 1 mA cm<sup>-2</sup> using a poly(2-acrylamido-2-  
678 methylpropanesulfonic acid potassium salt)/methyl cellulose with KOH 6 M. The outstanding  
679 overall results obtained for the gel 8 M KOH reported here looks therefore unprecedented  
680 (excluding some work with too different assembly and design for comparison) from a wide  
681 range of current densities 5-20 mA cm<sup>-2</sup>.

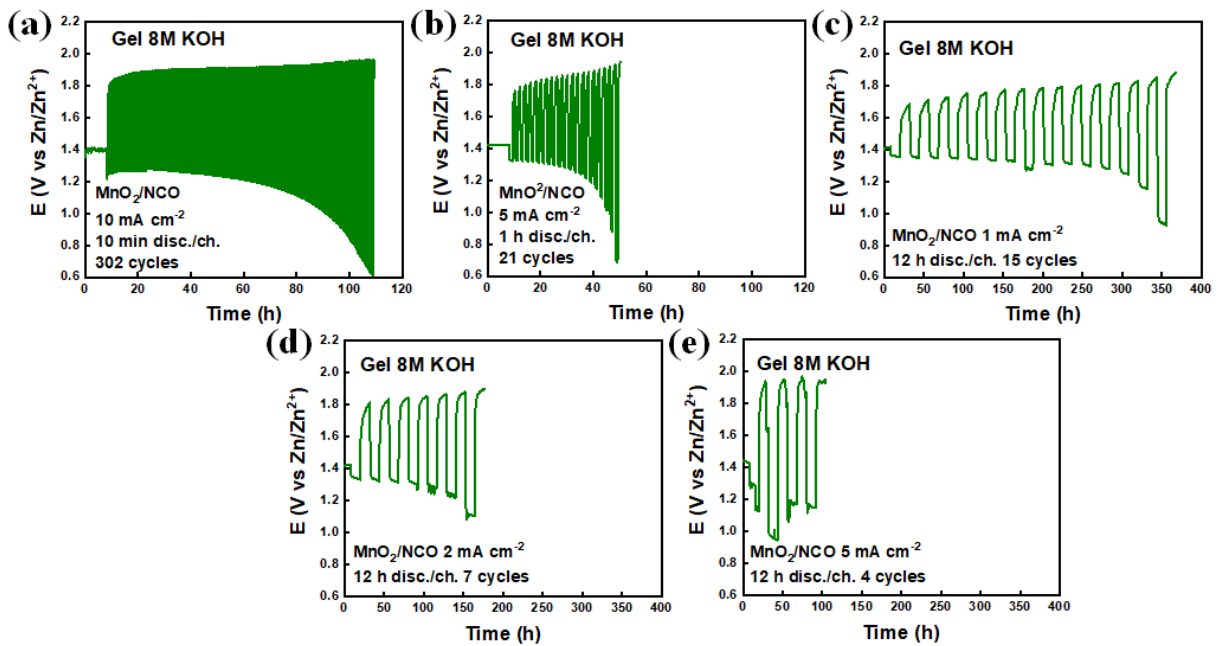
682 To further improve results at higher current densities, the mass of Zn could be better distributed  
683 by controlling the amount of anode paste, geometry of the anode compartment and thickness to  
684 increase discharged capacity, i.e., Zn utilization, and in turn, overall cell energy density. The  
685 same applies to the electrolyte because by reducing its thickness as much as possible, without  
686 compromising the overall cell operation, Zn weight fraction and energy density could be  
687 increased. However, for each current density in **Table 5**, it is demonstrated that the 8 M KOH  
688 gel performed better than 6 M KOH, because higher Zn utilization and specific discharged  
689 capacity were achieved.

### 690 *3.3.2. Use of 2 wt.% agarose biopolymer gel electrolyte 8 M KOH in secondary ZABs*

691 The 2 wt.% agarose biopolymer gel with 8 M KOH behaves properly as a solid electrolyte, has  
692 excellent electrolyte retention, high ionic conductivity, good flexibility, and robustness. Due to  
693 the encouraging performance in primary batteries and the outstanding Zn utilization –  
694 unprecedented in the literature –, these results support the possible application of this gel in  
695 electrically rechargeable ZABs (ERZAB).

696 In ERZABs, the validation of cyclability, rechargeability, and performance is complex, and  
697 reliable protocols are still under intense debate in the literature [52–54]. Moreover, the debate  
698 is centered on the cycling conditions (i.e., current density and cycling time) to be used to test  
699 and validate rechargeability. The most frequent approach is to apply mid-to-high current  
700 densities (5 or 10 mA cm<sup>-2</sup>) for very short times (10 or 20 min per cycle) to maximize the  
701 number of cycles because parasitic reactions and material degradation experienced by

702 components do not have enough time to occur. On the contrary, low current densities applied  
 703 for long times (>1-6 h per cycle) could hinder degradation phenomena, due to the low  
 704 overpotentials, but provide enough time for parasitic reactions to slowly occur after few cycles,  
 705 hence selecting cycling conditions is not trivial. Recently, to consider industrially relevant  
 706 applications, the value of 12 mAh cm<sup>-2</sup> for areal capacity (calculated as the product of current  
 707 density and discharge time per cycle) was proposed as threshold for ERZABs [54].  
 708 Therefore, in this work, at first two current densities and cycling times have been explored as  
 709 parameters to obtain small areal capacities (i.e., < 12 mAh cm<sup>-2</sup>) showing their combined effect  
 710 on number of cycles and calculated performance, and then only current density is varied as  
 711 parameter with a fixed cycling time of 12 h disc./ch. to obtain larger areal capacities (i.e., ≥ 12  
 712 mAh cm<sup>-2</sup>) to study cyclability and the effect of current density on the number of cycles.  
 713 The results of the cyclability tests are shown in **Figure 8**. Furthermore, in **Table S4**, quantitative  
 714 information and calculated metrics for the ERZAB cells in **Figure 8** (i.e., masses, Zn loading,  
 715 Zn weight fraction, energy density etc.) are fully reported.



716  
 717 **Figure 8.** Cyclability tests in ERZAB for short cycles: (a) 10 mA cm<sup>-2</sup>, 10 min disc./ch. (areal  
 718 capacity 1.67 mAh cm<sup>-2</sup>); (b) 5 mA cm<sup>-2</sup>, 1 h disc./ch. (areal capacity 5 mAh cm<sup>-2</sup>). Cyclability  
 719 tests in ERZAB for long cycles: (c) 1 mA cm<sup>-2</sup> 12 h disc./ch. (areal capacity 12 mAh cm<sup>-2</sup>); (d)  
 720 2 mA cm<sup>-2</sup>, 12 h disc./ch. (areal capacity 24 mAh cm<sup>-2</sup>); (e) 5 mA cm<sup>-2</sup>, 12 h disc./ch. (areal  
 721 capacity 60 mAh cm<sup>-2</sup>).

722  
 723 In **Figure 8a**, the cycling conditions used are similar to those frequently reported in the  
 724 literature (especially for liquid electrolyte). The calculated areal capacity is 1.67 mAh cm<sup>-2</sup>,

725 showing that the gel 8 M KOH achieved approx. 100 h of continuous operation and 302 cycles,  
 726 in line with the literature for ERZABs using GPE (see also **Table 7** below). These cycling  
 727 conditions, alleviating irreversible impacts from the zinc electrode rather than assessing a  
 728 notable rechargeability [54], are not feasible for practical uses because the areal capacity is far  
 729 below the indicated threshold, and often quantitative comparisons/calculations are tricky due to  
 730 missing information about zinc mass and liquid electrolyte in excess [53]. As complementary  
 731 information, the Voltage vs. Specific capacity plots of the cycled cells are reported in **Figure**  
 732 **S12** to show in detail the evolution of discharge/charge voltage over cycling as a function of  
 733 current density and time. It is possible to observe that discharged/charged capacity per cycle  
 734 are identical, hence providing a Coulombic efficiency of  $\approx 100\%$  (due to the CC cycling mode  
 735 used) that is retained along operations under all the conditions tested, showing the excellent  
 736 capacity retention behavior of the developed gel.

737 To demonstrate the combined and not trivial effect of current density and cycling time, in  
 738 **Figure 8b** current density was reduced to  $5 \text{ mA cm}^{-2}$ , while cycling time was increased to 2 h  
 739 and the calculated areal capacity is  $5 \text{ mAh cm}^{-2}$ . As a consequence, the operation time and  
 740 number of cycles drastically decreased to approx. 40 h and 21 cycles. Considering just the  
 741 number of cycles as parameter to evaluate rechargeability of ERZABs, one would say that the  
 742 cell achieving 302 cycles is better than the second cell achieving just 21 cycles. This is not  
 743 correct if one calculates the specific metrics per cycle, together with the round-trip efficiency.  
 744 This is done for all the cells in **Figure 8** in the following **Table 6**.

745 **Table 6.** Secondary cells value per cycle for performance calculation (**Figure 8**, active Zn mass  
 746 and loading are those reported in **Table S4**).

Current density [mA cm <sup>-2</sup> ]	Disch./ch. time [h]	N. of cycles [-]	Disch. capacity per cycle [mAh g <sub>Zn</sub> <sup>-1</sup> ]	DoD <sub>c</sub> per cycle [%]	Energy density per cycle [Wh kg <sub>cell</sub> <sup>-1</sup> ]	Disch. voltage, avg. [V]	Ch. voltage, avg. [V]	Round-trip efficiency [%]
10	0.167	302	1.25	0.15	0.52	1.11	1.92	57.81
5	1	21	4.40	0.53	1.82	1.20	1.86	64.52
1	12	15	9.30	1.14	4.06	1.25	1.78	70.22
2	12	7	22.50	2.74	9.53	1.25	1.85	67.57
5	12	4	54.80	6.70	20.77	1.12	1.90	58.95

747  
 748 The cell operated at  $10 \text{ mA cm}^{-2}$  and 0.167 h (areal capacity  $1.67 \text{ mAh cm}^{-2}$ ), gives the highest  
 749 number of cycles, and therefore the highest cumulative DoD and energy density (see **Table S4**),  
 750 but presents the lowest metrics per cycle. From **Table 6**, can be concluded that to increase the

751 number of cycles, very short cycle times can be applied, but when longer cycle times are used,  
752 the number of cycles decreases but the capacity and energy density per cycle are increased due  
753 to the higher areal capacity. This is the reason why large areal capacities are required to meet  
754 real applications. Moreover, to obtain a good round-trip efficiency, small current densities must  
755 be used to minimize overpotentials, and hence long cycling time are needed to meet the areal  
756 capacity threshold of 12 mAh cm<sup>-2</sup>. Therefore, in **Figure 8c-e**, the cycling time was fixed to a  
757 daily cycle (i.e., 24 h per cycle, 12 h discharge and 12 h charge), to test an application-oriented  
758 time representing an industrially relevant condition, while current density was varied as  
759 parameter from 1 mA cm<sup>-2</sup> to 2 and 5 mA cm<sup>-2</sup>. As expected, the areal capacity was  
760 progressively increased from 12 to 24 and up to 60 mAh cm<sup>-2</sup>, while the number of achieved  
761 cycles is progressively reduced, indeed almost halved (from 15 to 7 to 4 cycles, respectively at  
762 1, 2, and 5 mA cm<sup>-2</sup>). These results suggest that the correlation between current density and  
763 number of cycles is inversely proportional in these conditions. Cross-comparing **Figure 8b** and  
764 **Figure 8e** at the same current density of 5 mA/cm<sup>2</sup> it is demonstrated also that cycle life  
765 decreases (from 21 to 4 cycles) when cycling time is increased (from 1 h to 12 h). Therefore,  
766 the rate capability of the assembled cells using the gel 8 M KOH is demonstrated by changing  
767 both current density and cycling time.

768 Furthermore, the metrics per cycle under these conditions in **Table 6** are very interesting  
769 because, even if the number of achieved cycles is small, the delivered capacity (54.80 mAh g<sub>Zn</sub><sup>-1</sup>  
770 per cycle), the energy density (20.77 Wh kg<sub>cell</sub><sup>-1</sup> per cycle), and the round-trip efficiency  
771 (58.95%) are higher than the cell operated at 1.67 mAh cm<sup>-2</sup> for 302 cycles (1.25 mAh g<sub>Zn</sub><sup>-1</sup>,  
772 0.52 Wh kg<sub>cell</sub><sup>-1</sup>, and 57.81%, respectively). This represent a truly industrially relevant result  
773 for future scale-up and shows the importance to obtain high areal capacities, while considering  
774 only the number of cycles is less relevant for real use.

775 However, in the profiles of **Figure 8d** and **Figure 8e**, instabilities in discharge voltage, causing  
776 deformed cycle shapes and spikes, are visible for many cycles (in **Figure 8c** this randomly  
777 occurs only for one discharge cycle). As recently reported in the literature, we ascribe this to  
778 the combination of current density and long cycling time, possibly affecting the degradation of  
779 cathode during the charge phase [117], the irreversible passivation of zinc-to-zinc oxide, and  
780 dendrite formation at gel/anode interface [118]. Moreover, in terms of gel chemical stability  
781 under cycling, we observed a change in the color (from yellowish to dark brown) of the  
782 electrolyte under any cycling conditions (see **Figure S13**). This is probably due to two  
783 phenomena, dissolution of catalyst/carbon support from cathode and/or hydrolysis of gelled

784 liquid electrolyte. During long charges, (e.g., hours) these phenomena are promoted and  
 785 extended because of the longer time available to occur.

786 In addition, **Table 6** shows the calculated round-trip efficiency, demonstrating that the cells  
 787 operated under small areal capacity are not as efficient as the cells operated under higher areal  
 788 capacity. It is worth noticing that this is more related to the current density applied and  
 789 overpotentials rather than time and is not directly related to mass and cell assembly/design.  
 790 However, maximizing the number of cycles is extremely important to improve cyclability and  
 791 rechargeability, but it should be also obtained at high areal capacity and high round-trip  
 792 efficiency.

793 In conclusion, the comparison with the literature in terms of electrode types, electrolyte, cycling  
 794 conditions (i.e., calculated areal capacity to include both current density and discharge time),  
 795 the number of cycles, and calculated round trip efficiency is reported in **Table 7**.

796 **Table 7.** Comparison of cycling performance in ERZABs with a gel electrolyte.

Gel type	Anode type	Cathode type	Areal capacity [mAh cm <sup>-2</sup> ]	N. of cycles [-]	Round-trip efficiency <sup>(a)</sup> [%]	Refs.
<b>Agarose 8 M KOH</b>	Zn paste	MnO <sub>2</sub> /NCO	1.67	302	57.81	<b>This work</b>
<b>Agarose 8 M KOH</b>	Zn paste	MnO <sub>2</sub> /NCO	5	21	64.52	<b>This work</b>
<b>Agarose 8 M KOH</b>	Zn paste	MnO <sub>2</sub> /NCO	12	15	70.22	<b>This work</b>
<b>Agarose 8 M KOH</b>	Zn paste	MnO <sub>2</sub> /NCO	24	7	67.57	<b>This work</b>
<b>Agarose 8 M KOH</b>	Zn paste	MnO <sub>2</sub> /NCO	60	4	58.95	<b>This work</b>
Agar + melamine foam in 6 M KOH	Zn foil	Mn-Co-Fe@CNT	0.334	74	62.30	[78]
Starch gel saturated with KOH + ZnO	Zn foil	Mn-Co-Fe@CNT	0.167	216	63.54	[80]
PAA 6 M KOH	Electrodeposited Zn	Pt-Ir/C	0.33	100	61.52	[100]
Quaternary ammonium functionalized cellulose in 6 M KOH	Zn foil	S-C <sub>2</sub> N aerogel/stainless steel mesh	25	230	63.15	[101]
PAA 6 M KOH	Zn foil	Pt-Ru/C	0.041	25	79.00	[94]



PVA/guar hydroxy propyl trimonium chloride 2 M KOH	Zn foil	IrO <sub>2</sub> /Pt/C/carbon cloth	0.167	57	62.12	[119]
BC-PVA in 6 M KOH + 0.2 M Zn acetate	Zn foil	Co <sub>3</sub> O <sub>4</sub> @Ni foam	0.165	650	69.40	[120]
Crosslinked PVA/PAA in 6 M KOH	Zn powder/PEI/CNT	Co <sub>3</sub> O <sub>4</sub> @MWCNT	0.041	150	57.69	[121]
PAM crosslinked with MBAa in 6 M KOH	Zn foil	C-CoPAN900/carbon paper	1 mAh	55	60.91	[122]
PAM/Na-Alginate/KI	Zn foil	PtC/RuO <sub>2</sub>	0.167	330	79.14	[123]
PVA + Lecithin in 6 M KOH + 0.2 M Zn acetate	Zn foil	CoFeP@C	0.5	141	57.50	[124]
PVAA-cellulose in 6 M KOH + 0.2 M Zn acetate	Zn foil	CoFeP@C	0.5	162	57.60	[96]
Liquid 6 M KOH + 0.2 M ZnCl <sub>2</sub>	Zn foil	Mn <sub>0.5</sub> Ni <sub>0.5</sub> Co <sub>2</sub> O <sub>4</sub> /C	0.7	150	58.58	[125]
Liquid 7 M KOH + ZnO + KF + K <sub>2</sub> CO <sub>3</sub>	Zn paste	NCO/CNT	2	88	60.00	[126]

(a) Values have been extrapolated from published figures if not explicitly reported in the cited source.

797

798

799 In **Table 7**, ERZABs using a GPE are included together with a couple of examples with liquid  
800 electrolytes, and usually the areal capacities calculated are very small, although large numbers  
801 of cycles and good round-trip efficiency are reported. Compared to the literature, the ERZABs  
802 developed here using the agarose gel with 8 M KOH show a very competitive round-trip  
803 efficiency, even at far higher areal capacity than those in the literature, and that the longer  
804 cycling times used justify the small number of cycles achieved. This is the aspect to be improved  
805 and a better cell and component design could greatly help in achieving more cycles at high areal  
806 capacity with the outstanding gel developed in this work. Therefore, data reported above  
807 demonstrates that the developed gel 8 M KOH can be used in ERZABs, and can sustain quite  
808 well high areal capacities, not previously tested in the relevant literature, although optimizations  
809 are needed.

810

#### 811 4. Conclusions

812 The use of naturally occurring biopolymers to synthesize gel electrolytes for ZABs, and  
813 batteries in general, is a very appealing approach to replace the use of synthetic polymers,  
814 derived from petrochemicals, as alternative to standard liquid electrolytes and related issues.

815 However, a compromise between physical, chemical, mechanical, and electrochemical  
816 properties is needed to design a high-performance gel.

817 In this work, a more convenient, faster, and scalable synthesis method is proposed to obtain  
818 agarose gels directly embedding a highly alkaline and corrosive electrolyte which is applicable  
819 also to other biopolymers such as xanthan, agar-agar, and  $\kappa$ -carrageenan, which gave higher  
820 ionic conductivity compared to the literature, but still lower than the agarose gel developed  
821 within this work. A detailed study of the agarose gels, showing the effect of biopolymer amount  
822 and KOH concentration, is provided. Thorough characterization in terms of ionic conductivity,  
823 chemical structure, electrolyte retention, flexibility (qualitative) and compression modes  
824 (quantitative) is presented, which accounts for the best gel biopolymer electrolyte formulation  
825 being the gel with 2wt% agarose and 8 M KOH electrolyte. Indeed, it shows an ionic  
826 conductivity of  $0.45 \pm 0.05 \text{ S cm}^{-1}$  at room temperature, elastic modulus is  $2.1 \pm 0.2 \text{ kPa}$  and  
827 maximum compression strength of  $62.0 \pm 1.0 \text{ kPa}$ , at 25% of compression strain, with a  $\approx 100\%$   
828 electrolyte retention (i.e., negligible weight loss) up to 200-250 h at  $30 \pm 1^\circ\text{C}$  and environmental  
829 relative humidity of  $40 \pm 5\%$ . When this gel was used to for primary ZABs assembly, it provided  
830 unprecedented Zn utilization for GPEs in ZABs of  $\approx 97\%$  at  $5 \text{ mA cm}^{-2}$ , and between 75% and  
831 80% in the 1-20  $\text{mA cm}^{-2}$  range, on average.

832 The biopolymer gel electrolyte was further used in secondary ERZABs and tested under very  
833 small ( $\ll 12 \text{ mAh cm}^{-2}$ ) and large ( $\gg 12 \text{ mAh cm}^{-2}$ ) areal capacities to determine the effect of  
834 applied current density and cycling time. Promising results were obtained in terms of DoD<sub>c</sub>,  
835 energy density (total and per cycle), and delivered capacity while satisfying number of cycles  
836 were achieved. By using the gel 8 M KOH,  $>300$  cycles were obtained at  $10 \text{ mA cm}^{-2}$  and 20  
837 min per cycle, but the DoD<sub>c</sub> was 0.15% and round-trip efficiency was  $\approx 57\%$ , whereas at  $1 \text{ mA}$   
838  $\text{cm}^{-2}$  and 24 h per cycle, the DoD<sub>c</sub> was 1.14%, round-trip efficiency  $\approx 70\%$  on average of 15  
839 cycles. At the hardest cycling conditions tested ( $5 \text{ mA cm}^{-2}$  and 24 h per cycle, corresponding  
840 to an areal capacity of  $60 \text{ mAh cm}^{-2}$ ), a DoD<sub>c</sub> of 6.7% and a round-trip efficiency of 59% were  
841 achieved, with only four reversible cycles achieved. Cyclability results suggested that number  
842 of cycles alone is not enough to prove high performance or high round-trip efficiency, as  
843 generally reported in the literature, and, as also confirmed by the final EIS characterization on  
844 Zn paste/Zn paste symmetric cell, an overall optimization of components, anode mass  
845 distribution, cell design, and assembly is needed to better exploit the developed electrolyte and  
846 single cells, to increase the number of cycles at high areal capacities and long cycling times.  
847 Therefore, the results discussed in this work are a preliminary benchmark to push future  
848 research toward a more quantitative, engineered, and integrated approach for component

849 development and performance evaluation by adopting gelled electrolyte and relevant cycling  
850 times to assess concrete progress in ZABs and ERZABs.

851

## 852 **Supplementary materials information**

853 Supplementary materials are available online or from the authors.

854

## 855 **CRedit authorship contribution statement**

856 **Conceptualization:** N.O.V., E.G.G., M.C.M.M., D.F.; **Methodology:** All authors; **Formal**  
857 **analysis:** E.G.G., D.F., M.C.M.M., L.M.; **Data curation:** E.G.G., D.F.; **Visualization:** E.G.G.,  
858 D.F., N.O.V.; **Investigation:** E.G.G., D.F., M.C.M.M.; **Writing – original draft:** E.G.G., D.F.,  
859 L.M., N.O.V.; **Writing – review & editing:** All authors; **Supervision:** N.O.V., A.F., C.G.;  
860 **Funding acquisition:** N.O.V.

861

## 862 **Conflicts of interest**

863 There are no conflicts to declare.

864

## 865 **Acknowledgements**

866 E. Garcia thanks the Basque Government for the Bikaintek grant (1-AF-W2-2019-00003)  
867 N. Ortiz-Vitoriano acknowledges the “Ramón y Cajal” grant (RYC2020-030104-I / AEI /  
868 10.13039/501100011033). Authors are also very thankful to Ainhoa Bustinza Murguialday  
869 for her technical support during the experimental trials.

870

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