1 **Inherently multifunctional geopolymeric cementitious composite as electrical energy**
2 **storage and self-sensing structural material**

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8 **Abstract**

9 In this paper, we demonstrate for the first time that potassium-geopolymeric (KGP)

10 cementitious composites can be tuned to store and deliver energy, and sense themselves

11 without adding any functional additives or physical sensors, thus creating intelligent concrete

12 structures with built-in capacitors for electrical storage and sensors for structural health

13 monitoring. Density function theory (DFT)-based simulations were performed to determine

14 the electronic properties of the KGP cementitious composite and understand its conduction

15 mechanism. Experimental characterization was also conducted to determine the structure,

16 chemical composition, conduction mechanism, energy storage and sensing capabilities of the

17 KGP cementitious composite. The DFT simulations suggested that the KGP cementitious

18 composite relies on the diffusion of potassium (K^+) ions to store electrical energy and sense

19 mechanical stresses. The geopolymeric cementitious composite exhibited a good room

20 temperature ionic conductivity in the range of 12 (10^{-2} S/m) and an activation energy as high

21 as 0.97 eV. The maximum power density of the KGP capacitors is about 0.33kW/m^2 with a

22 discharge life of about 2 hours. The KGP stress sensors showed high sensitivity to compressive

23 stress: 11 Ω/MPa based on impedance measurement and 0.55 deg/MPa based on phase

24 measurement. With further development and characterization, the KGP cementitious

25 composite can be an integral part of concrete structures in the form of a battery to store and

26 deliver power, and sensors to monitor the structural integrity of urban infrastructure such as

27 bridges, buildings and roads.

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1. Introduction

Recently, there has been a growing interest in the development of advanced structures to enhance the safety and sustainability of civil infrastructure systems such as bridges, buildings, roadways and energy constructed facilities. Advanced structural materials of the future are being envisaged to provide new smart features such as self-condition monitoring to determine the magnitudes and locations of any deterioration occurring in structures so that proper actions can be taken to avoid failures. Ordinary Portland cement (OPC) is the most widely used material for the construction of civil infrastructure systems. When OPC is mixed with water, the resulting hydration products fulfil their primary function of mechanical load bearing, but lack the functionality needed for civil infrastructure systems of the future. Consequently, expensive and exotic functional additives are routinely used to induce self-sensing functionality in cement-based materials. For example, conductive fillers such as carbon fibers (CFs), carbon nanotubes/nanofibers (CNTs/CNFs) and graphene were employed to induce the piezoresistive effect in cement-based materials for structural health monitoring applications [1-3]. However, a large-scale deployment of conductive fillers in cementitious composites is limited due to serious issues including poor dispersibility, incompatibility with the host materials, costs and health risks.

Structural materials will also take on additional functions such as collection and storing power from solar and wind renewable energy sources. This function will not only improve the energy efficiency of structures but also enable better management of excess energy by feeding it to the grid to reduce energy peak demands [4] or using it to power auxiliary systems such as lighting posts, traffic lights, advertising boards, electric vehicle charging stations and structural health monitoring sensors. In the areas of aerospace and automotive engineering, several concepts of composite-based structural energy storage systems have been introduced that can simultaneously carry load and store electrical energy [5-7]. In these structural capacitors, the reinforcing carbon fiber mats act as electrodes and the specially formulated resin epoxies act

2

57   as ionic electrolytes [5-7]. Research into electrical energy storage in civil engineering

58   structures remains scarce and only a few concepts of OPC-based structural electrical energy

59   storage systems have been proposed to date [8, 9]. These cement-based energy storage systems

60   use the pore solution in the cement as electrolyte and cement with additives such as graphene,

61   black carbon, zinc and magnesium dioxide as electrodes [8, 9]. Unfortunately, the

62   manufacturing of these concepts is a very expensive and complex to process, and more

63   importantly they can only work in the wet state, thus preventing their commercial use.

64   Geopolymers are a new class cementitious composites and are being explored as a potential

65   replacement for OPC, which is a material with a large carbon footprint. The most commonly

66   used geopolymeric cementitious composites are formed by alkali activation of alumino silicate

67   materials such as fly ash [10-13]. The alkaline activators typically consist of a mixture of

68   sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH). Depending on the Si/Al molar ratio,

69   after reaction under controlled temperature, the resulting geopolymeric frameworks can be in

70   the form of sodium-poly(sialate) (Na-PS), (Na-PSS) sodium-poly(sialate-siloxo) (Na-PSS) or

71   sodium-poly(sialate-disiloxo) (Na-PSDS), [14]. These types of geopolymeric cementitious

72   composites have shown to exhibit good mechanical properties and durability characteristics

73   [15]. Like OPC, geopolymers are perceived as inherently "dumb" materials, thus, requiring

74   functional additives to enhance their electrical properties for self-sensing purposes [16-17].

75   However, we have shown that Na-PSS geoplymeric cementitious composites exhibit a fairly

76   good ionic conductivity which can be exploited for the design of self-sensing structures [18].

77   Indeed, we have demonstrated that when employed in conjunction with current collectors such

78   as graphene electrodes, Na-PSS geopolymeric cementitious composites can be used as a high

79   resolution gauge strain sensors for health monitoring of structures [18]. However, the

80   manufacturing process of this geopolymeric sensor is quite complex and expensive due to the

81   addition of graphene sheets. Another type of geopolymeric cement is postassium-based

82   geopolymeric (KGP) cementitious composites, also known as potassium-poly(sialate-siloxo)

83 (K-PSS), which is processed by reacting aluminosilicate materials with a reagent consisting of

84 potassium silicate (K_2SiO_3). KGP cementitious composites offer several advantages over Na-

85 PS, Na-PSS and Na-PSDS -based cementitious composites including high strength, good high

86 temperature resistance and thermal stability, excellent durability in harsh environments and

87 easy manufacturing [19].

88 Herein, we demonstrate that the inherent high ionic conductivity of KGP cementitious

89 composites can be exploited for the fabrication of multifunctional structural materials with

90 intelligent features such as load bearing, electrical energy storage and self-sensing of

91 mechanical stresses. To the authors' best knowledge, this is the first time KGP cementitious

92 composites have been proposed for both electric energy storage and stress sensing without

93 adding additives or physical sensors.

94 **2. Methodology**

95 *2. 1. Experimental program*

96 *2. 1.1. KGP capacitors/sensors design, materials, chemicals and fabrication*

97 As shown in Fig. 1a, the capacitors/sensors are KGP cementitious composites equipped with

98 two steel mesh electrodes for sensing and power storage purposes. The KGP matrix was

99 prepared by mixing fly ash into the alkaline activator with an alkaline activator-to-fly ash ratio

100 of 0.60. The alkaline activator consisted of potassium silicate (K_2SiO_3) solution with $SiO_2 =$

101 26.6%, $K_2O = 30.7\%$ and $H_2O = 42.7\%$. The manufacturing of the KGP capacitors/sensors is

102 quite simple. The fly ash powder was first added to the alkaline solution and mixed for 1

103 minute with a DAC 150 high centrifugal mixer. Upon mixing, the KGP paste was poured into

104 plastic molds to form the KGP capacitors/sensors with dimensions of 50 mm (W) x 50 mm (L)

105 x 10 mm (T). Subsequently, the two steel mesh electrodes were inserted into each KGP

106 capacitor/sensor and then the samples were vibrated to ensure good contact between the

107 electrodes and the KGP matrix. The distance between the electrodes represents the effective

108 thickness of the KGP capacitors/sensors and was 4 mm and 8 mm for capacitors/sensors 1 and

109   2, respectively. The fabricated KGP sensors/capacitors were cured at room temperature for 24

110   hours then cured in oven at 50°C for 24 hours. The KGP capacitors/sensors were then cooled

111   down in room temperature prior to characterization.

112   *2.1.2. Characterization*

113   A scanning electron microscope/energy-dispersive X-ray spectroscopy (SEM/EDX) was

114   employed to determine the microstructure and chemical composition of the KGP cementitious

115   composite. Electrochemical impedance spectroscopy (EIS) was used to investigate the energy

116   storage and self-sensing capabilities of the KGP capacitors/sensors using Gamry Interface 1000

117   with a frequency range of 0.04 Hz – 1 MHz (Fig. 1b). The ionic conductivity, activation energy

118   and dielectric constant of the KGP capacitors/sensors were determined under normal civil

119   engineering structures operating temperatures of -5, 5, 20 and 30°C.   The KGP

120   capacitors/sensors were placed in a controlled environmental chamber and were heated from -

121   5 to 30°C in 10 and 15 °C steps. Each temperature was kept constant for 1 hour to achieve

122   thermal equilibrium in the chamber.   This heating test procedure was also employed to

123   determine the temperature dependence of the capacitance of the KGP capacitors. The stress

124   dependence of the capacitance of the KGP capacitors was determined at room temperature at

125   loads of 3, 6, 10 and 15 kN using the setup shown in Fig. 1c. The electrical storage capacity

126   of the KGP capacitors was studied using their measured cyclic voltammetry (CV) response.

127   The CV response of the KGP capacitors was determined at scan rates of 25, 100 and 200 mV/s.

128   The charge-discharge behavior of the KGP capacitors was investigated using discharge tests at

129   currents between 50 and 400 μA. For each current, the voltage was measured until it dropped

130   to zero and the corresponding discharge time was determined.

131   The stress sensing capability of the KGP sensors was determined under monotonic compressive

132   load at constant ambient room temperature using the setup shown in Fig. 1c. The KGP sensors

133   were loaded from 3 to 15 kN in 3, 4 and 5 kN steps and their impedance and phase responses

134   were determined. It is worth noting that the configuration of the environmental test chamber

135   did not allow the authors to investigate the effect of the temperature on the stress sensing

136   response of the KGP sensors.

137   *2.2. Density function theory (DFT) simulations*

138   To elucidate the electrical energy storage and self-sensing mechanisms of the KGP

139   capacitors/sensors, basic understanding of the electronic properties of the KGP cementitious

140   composite is needed to uncover their conduction mechanism. The electronic properties of the

141   KGP cementitious composite were determined using the density function theory (DFT). The

142   geometry relaxation, band structure and density of state calculations were performed using the

143   SIESTA implementation of DFT [20]. SIESTA employs norm-conserving pseudopotentials to

144   account for the core electrons and linear combinations of atomic orbitals (LCAO) to construct

145   the valence states. The generalized gradient approximation (GGA) of the exchange and

146   correlation functional were employed in conjunction with the Perdew-Burke-Ernzerhof

147   parameterization (PBE) with an equivalent cut-off energy of 2040 eV. The lattice parameters

148   of the KGP composite were optimized until the forces on each atom are smaller than 20 meV/Å.

149   The band structure and the density of states (DOS) were determined using 5 x 5 x 5 Monkhorst-

150   Pack k-point for Brillouin-zone integrations.

151   **3. Results**

152   *3.1. Mineralogical composition, morphology and structure*

153   The XRD pattern for the KGP matrix is shown in Fig. 2. As seen, the primary crystalline phase

154   is hydrated leucite with secondary phases mainly mullitte and quartz. Figures 3 and 4 show

155   the EDX spectrum and the map of the chemical elements of the KGP matrix, respectively. The

156   average oxide molar ratio of SiO_2/A_2lO_3 is around 2, confirming that the KGP matrix is mainly

157   a 3D framework in the form of hydrated leucite type-poly(sialate-siloxo) (K-PSS or K (-Si-O-

158   Al-O-Si-O-) as demonstrated by Davidovits [12]. Figure 4 shows the x-ray maps of Si, Al and

159   K elements of the whole region shown in Fig. 4a. First, the SEM image in Fig. 4a shows

160   somewhat a homogenous sponge-like KGP matrix containing closed and unclosed pores as a

161   result of partially or fully reacted fly ash particles [18]. Second, it can be seen from Fig. 4b-d,

162   that the Si, Al and K elements are uniformly distributed across the bulk KGP matrix. Third,

163   Fig. 4e shows high concentration of K element across the bulk KGP matrix.

164   *3.2. Impedance response of KGP capacitors/sensors*

165   The Bode plot of the impedance for the 4 and 8 mm KGP capacitors/sensors is shown in Fig.

166   5. The measured total impedance Z is described by the following expression:

$$Z = Z' + jZ'' \qquad (1)$$

168   where Z' (Z' = R) and Z'' (Z'' = $1/\omega C$) are the real and imaginary impedances, respectively. *R*

169   and *C* are the resistance and the capacitance, respectively, and $\omega=2\pi f$ is the angular frequency

170   where *f* is the frequency of the electric field.

171   As seen in Fig. 5, both KGP capacitors/sensors have very similar impedance shape and trend.

172   Both KGP capacitors/sensors behave like a pure capacitor in the frequency range of 0.1 Hz-1

173   Hz, as the total impedance is largely capacitive over this frequency range. However, at higher

174   frequencies, their imaginary impedance ($Z'' = 1/\omega C$) is very small and their real impedance

175   becomes their bulk resistance ($Z' = R$) which is about 250 Ω and 100 Ω for the KGP

176   capacitors/sensors 1 and 2, respectively. This means that, in addition to storing electrical

177   energy, the KGP capacitors/sensors can function as piezoresistive stress sensors at frequencies

178   higher than 1 Hz.

179   *3.2. Permittivity, ionic conductivity and activation energy of KGP capacitors/sensors*

180   The frequency dependence of the dielectric constant of the KGP capacitors/sensors at different

181   temperatures is shown in Fig. 6. The dielectric constant ϵ' was calculated using the following

182   expression:

$$\epsilon' = \frac{dZ''}{2\pi f Z^2 \epsilon_0 A} \qquad (2)$$

184   Where *d* is the distance between the electrodes, ϵ_0 is permittivity of the free space, *f* is the

185   frequency of the electric field and *A* is the area of the steel electrode.

186   From Fig. 6, one can see that for both KGP capacitors/sensors, the dielectric constant decreases

187   as the frequency increases over the frequency range of 0.1 Hz - 10 Hz. This is because of the

188   dielectric dispersion within the KGP matrix and the interfacial polarization caused by

189   inhomogeneity in the KGP material. In this case, the dipoles are incapable to orient themselves

190   in the direction of the applied electric field. At higher frequencies, the dielectric constants level

191   off as they approach zero. Fig. 6 also shows that the dielectric constant of the KGP

192   capacitor/sensor 1 increases with increase in temperature due to the formation and orientation

193   of dipoles. On the other hand, the dielectric constant of the KGP capacitor/sensor 2 seems to

194   be somewhat insensitive to temperature. The measured room temperature dielectric constants

195   are 1.5×10^8 and 5×10^8 for the KGP capacitors/sensors 1 and 2, respectively. As the effective

196   thickness increases, the dielectric constant also increases due to the reduction of the interfacial

197   dead-layer effect [21].

198   The room temperature ionic conductivity of the KGP capacitors/sensors at frequencies of 0.1,

199   1 and 1000 kHz is given in Fig. 7. The ionic conductivity was calculated using the following

200   formula:

201    $$\sigma_{ac} = 2\pi f \epsilon'' \epsilon_0 \qquad (3)$$

202    $$\epsilon'' = \frac{dZ'}{2\pi f Z^2 \epsilon_0 A} \qquad (4)$$

203   where f is the frequency of the electric field and ϵ_0 is the dielectric constant of the free space

204   and A is the area of the electrode. As shown, the maximum room temperature ionic conductivity

205   is about 1.72 (10^{-2} S/m) and 11 (10^{-2} S/m) for the KGP capacitors/sensors 1 and 2, respectively.

206   The high ionic conductivity of the KGP capacitor/sensor 2 is presumably attributed to high

207   concentration of K^+ carriers.

208   The variation of log ionic conductivity (σ_{ac}) with inverse of temperature ($1/T$) for the KGP

209   capacitors/sensors is depicted in Fig. 8. As shown, the KGP capacitors/sensors show an

210   Arrhenius conductivity-temperature behavior governed by the following equation:

8

211
$$\sigma_{ac} = \sigma_0 \, exp\left(\frac{-E_a}{E_B T}\right) \tag{5}$$

212 where σ_0, E_a and E_B are the pre-exponential factor, the activation energy and the Boltzmann

213 constant, respectively. The activation energy E_a is defined as the slope of the Arrhenius plot

214 multiplied by the Boltzmann constant E_B. The calculated activation energy E_a of K^+ mobility

215 for the KGP capacitors/sensors at different frequencies is shown in Fig. 8. In the frequency

216 range of 100 Hz – 1 MHz, the activation energy for the KGP capacitor/sensor 1 is between 0.87

217 eV and 0.97 eV, whereas the activation energy for the KGP capacitor/sensor 2 is between 0.4

218 eV and 0.64 eV.

219 *3.3. Electronic properties and conduction mechanism of the KGP cementitious composite*

220 Based on the XRD results, the primary crystalline phase of the KGP cementitious composite is

221 hydrated leucite. The lattice structure of hydrated leucite is still not known. However, Bell et

222 al. [22] have shown that the molecule structure of hydrated leucite is similar to that of leucite

223 ($KAlSi_2O_6$). Leucite is part of the feldspathoid mineral group with a structure consisting of a

224 three-dimensional framework of $[SiO_4/AlO_4]^-$ tetrahedral. As such, the lattice structure of

225 leucite shown in Fig. 9 was adopted to calculate the band structure and density of states of the

226 KGP cementitious composite using DFT. The energy band gap and the density of states of the

227 structure are shown in Fig. 10. The band gap in Fig. 10a describes the energy required to move

228 electrons from the valence band into the conduction band to form current. The calculated gap

229 between the conduction band and the valence band is in the range of 3.3eV. This band gap

230 appears to be too large for current tunneling. Since the sample size is large and the current due

231 to such energy barrier is expected to be small, in the range of *pA*, the contribution from the

232 tunneling current to the total conductivity obtained in the experiment is low.

233 It is worth to note that, the Fermi energy is located about 0.1 eV above the valance band and 3

234 eV below the conduction band. This means that the KGP cementitious composite is similar to

235 p-type semiconductor solids where electron holes (i.e. K^+) are the majority carriers. As shown

9

236   in Fig. 10b, the density of states in the valance band is much higher than that in the conduction

237   band, thereby confirming that K^+ carriers dominate the conduction mechanism of the KGP

238   cementitious composite. We therefore conclude that the charge transport mechanism is an

239   ionic current flow due to the diffusion of K^+ in the KGP cementitious composite. In this case,

240   the K^+ atoms are the only type of mobile charge carriers in the KGP structure and their behavior

241   controls the overall ionic conductivity and dielectric properties of the KGP cementitious

242   composite. The K^+ atoms diffuse in the structure by hopping through vacancy sites to balance

243   the negative charge on the AlO_4^- tetrahedral.

244   The obtained low activation energy values support the above conclusion that the conduction

245   mechanism of the KGP cementitious composite is dominated by K^+ ions hopping through their

246   lattice structure. It is also interesting to note that the activation energies for the KGP

247   cementitious composites are in good agreement with those for the natural leucite mineral

248   ($KAlSi_2O_6$) [23]. Natural leucite crystal is a superionic conductor with an activation energy in

249   the range of 0.35 – 1 eV. This means that the KGP cementitious composite is an inherently

250   superionic material.

251   *3.4. Storage capability of KGP capacitors*

252   *3.4.1. Electrochemical behavior and electrical storage capability of KGP capacitors*

253   The cyclic voltammetry (CV) curves for the KGP capacitors 1 and 2 at different scan rates in

254   the potential window -0.5 - 0.5V are shown in Fig. 11. As displayed in this figure, for both

255   capacitors, all CV curves have somewhat symmetrical and slightly deformed rectangular

256   shapes, showing a good capacitive behavior for energy storage [24]. The rectangular shapes

257   also confirm the existence of an electrochemical double layer (EDL) mechanism in the KGP

258   capacitors. The energy storage mechanism in the KGP capacitors is due to the reversible

259   electrostatic accumulation of ions adsorbed onto the surface of the steel mesh electrodes.

260   Figure 12 shows the storage mechanism in the KGP capacitors. As depicted in Fig.12b, during

261   charging, the oppositely charged ions are separated where the positively charged K^+ ions are

262 adsorbed onto the negative electrode and the negatively charged $[SiO_4/AlO^4]^-$ ions (and

263 potentially OH^-) are adsorbed onto the negative electrode. This leads to the formation of two

264 layers of charges with opposite polarity separated by an effective distance d at the

265 electrode/KGP matrix interface (Fig. 12c). As a result, a capacitor for energy storage is formed

266 at the interface. The potential V_o at the electrode surface decreases when the effective distance

267 d increases. The K^+ and $[SiO_4/AlO^4/OH]^-$ ions separate from the electrode surface when the

268 electric charge of the electrode is discharged. As shown in Fig. 12c, the capacitance C_h of the

269 capacitor at the interface can be related to the Debye length λ_D, which defines the distance d

270 [25]. The capacitance C_h and the charge density σ of the capacitor at the interface are defined

271 by [25]:

272
$$C_h = \frac{1}{\lambda_D} \qquad (6)$$

273
$$\lambda_D = \sqrt{\frac{\varepsilon_0 \varepsilon' k_B T}{2 C_0 N_A e^2}} \qquad (7)$$

274
$$\sigma = C_h V_s \qquad (8)$$

275

276 where ε_0 and ε' are the the dielectric constant of the free space and KGP cementitious

277 composite, respectively, k_B is the Boltzmann constant, T is the temperature, C_0 is the ionic

278 strength of the KGP cementitious composite, N_A is the Avogadro constant, e is the elementary

279 charge, σ is the charge density and V_s is the voltage drop across the double layer. Equations

280 (6), (7) and (8) suggest that the overall performance of the KGP capacitors depends slowly on

281 the stability of their capacitance. The stability of the capacitance under temperature and

282 mechanical stress is discussed in *section 3.4.3*.

283 Figure 11 shows that the area of the enclosed CV curves for capacitor 2 is larger than that for

284 capacitor 1, indicating better electrochemical performance when the effective thickness

285 increases from 4 to 8 mm. This could be attributed to high concentration of K^+ ion charge

11

286   carriers in capacitor 2 which in return leads to higher capacitance as shown in Fig. 13. Figure

287   13 shows that for both KGP capacitors, the maximum capacitance during charging ($C = i/s$,

288   where i is the applied current and s is the scan rate) decreases as the scan rate increases. This

289   is because, at higher scan rates, the K^+ ions do not have sufficient time to diffuse inside the

290   KGP matrix, and adsorb and desorb on the surface of the steel mesh electrodes, thereby leading

291   to lower capacitance [26].

292   *3.4.2 Discharge behavior of KGP capacitors*

293   The discharge behavior of the KGP capacitors at different discharge currents is displayed in

294   Fig. 14. As can be seen, for both capacitors, the discharge life and the open-circuit voltage

295   decrease as the discharge current increases. The currents 200 and 400 µA appear to be too high

296   for discharging both KGP capacitors as can be witnessed by their short discharge-life and the

297   low open-circuit voltage. It is worth noting that the open-circuit voltage decay of the KGP

298   capacitors somewhat follows the exponential discharge behavior of capacitors and batteries

299   reported elsewhere [24]. Figures 15 and 16 compare the two KGP capacitors in terms of

300   discharge-life and storage capacity. These figures show that for both KGP capacitors, the

301   discharge-life and the capacity are strongly dependent on the discharge current. As shown in

302   Figs. 15 and 16, higher discharge current yields shorter discharge-life and lower capacity.

303   From Fig. 15, the longest discharge-life of the KGP capacitors is achieved at a current of 50

304   µA and estimated as 1.67 and 2.22 hours for capacitors 1 and 2, respectively. It can be observed

305   from Fig. 16 that capacitor 2 exhibits higher capacity than capacitor 1, reaching a maximum

306   value of 0.11mAh at 50 µA compared to 0.085mAh for capacitor 1 at the same current. Figure

307   17 shows the initial running voltage for the KGP capacitors discharged at different currents. It

308   can be seen that the initial voltage decreases with increasing the current. The highest initial

309   running voltage is achieved at current of 50 µA and estimated as 2.4 and 2.5 V for capacitors

310   1 and 2, respectively. The initial power density of the KGP capacitors (power output per unit

311   area) is depicted in Fig. 18. As shown, for both KGP capacitors, the initial power output

312   increases as the current density increases. Capacitor 2 slightly outperforms capacitor 1 with a

313   maximum power output of about 33mW/cm^2 at a current density of 16 µA/cm^2, compared to

314   27 mW/cm^2 for capacitor 1 at the same current density. Overall, the obtained data shows that

315   capacitor 2 works better than capacitor 1 in terms of discharge-life, open-circuit voltage, initial

316   running voltage, storage capacity and power output. This is because the effective thickness of

317   capacitor 2 is larger than that of capacitor 1, thus more K$^+$ ion charge carriers in KGP matrix

318   to store electrical energy.

319   *3.4.3. Stability of KGP capacitors*

320   For applications in civil engineering structures, the energy storage efficiency of the KGP

321   capacitors depends on the stability of their capacitance under temperature and stress. Figures

322   19 and 20 show the effect of temperature and stress on the capacitance of the KGP capacitors.

323   The capacitance was calculated from the EIS spectra using the following equation:

324
$$C = \frac{1}{2\pi f Z''} \qquad\qquad (9)$$

325   where f is the frequency of the electric field and Z'' is the imaginary part of the impedance. As

326   it can be seen from Fig. 19a, the capacitance of the capacitor 1 slightly decreases when the

327   temperature decreases from 30°C to 20°C then remains constant over the temperature range of

328   -5°C – 20°C. On the other hand, negligible change in the capacitance of the capacitor 2 is

329   observed over the full temperature range (Fig. 19b). Figure 20 shows that for both capacitors,

330   the applied load has no effect on their capacitance. This implies that the KGP capacitors exhibit

331   a good stability under the temperature and load ranges used in this study.

332   *3.5. Response of KGP sensors to compressive load*

333   Figure 21 shows the impedance of the KGP sensors at different loads in the frequency range

334   of 100 Hz – 10 kHz. Based on the measured real and imaginary impedances, the KGP sensors

335   exhibit a resistive-like behavior in this frequency range, because their impedance response is

336   largely dominated by the real impedance. It can also be seen from Fig. 21 that the impedance

337   of the KGP sensors decreases with increasing load. This could be attributed to the effect of the

338   applied load on the hopping mechanism of the K^+ ions through the KGP lattice structure.

339   Studies on the effect of stress on the ionic transport in solids are scarce. Equation (5), shows

340   that the hopping conductivity σ_{ac} of the KGP sensors is proportional to the activation energy

341   E_a at a temperature T. Equation (5) also shows that at a constant temperature T, the hopping

342   conductivity σ_{ac} of the KGP sensors increases as the activation energy E_a decreases. On the

343   basis of this, we hypothesize that the applied compressive load lowers the energy barrier in the

344   KGP matrix which, results in an increase in the hopping conductivity. This is reflected in the

345   decrease of the impedance of the KGP sensors as the applied compressive load increases

346   (Fig.21). One possible reason for the decrease of the activation energy barrier under

347   compressive load is the change in the hopping distances d along the diffusion path for the K+

348   ions (Fig. 22b). We hypothesize that the applied compressive load changes the lattice structure

349   of the KGP matrix, allowing the individual K^+ ions to jump shorter distances from one lattice

350   site to another through the inter-connected diffusion channels in the KGP crystal structural

351   framework. The activation energy for the hopping conductivity decreases as the applied

352   compressive load increases because the hopping distance between lattice sites decreases under

353   compressive stress (Fig. 22c) [27]. When the hopping distances are reduced, the need for

354   vacancies is eliminated and the hopping conductivity of the KGP sensors is increased as a result

355   [27].

356   Figure 23 plots the variation of the total impedance of the KGP sensors as a function of the

357   applied load at three representative frequencies of 0.1, 0.5 and 2 kHz. For both KGP sensors,

358   Fig. 23 shows that there is a strong linear relationship between the real impedance and the

359   compressive load. The impedance sensitivity values obtained from the linear fits are displayed

360   in Fig. 23. As shown, KGP sensor 2 exhibits higher sensitivities than KGP sensor 1 due to

361   higher conductivity and lower activation energy. KGP sensor 1 exhibits an impedance

362   sensitivity between 2.86 and 3.44 Ω/kN whereas KGP sensor 2 exhibits an impedance

363   sensitivity between 4.15 and 4.44 Ω/kN.

14

364 Figure 24 shows the phase of the KGP sensors at different loads in the frequency range of 100

365 Hz – 10 kHz. As shown, for both KGP sensors, the phase increases as the load increases due

366 to the decrease in the impedance. Figure 25 plots the variation of the phase as a function of the

367 applied load at three representative frequencies of 0.1, 0.5 and 2 kHz. For both KGP sensors,

368 Fig. 25 shows that there is a strong linear relationship between the phase and the compressive

369 load. The phase sensitivity values obtained from the linear fits are displayed in Fig. 25. As

370 can be seen, KGP sensor 2 exhibits higher phase sensitivities than KGP sensor 1. The phase

371 sensitivity of the KGP sensor 1 is between 0.089 and 0.115 deg/kN and the phase sensitivity

372 of the KGP sensor 2 is between 0.21 and 0.22 deg/kN. The KGP sensor 2 shows better

373 sensitivity to load than the KGP sensor 1 as a result of higher conductivity.

374 **Discussion**

375 In this paper, we show for the first time that plain KGP cementitious composites can be used

376 as multifunctional structural materials for electrical energy storage and structural health

377 monitoring without adding any functional additives. The KGP cementitious composite was

378 synthesized by simply activating fly ash with potassium silicate. The conduction mechanism

379 of the KGP cementitious composite is based on the hopping of the K^+ ions from one lattice

380 structure to another through diffusion channels in the KGP crystal structure framework. The

381 KGP cementitious composite exhibits two types of behavior: capacitive behavior at low

382 frequencies and piezoresistive behavior at high frequencies. This indicates that the proposed

383 KGP cementitious composite can be used as both a capacitor for electrical energy storage and

384 a sensor for stress and crack sensing, thereby inducing new functionalities in concrete

385 structures for improved efficiency and sustainability. The EIS results have shown that the KGP

386 cementitious composite is a superionic type material with a maximum room temperature

387 conductivity of about 11 (10^{-2} S/m). The conductivity values obtained in this investigation are

388 in the range of recently reported solid state ionic conductors used in energy storage systems

389 [28]. The KGP capacitors/sensors also exhibit low activation energy barriers ranging from

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390   0.40 to 0.97 eV. This means that the conduction mechanism of the KGP cementitious

391   composite is predominantly ion hopping instead of tunneling as confirmed by the DFT

392   simulations. This is significant because it eliminates the need for conductive additives in

393   geopolymeric materials.

394   The KGP capacitors behaves like double-layer energy storage capacitors with almost

395   rectangular CV curves. The KGP capacitors show great stability under stress and normal civil

396   infrastructure operating temperatures. The KGP capacitors could be manufactured in the form

397   of panels and can be an integral part of structures such as buildings and bridges. When

398   interfaced with solar panels, the proposed structural KGP capacitors could store up to

399   0.33kW/m^2, enough to power systems such as structural health monitoring sensors, internet of

400   things devices, LED street lights, household appliances, and healthcare tools during power

401   outages. The power density and the discharge life of the KGP capacitors can be increased by

402   using electrodes with high ion adsorption capacity. Furthermore, the performance of the KGP

403   capacitors can be enhanced by hermitically insulting them from the surrounding environment

404   to minimize the effect of moisture and chemical contamination.

405   The KGP sensors exhibit measureable changes in impedance and phase under stress. The

406   highest measured compressive stress sensitivities are 11 Ω/MPa and 0.55 deg/MPa. This means

407   that even small changes in stress cause a measurable change in the impedance and phase of the

408   KGP sensors. This is particularly appealing as sensitivity to small stresses enables the KGP

409   sensors to detect micro cracks in structures which typically appear in brittle materials at low

410   load levels.

411   The effect of thermomechanical coupling on the response of the KGP sensors was not

412   investigated in this paper. However, we recognize that temperature and the surrounding

413   environment will likely affect the response of the KGP stress sensors. To reduce the effect of

414   temperature, a separate temperature from mechanical load can be utilized as a reference sensor

415   to compensate for the temperature effect. To minimize the effect of the surrounding

environment such as moisture and chemicals, the KGP sensors can be insulated using a hermetic package. Owing to their low-cost and easy manufacturing, the KGP sensors can be deployed in a large number in areas where high stresses are known to occur. The KGP sensors draw very low power in the μW-mW range. As such, the proposed KGP capacitors can be integrated into the structure to store electrical power for the KGP sensors.

The KGP sensors were studied under compression, further work is needed to study their response under tensile loading. The repeatability, stability, accuracy and the hysteresis behavior of the KGP sensors under cyclic loading require further investigations.

Conclusions

In this paper, a novel geopolymeric cementitious composite has been designed and investigated for electrical energy storage and stress sensing. The density function theory (DFT)-based simulations revealed that the KGP cementitious composite relies on the diffusion of potassium (K^+) ions to store electrical energy and sense mechanical stresses The electromechanical characterization indicated that the KGP capacitors are electrochemical double layer (EDL)-type capacitors with rectangular CV shapes. It is also revealed that temperature and load had little effect on the capacitance of the KGP capacitors, suggesting good stability under thermal and mechanical load conditions. The KGP capacitors can store power up to 0.33 kW/m^2, enough to power systems such as health monitoring sensors, LED light poles and internet of things devices.

The EIS characterization revealed that the KGP sensors were able to measure compressive stress with high phase and impedance sensitivities, in the order of 11 Ω/MPa and 0.55 deg/MPa, respectively. Once fully designed and characterized under compressive and tensile stress, the KGP sensors can easily be manufactured with different lengths to measure bulk stresses in large civil engineering structures.

Owing to their low-cost and easy manufacturing and scale-up process, the developed KGP capacitors/sensors can be embedded or retrofitted onto existing large structures to

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simultaneously store electrical energy and monitor their structural integrity for improved

performance and resilience.

Acknowledgments

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