

Utilization of geopolymer cements as supercapacitors: influence of the hardeners on their properties

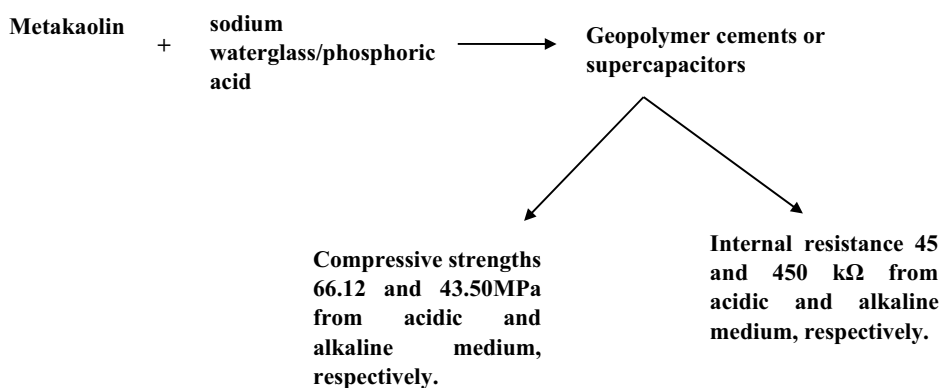
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Abstract

The main target of this work was to investigate the influence of the hardeners on the properties of the prepared supercapacitors named geopolymer cements. The supercapacitors were obtained by mixing an aluminosilicate source (metakaolin) and hardeners (sodium waterglass or phosphoric acid solution). The obtained supercapacitors were characterized by measuring the compressive strengths, infrared spectroscopy and scanning electron microscope. The electrochemical properties of the prepared supercapacitors were carried out by cyclic voltammetry and electrochemical impedance spectroscopy. The obtained results show that the compressive strengths of geopolymer cements from sodium waterglass and phosphoric acid solution are 43.50 and 66.12 MPa, respectively. The micrograph images indicate that both supercapacitors are compact, homogeneous and denser matrix. It appears that the supercapacitors from acidic medium have a lower internal resistance (45 kΩ), i.e. higher ionic conductivity, whereas, the one from alkaline medium indicates the higher value of the internal resistance (450 kΩ). It was typically found that the geopolymer cements from acidic medium have a higher electrical conductivity making it a potential electrode material for structural supercapacitor compared to the one obtained in alkaline medium.

Graphic abstract



Keywords Metakaolin · Sodium waterglass · Phosphoric acid · Supercapacitors · Internal resistance

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1 Introduction

Geopolymers refer to amorphous inorganic polymers obtained by mixing a semi-crystalline aluminosilicate source with a hardener [1]. According to Davidovits [1], geopolymer cement can be obtained by two different routes such as in alkaline medium (sodium or potassium waterglass) and in acidic medium (phosphoric acid solution or humic acids). Geopolymer cement produced in an alkaline medium consists of repeating units such as poly(sialate), $-\text{Si}-\text{O}-\text{Al}-\text{O}-$, poly(sialate-siloxo), $-\text{Si}-\text{O}-\text{Al}-\text{O}-\text{Si}-\text{O}-$, and poly(sialate-disiloxo), $-\text{Si}-\text{O}-\text{Al}-\text{O}-\text{Si}-\text{O}-\text{Si}-$ created through the geopolymerization process [1]. The synthesized product from the phosphoric acid solution which is usually used as a hardener is called poly(phospho-siloxo), $-\text{Si}-\text{O}-\text{P}-\text{O}-\text{Si}-\text{O}-$. Recent studies have shown that this inorganic polymer produced in acidic medium is obtained after curing the fresh samples for 24 h in an oven at 60 °C [2–5]. Up to now, geopolymer cements are generally used for the construction materials, immobilization of the heavy metals and so on. A recent study by Xu and Zhang [6] investigated the structural supercapacitors from graphene and geopolymer cement. In this study, the authors used the sodium waterglass at different modulus (molar ratio $\text{SiO}_2/\text{Na}_2\text{O}$) as a hardener for producing geopolymer cements. They reported that geopolymer cement from the modulus 1.6 exhibits the best level of multifunctionality, with compressive strength of 33.85 MPa. The internal resistance increases on decreasing the modulus and curing age. The recent study indicated that graphene has been recognized as an ideal material for electrochemical energy storage, due to its unique properties of high electrical conductivity, large surface area, and chemical stability [7]. Douiri et al. [8] investigated the dielectric constant conductivity and loss tangent of phosphoric acid-based geopolymers using different molar ratios Si/P. The hardener used by these authors is a phosphoric acid solution. They reported that the dielectric values increase with decreasing the molar ratio Si/P. The increase of the dielectric constant and loss tangent could be related to the enhancement of the ionic conduction phenomenon that was observed at low-frequency ranging from 1 to 10^6 Hz. For the highest amount of H_3PO_4 , the conductivity did not exceed 10^{-6} S/cm. Malkawi et al. [9] studied the dielectric constant and the dielectric loss factor of fly ash-based geopolymer binders using sodium waterglass as a hardener. They concluded that the dielectric properties of geopolymer binder from alkaline solution are between 0.1 and 60 MHz. Supercapacitors are high-capacity capacitors with a capacitance value much higher than other capacitors. For example, the

capacities of Ti_3C_2 as supercapacitor electrode were 350 F/cm^3 in the KOH electrolyte and 415 F/cm^3 in the H_2SO_4 electrolyte. They can accept and deliver charge much faster than batteries, and tolerates many more charge and discharge cycles than rechargeable batteries [10, 11]. Supercapacitors are used in applications requiring many rapid charge/discharge cycles, rather than long term compact energy storage—in automobiles, buses, trains, cranes and elevators, where they are used for regenerative braking, short-term energy storage, or burst-mode power delivery [12, 13]. In recent work, Jiaming et al. [6] demonstrated that it was possible to fabricate a supercapacitor based on geopolymer. Geopolymer is a porous material with many excellent properties such as high compressive strength, good electrical insulation and resistance to chemical corrosion. Furthermore, the widespread pores in geopolymer matrix provide enough channels for ion storage and motion [6, 14].

The main objective of this work is to investigate the influence of the hardeners on the properties of the novel supercapacitors denoted as geopolymer cements. Sodium waterglass and the phosphoric acid solution was used as hardeners and metakaolin was used as an aluminosilicate source. The obtained geopolymers were characterized by the determination of their compressive strengths, infrared spectroscopy, X-ray diffractometry and scanning electron microscope (SEM). The electrochemical techniques used in this work to monitor the properties of supercapacitors are cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

2 Materials and experimental methods

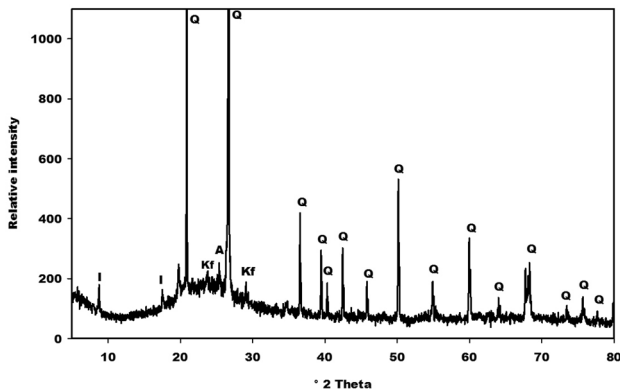
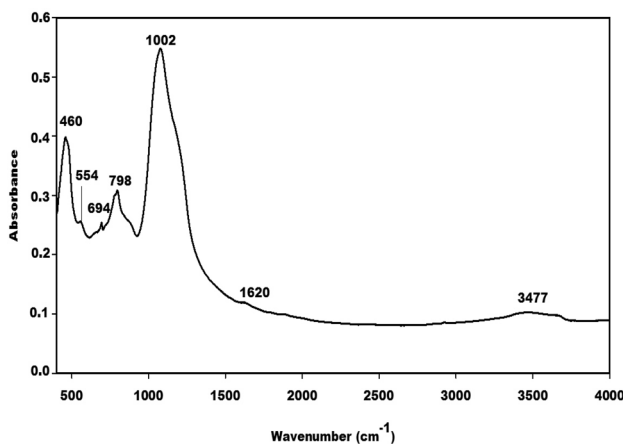
2.1 Materials

Kaolin used in this study was extracted from Mayouom in the West region of Cameroon. This raw material was crushed in a rapid ball mill (MGS Srl, type 1000/2) for 30 min with a porcelain jar and microspheres of higher-grade alumina as grinding medium in order to obtain fine particles of kaolin. The obtained sample was calcined at 700 °C in a programmable electric furnace (MGS Srl) for 4 h with a heating and cooling rate of 5 °C/min to obtain metakaolin denoted MK. The physico-chemical characterization of kaolin was already studied by Tchakouté et al. [15, 16]. The chemical composition of this kaolin is given in Table 1. The X-ray pattern and infrared spectrum of metakaolin are given in Figs. 1 and 2, respectively. Commercial phosphoric acid (H_3PO_4 85%, puriss. p.a., Reag. ACS, Reag. ISO, Reag. Ph. Eur. d = 1.69) was used to prepare acid hardener. Commercial silica fume, $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ (Merck,

Table 1 Chemical composition (wt %) of kaolin

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	TiO ₂	MgO	Na ₂ O	CaO	P ₂ O ₅	MnO	LOI
Kaolin	41.46	31.47	7.65	0.51	1.50	0.65	0.69	0.15	0.09	0.06	15.76

LOI: Loss on ignition at 1000 °C

**Fig. 1** X-ray pattern of metakaolin, MK. (I, A, Q and Kf denote peaks of Illite, Anatase, Quartz and K-feldspar respectively)**Fig. 2** IR spectrum of metakaolin (MK)

N° 10,279-57-9) was used as a silica source for producing the alkaline hardener.

2.2 Experimental methods

2.2.1 Preparation of hardeners

The acid solution was prepared by mixing distilled water and commercial phosphoric acid in order to get the hardener with molar concentration 10 M. The alkaline solution was prepared by adding commercial silica fume to NaOH pellets and mixed with distilled water. The whole was treated for 1 h at 100 °C using a magnetic stirrer to obtain the reactive ingredient with the molar ratios SiO₂/Na₂O

and H₂O/Na₂O kept constant at 1.6 and 10, respectively. The molar ratio SiO₂/Na₂O equal to 1.6 was chosen according to the findings work of Xu and Zhang [6]. The aforementioned hardeners (acid and alkaline hardeners) were allowed to mature in the laboratory at room temperature for 24 h prior to use.

2.2.2 Synthesis of geopolymer cements

Both geopolymer cements were prepared by adding each hardener gradually to metakaolin in a porcelain mortar and mixing mechanically for 5 min, obtaining the specimens GA and GB. GA and GB correspond to geopolymer cements from phosphoric acid and sodium waterglass as hardeners, respectively. The liquid/solid mass ratio for both specimens was kept constant at 0.80. The fresh geopolymer cements were poured into cube mould (40 × 40 × 40 mm) for compressive strength measurement and into cylindrical PE-containers (7 × 15 mm) for electrochemical characterization. These samples were closed in order to hinder the evaporation of water during the setting. The specimens GB were kept at room temperature for 24 h while the one of GA were cured at 60 °C in an oven for 24 h. After 24 h, the obtained geopolymer cements (GA and GB) were demoulded and conserved at room temperature for 28 days before compressive strengths and electrochemical tests. GA was cured at 60 °C according to the findings works of Davidovits [1]. He reported that geopolymer cement from acidic medium needs an energy gradient which favours the formation of the poly(phospho-siloxo) chain.

2.2.3 Methods of characterization of geopolymer cements

The compressive strengths of both geopolymer cements were measured after 28 days at room temperature using a 250 kN cement/mortar automatic machine (Impact Test Equipment Limited) according to the EN196/01 standard. The specimens were subjected to a compressive force until the specimen failed. Six samples were tested for each measurement and the mean values for the closest five were determined. After compressive strength testing, the fragments of each geopolymer were crushed and the obtained powders were used to measure X-ray diffractometry (XRD) and Fourier transforms infrared spectroscopy (FT-IR). The other fragments were used for SEM observations. XRD patterns were taken using CuKa

radiation between 5 and 80° in 7 h in steps of 0.03° (Bruker D4). Infrared (FT-IR) absorption spectra were taken by the ATR method (about 1 mg sample, Bruker, 2 cm⁻¹, 16 scans). Fragments from the mechanical testing, after gold coating and drying, were used for microstructure observations using a JEOL JSM-6390A Scanning Electron Microscope (SEM) with an acceleration voltage of 15.0 kV.

The electrochemical experiments were performed in a thermostated electrochemical cell with three electrodes: The working electrode is a cylindrical geopolymer bar, the auxiliary electrode a platinum wire and the reference electrode a saturated calomel electrode (SCE). These electrodes were connected to an Autolab PGSTAT 12 (EcoChemie) potentiostat/galvanostat controlled by the software FRA (Frequency Response Analysis) for electrochemical impedance measurements, and GPES (General Purpose Electrochemical System) for the cyclic voltammetry (CV) experiments. Cyclic voltammetry experiments were carried out with working voltage between -0.5 and 0.5 V, at a scan rate of 100 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) is well established as a powerful tool for measuring the dielectric and transport properties of materials and for exploring the properties of porous electrodes. The electrochemical impedance spectroscopy (EIS) plots were measured with the frequency ranging from 0.1 to 10 kHz. The low-frequency in the range 0.1 Hz–10 kHz was chosen to avoid complications due to pseudo-inductances. In order to obtain reproducible and reliable results, the experiments were repeated three times with three different specimens under the same experimental conditions. The initial voltage was set to open circuit potential. The electrochemical tests were evaluated in a 2 M of potassium hydroxide solution at room temperature.

3 Results and discussion

3.1 X-ray patterns

The X-ray patterns of geopolymer cements from alkaline (GB) and acid (GA) solutions are given in Fig. 3. Both X-ray patterns exhibit the broad hump structure between 5 and 15° (2θ) and between 20 and 38° (2θ). These hump structures appear between 18 and 30° (2θ) on the X-ray pattern of metakaolin (Fig. 1). The shift of this broad reflection at 20 and 38° (2θ) and the apparition of the one at 5 and 15° (2θ) on the X-ray patterns of geopolymer cements could be related to the formation of poly(sialate-siloxo) and poly(phospho-siloxo) networks for GB and GA, respectively. The hump structure between 5 and 15° (2θ) observed on the X-ray patterns of both geopolymer cements could be related to the additional amorphous phase contained in the structure of these specimens

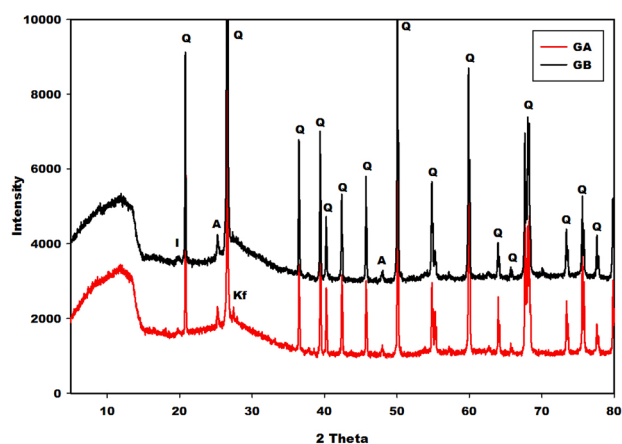


Fig. 3 X-ray pattern of geopolymer cements, GA and GB. (I, A, Q and Kf denote peaks of Illite, Anatase, Quartz and K-feldspar respectively)

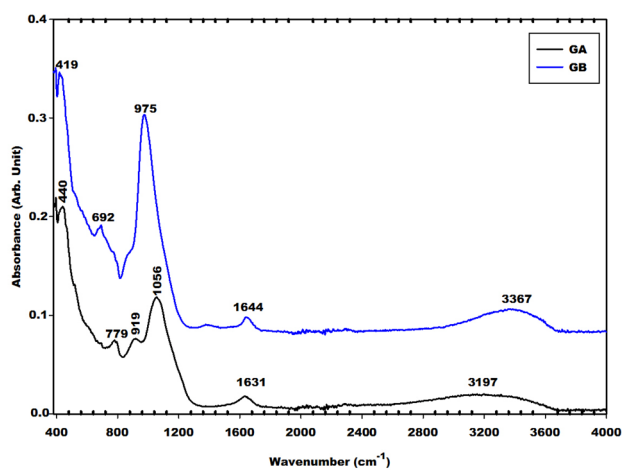


Fig. 4 IR spectra of geopolymer cements, GA and GB

[15]. In addition, a few crystalline peaks corresponding to quartz, illite, anatase and K-feldspar are also observed. These crystalline phases are also present on the X-ray pattern of metakaolin suggesting thus, these minerals remain unaffected during the depolymerization and the polycondensation reactions.

3.2 Infrared spectra

The infrared (IR) spectra of GB and GA are shown in Fig. 4. The broad bands that appear at 3197 and 3367 cm⁻¹ for GA and GB, respectively correspond to the deformation vibration modes of -OH. Those that appear at 1644 and 1631 cm⁻¹ belong to the bending vibration modes of H-O-H of water molecules [17]. The absorption bands at 440 cm⁻¹ for GA and 419 cm⁻¹ for GB are assigned to

Si–O–Si in-plane vibration [15]. These bands appear at 460 cm^{-1} in the IR spectrum of metakaolin (Fig. 2); the shift of this band toward lower wavenumber on the IR spectrum of geopolymer cements could be related to the reorganization of the structure of geopolymer cements during the polycondensation reaction. The band at 712 cm^{-1} that appears only on the IR spectrum of GB is attributed to sialate (Si–O–Al^{IV}) bonds in the geopolymer networks [15]. The bands at 779 and 919 cm^{-1} on the IR spectrum of GA is ascribed to phospho-siloxo, Si–O–P and P–O bonds, respectively in the structure of acid-based geopolymer cements [5]. The band that appears at 1002 cm^{-1} on the IR spectrum of metakaolin shift toward lower wavenumber, i.e. 975 cm^{-1} for GB and toward higher wavenumber (1058 cm^{-1}) for GA [18]. This is related to the inclusion of Al and P in the tetrahedral network of GB and GA, respectively. This confirms the formation of poly(sialate-siloxo) and poly(phospho-siloxo) networks in the structure of GB and GA, respectively.

3.3 Compressive strengths and micrograph images

The compressive strengths of geopolymer cements GA and GB were 66.12 ± 0.56 and 43.50 ± 0.75 MPa, respectively. The higher compressive strength of GA compared to the one of GB could be related to the higher cross-linking geopolymer framework. Similar results have been obtained by Tchakouté et al. [5]. The micrograph images of both geopolymer cements are compact due to the more depolymerization of the hardeners used (Fig. 5). The denser matrices indicate the good connectivity of acid and alkaline hardeners-based geopolymer cements.

3.4 Electrochemical properties of geopolymer cements

3.4.1 Electrochemical impedance spectra

The conductivities of geopolymers from alkaline (GB) and

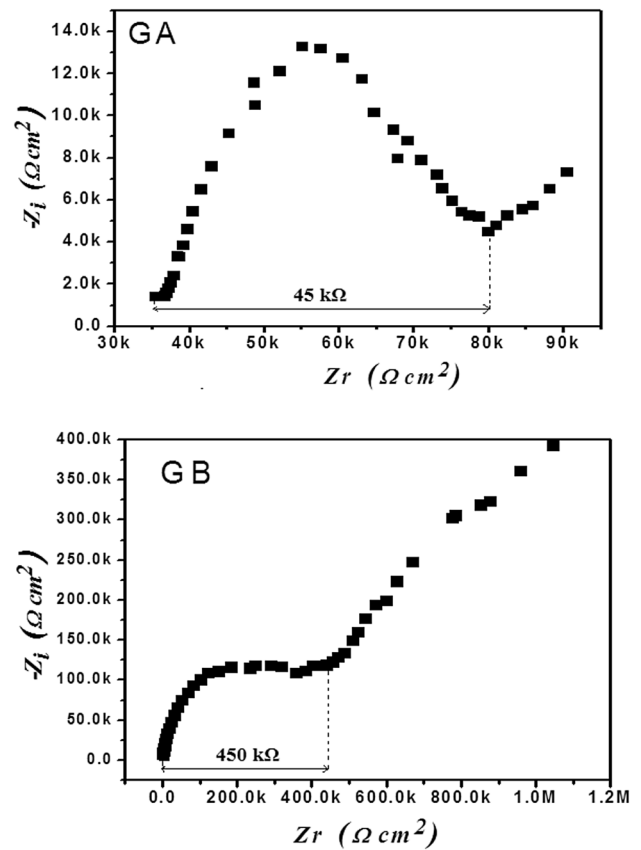


Fig. 6 Diagram of Nyquist of the geopolymer GA and GB

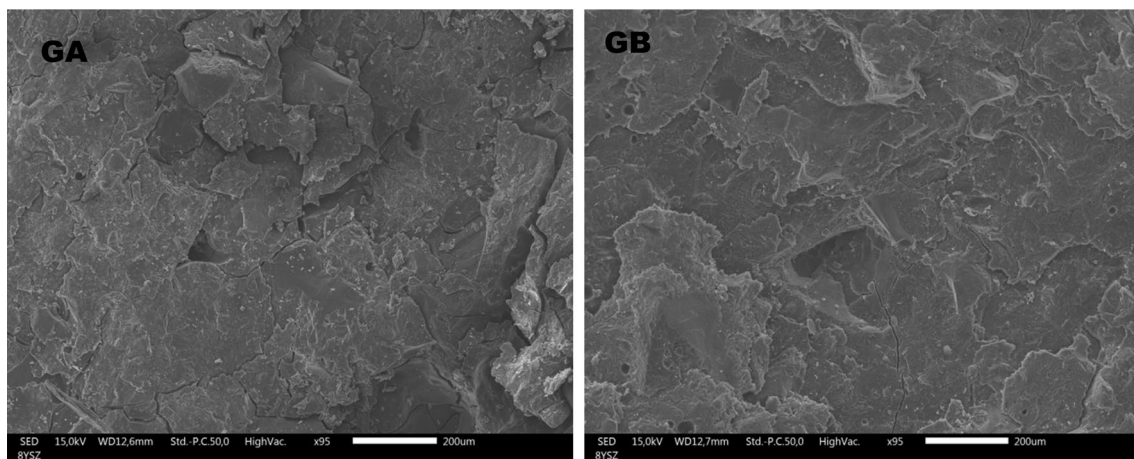


Fig. 5 Micrograph images of geopolymer cements GA and GB

acid (GA) solutions are shown in Fig. 6. It appears that the Nyquist diagrams of geopolymer separator exhibit ionically-conducting function. In the present study, we plotted the imaginary impedance component (Z'') versus real impedance component (Z') at each excitation frequency. In this plot, two separate processes are very well differentiated. A semicircle (high frequency) relating to a charge-transfer-controlled process [19]. At low frequencies, the linearity observed on the Nyquist diagrams is due to the scattering of species indicating a nearly ideal capacitor response according to Gong et al. [7] and Gabrielli [20]. The charge transfer resistors (R_{ct}) of geopolymer separator could be determined from EIS by the intersection point of the curves with the horizontal axis. The semicircle corresponds to the domain of charge transfer following a sinusoidal disturbance which is a function of the ionic conductivity of the material. It is important to note that a lower charge transfer resistance implies a higher performance of materials. It appears that the geopolymer cement, GA has a lower internal resistance (45 k Ω), higher ionic conductivity compared to the one of GB (450 k Ω). According to Xu and Zhang [6], the higher value of the internal resistance of geopolymer cement from alkaline hardener, GB, could be due to the smaller pore size of the specimen and therefore the lower ionic conductivity. We expected that GB has a higher ionic conductivity due to the lower value of its compressive strength. Indeed, the electrode of GA possesses high conductivity owing to the good interfacial contact with electrolyte, which provides fast ion transport channels. This behavior could be assigned to the higher ionic conductivity of the H_3O^+ (34.98 mS m 2 mol $^{-1}$, à 25 °C) compared to the one of Na^+ (5.01 mS m 2 mol $^{-1}$, à 25 °C) [21]. Gao et al. [10] investigated the electrochemical performance of Ti_3C_2 supercapacitors in KOH electrolyte. They reported that the addition of the black carbon increases the ion diffusion channel and reduces the diffusion resistance of ion. Equivalent resistance was decreased from 16.7 to 3.5 Ω . It was found that geopolymer cement has a higher internal resistance compared to Ti_3C_2 supercapacitors.

3.4.2 Cyclic voltammetry

Figure 7 shows the cyclic voltammetric (CV) curves of supercapacitor from an acid (GA) and in alkaline medium (GB). It seems that both curves have the same shape with a low capacitive current indicating the identical porosity for both geopolymers. The absence of oxidation and reduction peaks indicates that geopolymer is not electro-active in the range of potentials explored or electrodes were excellent electrochemical stability Gong et al. [7]. In both geopolymer materials, conducting ions are distinguished from other elements by the significant occupation of the

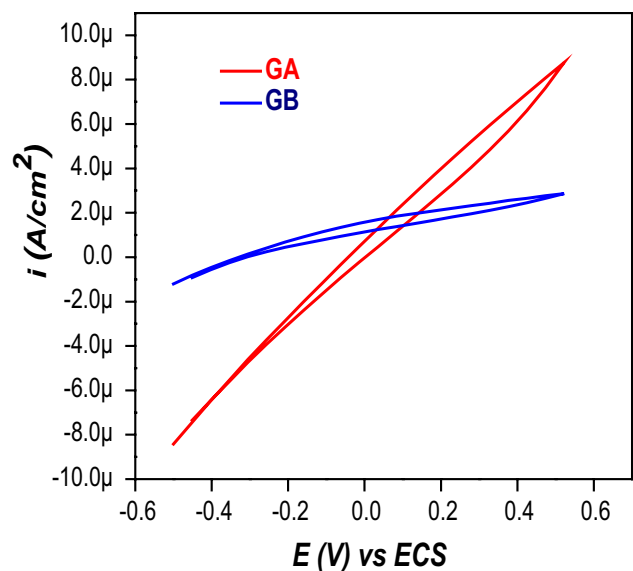


Fig. 7 Voltametric curves of geopolymers GA and GB

material sites. The latter are more numerous in the acidic medium than in alkaline medium, that is why the geopolymer hardened in alkaline medium has a current density lower than that the one impregnated in an acid medium. These results are consistent with those of the impedance diagrams. As a porous and dielectric material, the geopolymer plays a role in the energy storage system. The pores in the matrix have channels for ion storage and charge movement so that the geopolymer separator has an ionic conduction function Xu and Zhang [6].

4 Conclusion

Sodium waterglass with molar ratio SiO_2/Na_2O equal to 1.6 and phosphoric acid with molar concentration 10 M were used as hardeners in order to study their influences on the properties of the supercapacitors. The results show that geopolymer cement obtained in the acidic medium have a lower internal resistance (45 k Ω) compared to the one obtained in alkaline medium (450 k Ω). The result shows that the obtained supercapacitor from acidic medium exhibits the higher value of the compressive strength (66.12 MPa), lower internal resistance and higher ionic conductivity. It was found that geopolymer cement obtained in the acidic medium could be used as a supercapacitor and making a multifunctional material.

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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