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A Gel Polymer Electrolyte for Aluminum Batteries

Giuseppe Antonio Elia,* Carlos Islas Acevedo, Reyhaneh Kazemi, Sebastien Fantini, Rongying Lin, and Robert Hahn

Herein, the use of a gel polymer electrolyte (GPE) comprising polyacrylonitrile and 1-ethyl-3-methylimidazolium chloride:aluminum trichloride (EMIMCl:AlCl₃) ionic liquid in aluminum batteries is investigated. The investigated GPE is characterized in terms of conduction properties. The obtained ionic conductivity values are suitable for battery applications. The ability of the GPE to sustain an efficient aluminum stripping deposition process is verified, revealing the need of a swelling process to enable the aluminum plating/stripping. The mitigation of the chloroaluminate corrosivity in the GPE is confirmed by evaluating the corrosion current of stainless steel 316 current collectors. The long-term ability of GPE to sustain the stripping deposition process is tested, evidencing a good Al/GPE interface stability. Finally, the GPE electrolyte suitability in the Al battery is verified by assembling an Al/GPE/pyrolytic graphite (PG) cell. The test cell shows a good cycling ability, demonstrating the suitability of the GPE electrolyte for the realization of aluminum batteries.

graphite anode in Li ion 1066 mAh cm⁻³), and by a satisfactory specific capacity of 2980 mAh g⁻¹.^[1,2] One of the main drawbacks of secondary Al batteries is the extremely high corrosivity of the chloroaluminate electrolyte conventionally used for this system.^[3–8] Most of the polymers used as binders or separators and cell cases are not stable in the chloroaluminate melt electrolyte.^[9–11] Furthermore, the metal current collector's corrosion limits the choice to molybdenum or tungsten, unsuitable in practical application for their elevated cost.^[7] The identification of chlorine-free electrolytes, characterized by higher stability against cell components, can overcome these issues. Several efforts have been dedicated to realizing an electrolyte composition with the ability

1. Introduction


Aluminum batteries are considered a valid alternative electrochemical storage system, characterized by low cost and high sustainability. Using Al metal as an anode has several advantages: it is the most abundant metal element on the Earth crust, it is characterized by an extremely good volumetric capacity of 8040 mAh cm⁻³ (Li metal anode 2063 mAh cm⁻³,

to efficiently strip and deposit aluminum metal and be noncorrosive.^[12–14] Unfortunately, up to now, an efficient electrolyte able to sustain the Al stripping deposition process with an efficiency close to the chloroaluminate melt electrolyte is not available. For that reason, an alternative approach is to mitigate the chloroaluminate electrolyte reactivity while maintaining their activity^[15] or trap the electrolyte in a polymeric matrix obtaining a gel polymer electrolyte (GPE).^[16,17] The inclusion of the reactive chloroaluminate melt in the polymer matrix can mitigate the high reactivity. Sun et al.^[17] reported a GPE obtained via free radical polymerization capable of maintaining its activity after exposure to air. Yu et al.^[16] reported a GPE obtained with a similar preparation procedure achieving excellent performance in the Al/graphite battery. Herein, we propose the preparation of a GPE via solvent casting method, easier to scale up compared with the radical polymerization methods. The obtained GPE has been fully characterized in terms of electrochemical properties, evidencing a good ionic conductivity and efficiently sustaining the aluminum stripping deposition process. The reduced reactivity of the prepared GPE has been verified by comparing the corrosion behavior of stainless steel 316 in the GPE and the conventional EMIMCl:AlCl₃ electrolyte, thus reducing one order of magnitude of the corrosion current for the GPE electrolyte. Finally, the suitability of the prepared GPE in the Al battery has been verified by assembling an Al/GPE/pyrolytic graphite (PG) cell. The assembled cell prototype is characterized by good electrochemical performance and good stability, but by a poor rate capability. The results obtained evidenced the feasibility of a solvent casting approach to fabricate the GPE for Al batteries.

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2. Experimental Section

2.1. Material

The electrolyte 1-ethyl-3-methylimidazolium chloride:aluminum trichloride EMIMCl:AlCl₃ in a 1:1.5 mole ratio was provided by IOLITEC. The water content of the electrolyte was lower than 100 ppm. The polyacrylonitrile (Sigma Aldrich PAN, $M_w = 150\,000\text{ g mol}^{-1}$) and ethylene carbonate (EC, Sigma Aldrich anhydrous, 99%) were used to prepare the GPE. The PAN was dried under vacuum at 110 °C for 3 days before use. Water traces in the EC solvent were removed using 4 Å zeolite, keeping the EC liquid at 40 °C in an oven placed in the glovebox (MBraun with water and oxygen content lower than 0.1 ppm) for several days, until the water content was below 5 ppm (the water content was measured by Karl Fischer titration). The electrochemical tests were carried out using high purity aluminum (Al 99.99%, Alfa Aesar) as anode and PG with a thickness of 25 μm and a loading of 4.71 mg cm⁻² as the cathode material.^[18,19]

2.2. Gel Electrolyte Preparation

The GPE preparation procedure scheme is shown in **Figure 1a**. The first step involves the solubilization of the PAN in EC at

60 °C forming a 5% w/w PAN solution in EC (step 1). Following the EMIMCl:AlCl₃, electrolyte was added to the solution to have a 4:1 weight ratio of EMIMCl:AlCl₃:PAN (step 2). Afterward, the blend was mixed until a homogeneous solution was obtained (step 3). Then, 6 mL of the final solution were poured into a 100 mm Petri dish (step 4), and the solvent (EC) was evaporated at 80° under vacuum for 6 h, obtaining the desired homogeneous and mechanically stable membrane (see Figure 1b). The thickness of the membrane varied between 200 and 300 μm.

2.3. Electrochemical Test

The electrochemical measurements were carried out using Teflon Swagelok type T cells.^[18] All potentials quoted in this article refer to the quasi reference Al/Al³⁺ electrode. The ionic conductivity of the GPE was evaluated by potential electrochemical impedance spectroscopy (PEIS) in a 25–55 °C temperature range applying a 10 mV amplitude signal in a frequency ranging from 200 kHz to 10 Hz. Glassy carbon electrodes and a Teflon spacer of known dimension were used in the T cell to fix the cell constant. The aluminum stripping deposition properties were evaluated by cyclic voltammetry in a –0.5 to 0.5 V potential range at a 0.1 mV s⁻¹ scan rate employing a nickel foil working electrode.

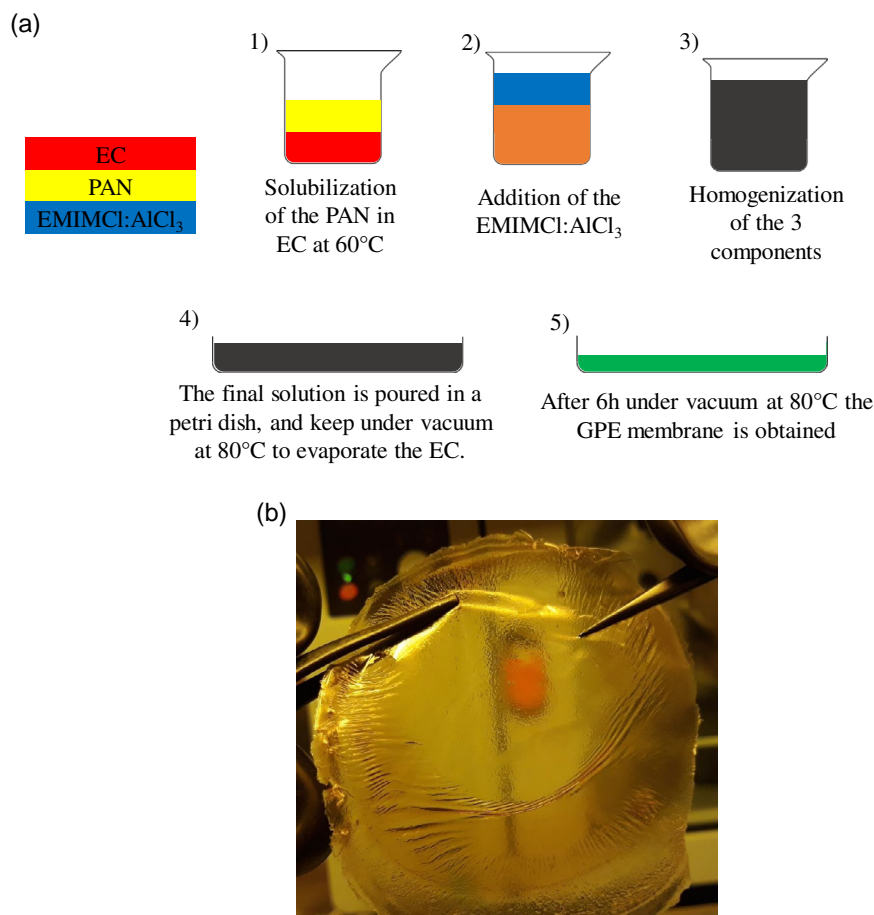


Figure 1. a) Scheme of the GPE preparation. b) Photographic image of the prepared GPE membrane.

The aluminum metal's cycling stability was evaluated by continuous stripping/deposition tests on symmetrical Al/Al cells with a current of 0.1 mA cm^{-2} and a stripping/deposition time of 1 h, using a Maccor 4000 battery test system. The evolution of the interface stability upon cycling was evaluated by impedance measurements (using Solartron PARSTAT MC potentiostat) in the frequency range of 75 kHz to 10 MHz at 10 mV sinusoidal amplitude. The corrosion measurement was carried out by linear sweep voltammetry (LSV) performed between the open circuit voltage (OCV) and 2.4 V versus Al/Al³⁺ using a stainless steel 316 rod as the working electrode and Al metal counter and the reference electrode. The cycling tests of Al/GPE/PG cells were carried out by applying increasing specific currents (from 25 to 100 mA g⁻¹) in the voltage range of 0.4–2.4 V. All the electrochemical measurements were carried out at 25 °C in a thermostatic climatic chamber (with a possible deviation of ± 1 °C).

3. Results and Discussion

Figure 1 shows the scheme of the procedure used to prepare the GPE. The PAN has been selected to prepare GPE, for its stability against the EMIMCl:AlCl₃ electrolyte.^[9] The EC has been selected for the GPE preparation for its ability to solubilize PAN and the stability against EMIMCl:AlCl₃ electrolyte. Other solvents in which the PAN is soluble have been evaluated for the preparation, such as dimethylacetamide (DMAC), dimethylformamide (DMF), and *N*-methyl pyrrolidone (NMP). The DMAC and the DMF are not stable against the EMIMCl:AlCl₃ electrolyte, whereas the addition of EMIMCl:AlCl₃ to NMP results in the precipitation of a white powder, most likely the AlCl₃. EC is not the ideal solvent medium for the preparation of a GPE due to the high boiling point. The EC has been removed at 80 °C under vacuum (10^{-3} mbar) for 6 h (step 5) after the obtainment of a homogeneous solution of PAN, EC, and EMIMCl:AlCl₃ (step 3). This procedure leads to a homogeneous and transparent membrane characterized by good mechanical stability and a thickness of 200–300 μm . The stability of the prepared GPE should be evaluated, considering the EMIMCl:AlCl₃ elevated corrosivity. The membrane's conductivity has been measured upon storage time to evaluate possible degradations of the GPE. The membrane degradation should result in a variation of the conduction proprieties. The measurement shown in **Figure 2a** evidences that the conductivity of the membrane remains stable at a value of about 0.25 mS cm^{-1} , suggesting the stability of the GPE. The obtained ionic conductivity value is comparable with GPE developed for Li and Na systems.^[20–22] The measured room temperature (25 °C) conductivity is comparable with the conductivity values of GPEs used in lithium batteries,^[11,23–27] indicating the suitability of the GPE for battery application. **Figure 2b** shows the trend of the conductivity of the GPE as a function of the temperature from 25 to 55 °C. The data fit well with an Arrhenius trend with an activation energy of 0.15 eV. The prepared membrane's ability to sustain the Al stripping deposition process has been verified by performing cyclic voltammetry on a nickel foil current collector in the -0.6 to 0.6 V versus Al/Al³⁺ voltage range. **Figure 3a** shows the current versus voltage signature of the CV carried out with the Al/GPE/Ni cell. No electrochemical activity can be observed, indicating

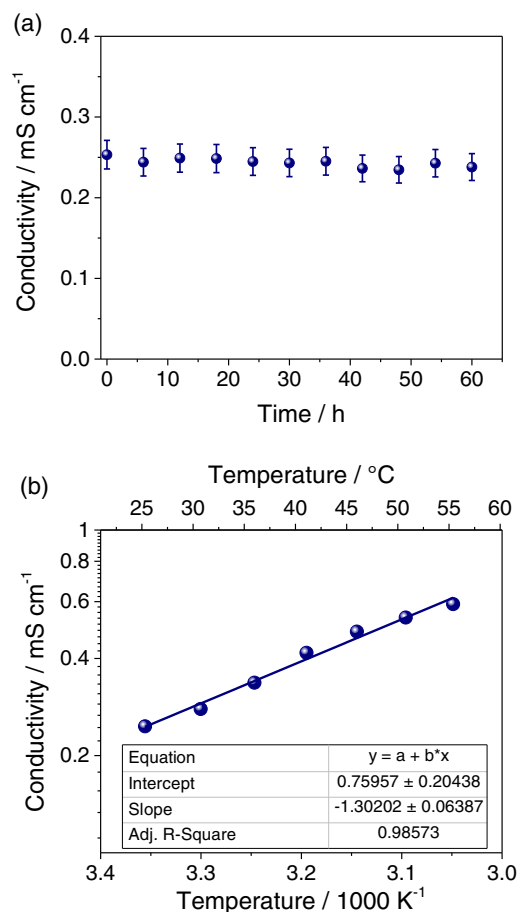


Figure 2. a) Evolution of the prepared GPE membrane conductivity upon different storage times. b) Arrhenius plot of the prepared GPE membrane.

that the membrane cannot sustain the aluminum stripping/deposition process, although the ionic conduction is high. **Figure 3b** shows the same measurement carried out using a GPE membrane immersed for 6 h in EMIMCl:AlCl₃ electrolyte (swelled). The measurement reveals that after swelling, the GPE can sustain the aluminum stripping deposition process. The need for the swelling to activate the membrane can be associated with the presence of Al₂Cl₇⁻. It is known that to have a reversible stripping deposition process, the dimeric species Al₂Cl₇⁻ must be formed, and the mole ratio of AlCl₃ with respect to the EMIMCl must be higher than one.^[28–31] The Al₂Cl₇⁻ has been identified as a key compound for the reversible Al stripping/deposition process.^[32–35] We suppose that the preparation process leads to a dilution of the salt (sublimation point of the AlCl₃ is 180 °C), reducing its concentration in the membrane. The immersion of the GPE in the electrolyte regenerates the lost AlCl₃. A second possibility can be associated with the residual EC solvent in the GPE membrane, compromising the Al metal deposition. In both cases, a more volatile solvent should be used to avoid this issue. Unfortunately, up to now, we were not able to identify an alternative solvent that is chemically stable in the system and solubilize the PAN and the EMIMCl:AlCl₃ in high concentration. The reduced corrosivity of the GPE

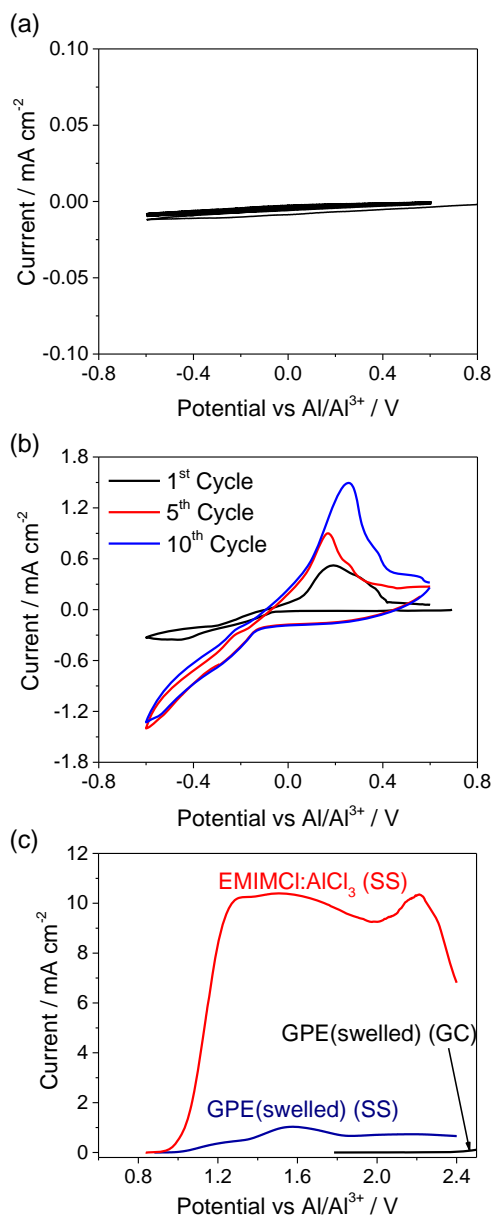


Figure 3. Current versus voltage plot of the CV measurement of the Al/GPE/Ni cells carried out with a) the pristine GPE electrolyte and b) the swelled GPE electrolyte. c) Current versus voltage plot of the linear sweep voltammetry of the Al/EMIMCl:AlCl₃/SS316 cell (in red), of the Al/GPE(swelled)/SS316 cell (in blue), Al/GPE(swelled)/GC cell (in black) between OCV and 2.4 V versus Al/Al³⁺. Measurement carried out at 0.1 mV s⁻¹ scan rate at room T.

in respect to the conventional EMIMCl:AlCl₃ electrolyte has been verified by measuring the corrosion current of a stainless steel 316 current collector used as a working electrode. Figure 3c shows the comparison of the current versus voltage signature of the LSV measurement carried out with the Al/EMIMCl:AlCl₃/SS316 cell (in red) and the Al/GPE(swelled)/SS316 cell (in blue), indicating a reduction of one order of magnitude of the corrosion current at the stainless steel current collector with the GPE electrolyte. The reference curve (in black), obtained using glassy

carbon (GC) as the working electrode, indicate that the GPE electrolyte is stable up to 2.45 V versus Al/Al³⁺. The corrosion current using the GPE electrolyte is in the range of 1 mA cm⁻², much lower in respect to the conventional liquid electrolyte but still too high to use SS316 as current collector in the system. **Figure 4** shows the voltage versus time plot of the stripping deposition measurement carried out on symmetrical Al/GPE(swelled)/Al cell carried out using a current of 0.1 mA cm⁻² and a deposition time of 1 h. The measurement evidence that the cell initial overpotential of 75 mV decreases during cycling, reaching 50 mV at steady-state condition. The overpotential decrease is associated to the electrode/electrolyte interface stabilization, as evidenced by the Nyquist plot of the PEIS measurement carried out on the cell during cycling, reported in Figure 4b. The impedance measurements show a huge decrease in the interface resistance after the initial 10 h, which stabilizes after 20 h of cycling. The stability of the GPE in operative conditions indicates its suitability for application in aluminum batteries. This hypothesis was verified by assembling a cell employing aluminum metal as anode and PG as a

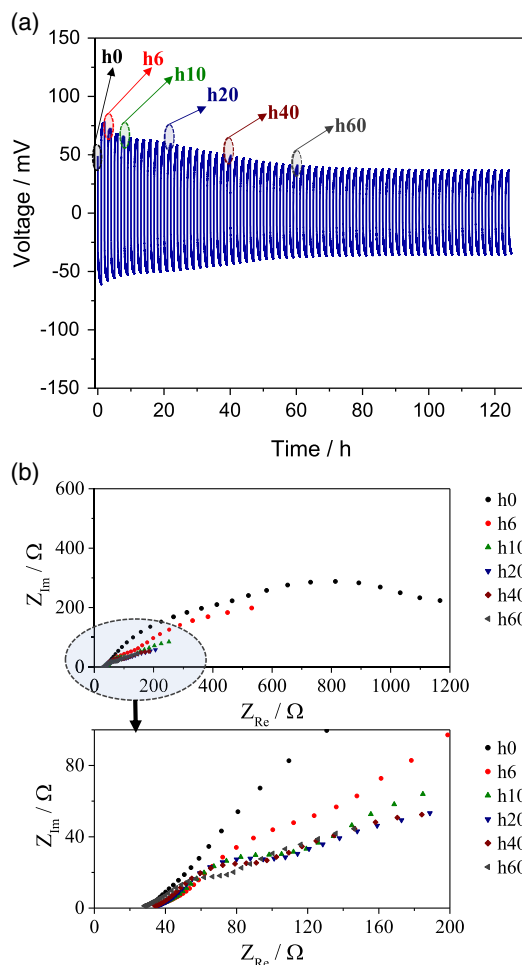


Figure 4. a) Stripping deposition measurement of a symmetrical Al/GPE(swelled)/Al cell using a current of 0.1 mA cm⁻² a deposition time of 1 h. b) Nyquist plot of the PEIS measurement carried out on the symmetrical Al/GPE(swelled)/Al cell at different cycling times.

cathode.^[18,36] **Figure 5** shows the cycling result of the Al/GPE(swelled) PG cell. Figure 5a shows the voltage signature of the Al/GPE(swelled) PG cell at various current rates, revealing that for the low current value (25 mA g^{-1}), the cell can deliver a capacity of about 63 mAh g^{-1} , similar to the one obtained in conventional liquid electrolyte.^[18,36,37] On the contrary, increasing the current rate result in a significant capacity decrease. At 50 mA g^{-1} , only 28 mAh g^{-1} can be delivered, less than 20 mAh g^{-1} at 75 mA g^{-1} , 13 mAh g^{-1} at 100 mA g^{-1} , and practically no capacity can be measured for a current of 200 mA g^{-1} . The increase in the current limits the side reactions taking place at the expense of the anion (AlCl_4^-).^[1] The system's limited rate

capability can be associated with a high polarization at the anode and to the lower ionic conductivity of the GPE in respect to the liquid electrolyte. Although the limited rate capability, the system is characterized by very good stability. As shown in Figure 5b, the system stabilizes back to the initial capacity value when put back to 25 mA g^{-1} . Figure 5c shows the long Al/GPE(swelled)/PG cycling test extended to 200 cycles, evidencing the system's good stability. This measurement illustrates that the cell is stable after increasing the upper cut-off voltage to 2.5 V at the 60th cycle. The new cut-off voltage allows the increase of about 10 mAh g^{-1} but sacrifices the cell Columbic efficiency that decreases from 97.5% to 94.7%.

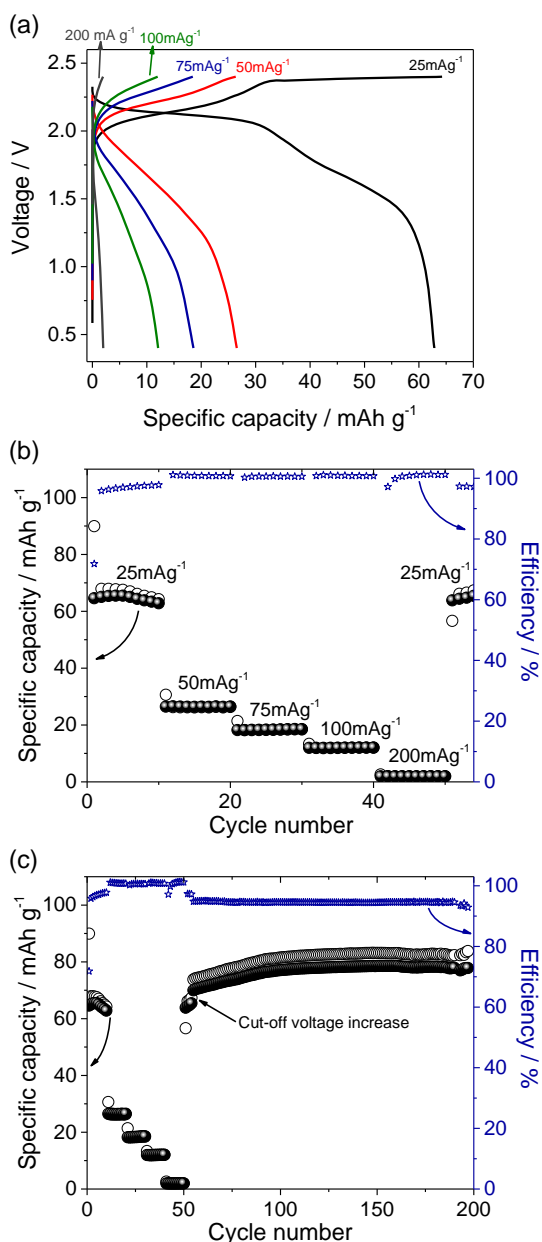


Figure 5. a) Voltage profile and b,c) cycling behavior of the galvanostatic cycling test of the Al/GPE(swelled)/PG cell, at various current rates (25, 50, 75, 100, and 200 mA g^{-1}) at room T.

4. Conclusions

In summary, the preparation of a GPE using a solvent casting approach has been demonstrated, obtaining a stable ionically conductive polymer electrolyte. Upon activation, the GPE can efficiently sustain the aluminum stripping deposition process. The prepared GPE electrolyte is characterized by lower corrosivity with respect to the conventional IL electrolyte against stainless steel 316. Finally, the realized GPE has been successfully used as an electrolyte in an aluminum battery with PG cathode, revealing the suitability of the prepared GPE for the realization of Al cells. The approach proposed here represents a possible alternative to the corrosive liquid electrolyte conventionally used in aluminum battery systems.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

aluminum batteries, aluminum stripping deposition, corrosion, gel polymer electrolytes, ionic liquids, polyacrylonitrile

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