



# Xanthan and $\kappa$ -carrageenan based alkaline hydrogels as electrolytes for Al/air batteries



T.M. Di Palma<sup>a</sup>, F. Migliardini<sup>a</sup>, D. Caputo<sup>b</sup>, P. Corbo<sup>a,\*</sup>

<sup>a</sup> Istituto Motori, National Research Council of Italy, Via Marconi, 4, 80125 Naples, Italy

<sup>b</sup> Applied Chemistry Laboratories, Department of Chemical Engineering, Materials and Production, University of Naples "Federico II", P.le Tecchio, 80, 80125 Naples, Italy

## ARTICLE INFO

### Article history:

Received 2 August 2016

Received in revised form 7 September 2016

Accepted 24 September 2016

Available online 26 September 2016

### Keywords:

Xanthan

$\kappa$ -Carrageenan

Alkaline hydrogels

Gel polymer electrolytes

Al/air batteries

## ABSTRACT

Xanthan and  $\kappa$ -carrageenan were used to prepare alkaline hydrogels to be used as electrolytes in aluminium air primary batteries. Two pasty gels were obtained starting from xanthan and KOH solutions (1 M and 8 M), while only the 8 M KOH solution permitted the formation of a stable, elastic and gummy hydrogel with  $\kappa$ -carrageenan. Discharge tests, performed on three Al/air cells assembled with Al anodes, electrolyte gels and Pt based cathodes, evidenced that all hydrogels exhibited appreciable properties of Al ion conductivities, according to the following performance order: xanthan with KOH 1 M < xanthan with KOH 8 M <  $\kappa$ -carrageenan KOH 8 M.

Characterization measurements (XRD, Ionic conductivity by EIS, SEM-EDS) were effected on hydrogels and galvanic cells to explain the behaviour differences detected between the hydrogels.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

The possibility to use solid ion conductors as electrolytes in electrochemical devices is currently investigated thanks to their well known advantages with respect to liquid ones, i.e. absence of leakage, high electrochemical stability at high voltages and excellent temperature stability, all characteristics that enhance safety issues (Yue et al., 2016; Zhang et al., 2014). In this context gel polymer electrolytes (GPE), including biopolymers materials, have been recently proposed for numerous electrochemical applications, such as fuel cells (Purwanto et al., 2016), batteries (Colò, Bella, Nair, Destro, & Gerbaldi, 2015; Isa & Samsudin, 2016), supercapacitors (Syahidah & Majid, 2013), sensors (Vaghela, Kulkarni, Haram, Karve, & Aiyer, 2016) and solar cells (Aziz, Buraidah, Careem, & Arof, 2015; Chiappone et al., 2014; Singh, Jadhav, Majumder, Bhattacharya, & Singh, 2013). They can be manufactured by simple and reliable processes, and could have ion conductivities comparable to those of liquid electrolytes ( $10^{-2}$ – $10^{-3}$  S/cm). Among GPEs, hydrogels prepared starting from some carbohydrate polymers (cellulose, starch, chitosan, agarose) have been extensively studied for electrochemical devices (Finkenstadt, 2005; Kadokawa, Murakami, Takegawa, & Kaneko, 2009; Yoshida, Takei, & Sawatari,

2002). They present the advantage to use a renewable, very cheap and environment-friendly source, meanwhile guarantying high conductivity values.

In this paper we present the results of a study of preparation and characterization on different GPEs obtained from two natural polysaccharides, characterized by low cost and manufacturing easiness (i.e. xanthan and  $\kappa$ -carrageenan), in view of a their utilization as electrolytes. Xanthan gum is a bacterial polysaccharide commercially produced by secretion from the bacterium *Xanthomonas campestris* in aerobic fermentation conditions. The structure consists of a cellulose backbone ( $\beta$ -(1  $\rightarrow$  4)-D-glucose) substituted at C-3 on alternate glucose residues with a tri-saccharide side-chain (Morris, 2006). It is widely used as a food additive and rheology modifier (Katzbauer, 1998), but electrochemical applications are not known.

Carrageenans are linear, sulphated polysaccharides extracted from various species of marine red algae. Their primary structure can vary with the algal source, but its backbone is essentially based on a repeating sequence of  $\beta$ -D-galactopyranose residues linked glycosidically through positions 1 and 3, and  $\alpha$ -galactopyranose residues linked glycosidically through positions 1 and 4 (Piculell, 2006; Tecante, & Nunez Santiago, 2012). The regular underlying structure is affected by the occurrence of substituents, mainly sulphate hemi-ester groups, in dependence of the algal source. A specific nomenclature based on Greek letters is used to distinguish between different samples.  $\kappa$ -Carrageenan presents one

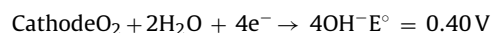
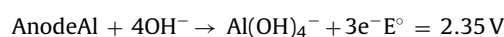
\* Corresponding author.

E-mail address: [p.corbo@im.cnr.it](mailto:p.corbo@im.cnr.it) (P. Corbo).

SO<sub>3</sub><sup>-</sup> group in the ideal repeating disaccharide unit, and is well known for its gelling capabilities in the presence of counter-ions, especially K<sup>+</sup>, that are the base of its rheological behaviour and consequent applications in the food field (Smidstrod & Grasdalen, 1982). Recent investigations have showed the promising properties of κ-carrageenan based hydrogels also in the electrochemical field (Prasad, Kaneko, & Kadokawa, 2009; Ueno, Endo, Kaburagi, & Kaneko, 2004).

In this work the two above polysaccharides were used as starting solid matrix to prepare hydrogels with alkaline solutions (KOH 1 M and 8 M). These solutions are known to effectively work as liquid electrolytes in many types of electrochemical devices, while the potassium counter-ion was selected for its property to enhance the gelling process of κ-carrageenan. The products obtained were tested as GPEs in an Al/air electrochemical cell. This system was chosen for the interesting electrochemical properties of Al that theoretically could provide very high energy and power densities and compete with Li batteries for different applications, from mobile to automotive. In fact, the theoretical specific capacity is 2.98 Ah/g, comparable to that of Li (3.86 Ah/g), but with less issues regarding metal abundance, price and safety (Egan et al., 2013). Most studies available in literature about Al/air batteries have investigated the properties of liquid electrolytes based on alkaline solutions (KOH and NaOH) (Mokhtar et al., 2015), while the possibility to use solid state electrolytes has been explored with reference to polyacrylic acid based alkaline gels (Zhang et al., 2014) and hydroponics polymer gels (Mohamad, 2008). However, to the best of our knowledge, no data are available in literature for Al/air batteries using polysaccharides based gels.

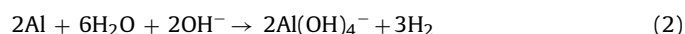
An Al/air battery operates by the following electrode semi-reactions:



Then the overall Al/air battery reaction is the following:



This type of battery is classified as a primary battery since it is not electrically rechargeable. This is essentially due to anode corrosion phenomena, occurring through the following parasitic reaction:



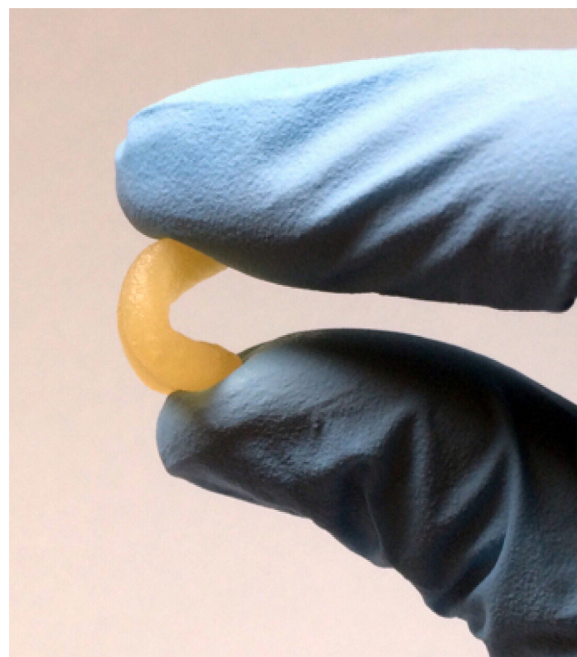
This reaction limits both the metal utilization and the cell practical voltage, that is usually comprised in the range 1–2 V. The corrosion level is a function of Al purity and of electrolyte nature. Recent investigations have evidenced that non-aqueous ionic liquids could introduce some grade of electric recharge ability (Revel, Audichon, & Gonzalez, 2014).

The performance of gels as electrolytes for this type of batteries were studied by discharge tests at constant current. The single gels were then characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS) in order to explain the electrochemical properties of materials.

## 2. Experimental

### 2.1. Materials

Xanthan gum (MW=2 10<sup>6</sup> g/mol) and KOH solutions (1 M and 8 M) were provided by Sigma-Aldrich, while κ-carrageenan (MW=789 g/mol) by Acros Organics. Aluminum anodes for Al/air cells were cut from a foil 0.5 mm thick (Puratronic, 99.998%) provided by Alfa Aesar, obtaining discs of 13 mm diameter. Cathodes



**Fig. 1.** GEL03 prepared by dispersion of κ-carrageenan in KOH 8 M. It looks like a gummy, quasi-solid state material.

were prepared starting from a Ni foam provided by MTI Corporation (1.6 mm thick, 350 g/m<sup>2</sup>). A 13 mm diameter disc was cut from this foam and used to sustain a Pt based catalyst. The Ni foam disc was immersed in a suspension obtained by mixing a Pt catalyst supported on active carbon (10% Pt, powder form, supplied by Aldrich) with polyvinylidene fluoride as a binder (powder form, supplied by Aldrich) in the weight ratio 10:1. The resulting mixture was then suspended in 1-methyl-2-pyrrolidinone. The amount of solvent in suspension preparation was adjusted to obtain a Pt concentration in the final cathode of 3 wt%. The Ni foam disc, after immersion in this suspension, was dried at 50 °C for 4 h.

### 2.2. Preparation of gels

Table 1 reports the list of different gels prepared starting from xanthan and κ-carrageenan with the details of preparation methods and product characteristics.

When xanthan was used as starting solid phase a pasty gel was obtained by stirring in both KOH solutions, while a clear and effective gelling process was observed with κ-carrageenan only with KOH 8 M. This sample presented an aspect elastic and gummy, as shown in the picture of Fig. 1.

### 2.3. Characterization measurements

X-ray diffraction studies were performed to determine the crystallinity of materials by using an X-ray diffractometer (Philips X'Pert PRO) with 2θ ranging from 5 to 80°. The X-ray source was Cu-κ<sub>α</sub> radiation with the wavelength λ = 1.540598 Å.

An Al/air galvanic cell was used to investigate the electrochemical properties of gels. The Al/air cells studied in this work were prepared by inserting the gels described in Table 1 as electrolytes between anode and cathode discs described in Section 2.1. The thickness of electrolyte was 1 mm electrochemical impedance spectroscopy (EIS) spectra were acquired on cells as prepared in order to determine the ionic conductivities of gels. A Zahner Zennium electrochemical workstation was used in potentiostatic mode, ranging the applied frequency between 4 MHz and 4 mHz,

Download English Version:

<https://daneshyari.com/en/article/5157805>

Download Persian Version:

<https://daneshyari.com/article/5157805>

[Daneshyari.com](https://daneshyari.com)