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SYNTHESIS, CHARACTERIZATION AND SENSING APPLICATION OF A SOLID ALUM/FLY ASH COMPOSITE ELECTROLYTE

SINTEZA, KARAKTERIZACIJA IN MOŽNOST UPORABE TRDNEGA KOMPOZITNEGA ELEKTROLITA GALUN-LETEČI PEPEL

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A new composite system using low-cost materials, potash alum and fly ash, was prepared and characterized using various techniques. Complex impedance spectroscopy was used for the conductivity measurement. A conductivity enhancement due to an addition of fly ash was observed and the maximum value was obtained with the 65 : 35 compositions. The maxima in conductivity can be explained with the percolation theory. Infrared spectroscopy (IR) as well as X-ray diffraction (XRD) confirmed the composite nature of the samples. Scanning electron microscopy (SEM) shows a good homogeneous mixture of the composite material which is essential for the conductivity enhancement. Based on the maximum-conductivity composition, a humidity sensor was fabricated which showed a good sensing behavior.

Keywords: composite, conductivity, IR, XRD, humidity sensor

Pripravljen in karakteriziran z različnimi tehnikami je bil nov kompozitni sistem iz poceni kalijevega galuna in letečega pepela. Za meritve prevodnosti je bila uporabljena kompleksna impedančna spektroskopija. Opaženo je bilo maksimalno povečanje prevodnosti zaradi dodatka letečega pepela pri razmerju sestave 65 : 35. Maksimum prevodnosti lahko razložimo s teorijo pronicanja. Infrardeča spektroskopija (IR) in rentgenska difrakcija (XRD) sta potrdili kompozitno osnovo vzorcev. Vrstična elektronska mikroskopija (SEM) je pokazala homogeno mešanico kompozitnih materialov, ki je ključna za povečanje prevodnosti. Na osnovi sestave z največjo prevodnostjo je bil izdelan senzor vlage, ki je pokazal dobro občutljivost.

Ključne besede: kompozit, prevodnost, IR, XRD, senzor vlage

1 INTRODUCTION

Composite materials are well known materials playing a dominant role in the industrial areas such as sport, aerospace, automotive industry and transportation. Due to the pioneering work of Liang and the subsequent efforts of many researchers, solid-composite electrolytes have been widely studied for their attractive behavior.[1] A significant enhancement in the conductivity has been observed in the multiphase materials with very small amounts of dispersoids. Fly ash, one of the dispersoids, has led to a multifold increase in the ionic conductivity when together with alumina. Several theoretical approaches have also been made to explain such a behavior. A comparison of a pure system and a two-phase mixture reveals that the two-phase mixtures in general exhibit a higher conductivity than those of the starting materials.[2–5] In this paper we report on an increase in the conductivity for a new composite using two low-cost materials, i.e., potash alum and fly ash.

Fly ash is a waste product produced from coal-fired thermal-power stations during the combustion of coal. It is an alkaline grey powder which causes serious environmental problems. Due to the environmental regulations, new ways of utilizing fly ash have to be explored in order to safeguard the environment and provide useful ways for its disposal. Hence, there is a considerable interest in utilizing fly ash as a raw material. More recently, materials scientists and engineers have suggested and devised various methods of using this waste product for the synthesis of some useful composites.[6–8] Raw fly ash consists of quartz and mullite as the crystalline phases and an amount of a glassy phase.[9] Efforts have been made to understand the electrical conductivity and dielectric behavior of fly ash and it was observed that this material possesses a very high relative dielectric constant of the order of 10^4. Such a high dielectric constant is one of the important parameters in a capacitor fabrication and microwave absorption applications.[8–14] The common alum is a double sulphate of potassium and aluminum, $K_2Al_2(SO_4)_4 \cdot 24H_2O$, which is a white crystalline powder readily soluble in water.

Through this work we have made a successful effort in preparing potash alum/fly ash composites and develop a humidity sensor which gives newer ways of a better utility of fly ash.

2 EXPERIMENTS

2.1 Preparation of the sample

Potash alum was purchased and used without any further purification while fly ash of an unknown purity and composition was collected from a local supplier. Appropriate amounts of potash alum and fly ash were weighed and thoroughly mixed in an agate mortar and pestle (≈2 h) and this was followed by a pulverization and pelletization in a nickel-plated steel die at the pressure of 2.5 t using a hydraulic pelletizer machine. The circular-shaped pellets thus obtained were 0.15 cm^2 in area and 4–6 mm in thickness. Infrared spectroscopy (Perkin Elmer 883) was carried out to study the composite nature and the functional groups present in the composite electrolyte. For further confirmation, X-ray diffraction was obtained using a Rigaku D/max-2500 in the range of 2θ = 20–55° with a scan rate of 1° min^{-1}. Scanning electron microscopy (SEM) was used to check the surface morphology. SEM micrographs were recorded using SEM (Hitachi S-570). For all the electrical measurements, a conductive silver paste was coated onto both surfaces of the pellets and dried under room environment. The complex impedance spectroscopy was used to calculate the bulk electrical conductivity of the polymer electrolyte films. In our laboratory we used pressure-contacted stainless-steel electrodes and connected them with a CH instruments electrochemical workstation (Model CHI604D) with a frequency range of 0.00001 Hz to 100 kHz. The electrical conductivity (σ) was evaluated using the following formula:

$$\sigma = R_b\ (l/A)$$

where σ is the ionic conductivity, R_b is the bulk resistance, l is the thickness of the pellet and A is the area of a given sample.

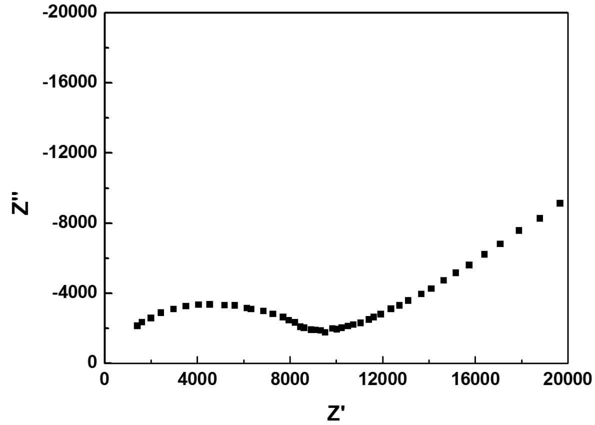

Figure 1: Complex impedance plot of a typical potash alum/fly ash solid electrolyte system
Slika 1: Kompleksno impedančno področje značilnega trdnega elektrolita kalijev galun-leteči pepel

Table 1: Room-temperature electrical conductivity of a potash alum/fly ash composite system
Tabela 1: Električna prevodnost kompozitnega sistema kalijev galun-leteči pepel pri sobni temperaturi

Composition, mass fraction, w/% Potash alum/fly ash	Electrical conductivity σ/(S/cm)
95 : 5	3.2×10^{-6}
85 : 15	5.3×10^{-6}
75 : 25	9.2×10^{-6}
65 : 35	1.5×10^{-5}
60 : 40	1.2×10^{-5}
40 : 60	5.4×10^{-6}
10 : 90	4.6×10^{-6}

3 RESULTS AND DISCUSSION

3.1 Complex impedance spectroscopy

The ionic conductivity of pure potash alum and the alum doped with fly ash pellets were measured using the complex impedance spectroscopy. The bulk resistance (R_b) was determined from an intersection at a high frequency with the real axis in the impedance plots. The complex impedance plot of a typical potash alum/fly ash composition is shown in **Figure 1**. The ionic conductivity values were calculated from the impedance spectroscopic data and are listed in **Table 1** and plotted in **Figure 2**.

It is observed that initially the electrical conductivity of the composite increases with the increasing content of fly ash. It attains its maximum at 65 % fly ash and then decreases gradually. To interpret such variations in conductivity, several theoretical models have been proposed in the literature. The percolation model considers the highly conducting paths that were created along the interface between the host electrolyte and the dispersoid. In the present system the conductivity maxima could be explained with the percolation model.[9] The maximum is obtained for the composition, with which the percolation threshold is achieved. The water of crystallization

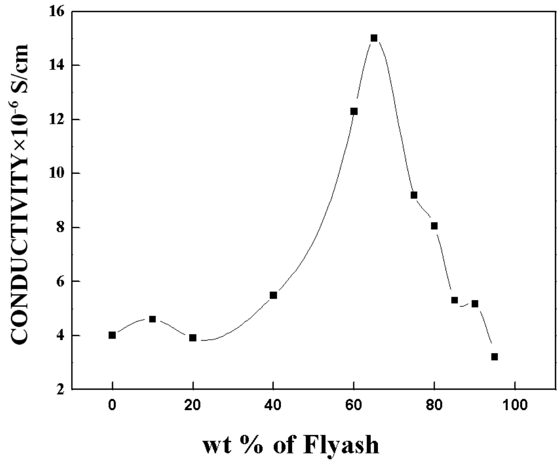

Figure 2: Variation in conductivity with the concentration of fly ash in a potash alum/fly ash composite system
Slika 2: Spreminjanje prevodnosti s koncentracijo letečega pepela in kalijevega galuna v kompozitnem sistemu

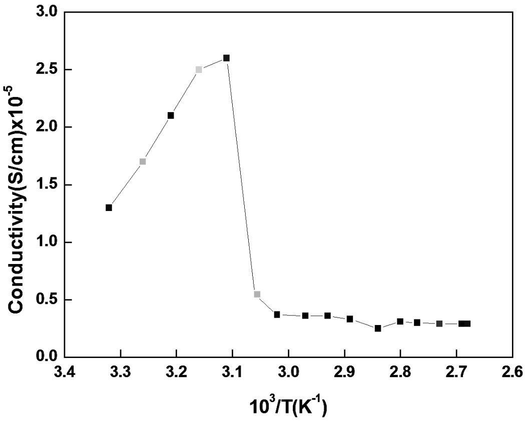

Figure 3: Variation in conductivity with temperature (maximum conductivity)

Slika 3: Spreminjanje prevodnosti s temperaturo (maksimalna prevodnost)

present in the alum gets adsorbed on the surface of the composite, in which the movement of H^+ and $OH^–$ ions is responsible for an increase in the conductivity. The decrease in the conductivity after the maximum is similar to those obtained in similar composite systems.[15–17]

3.2 Temperature dependence of conductivity

Figure 3 shows the variation in conductivity with the temperature of the maximum conductivity composition of the composite. The variation in conductivity indicates that the physisorbed water present in potash alum plays an important role in the conductivity enhancement. The conductivity rises with an increase in the temperature up to ≈50 °C and then begins to fall; after this a constant value is attained. This is because the physisorbed water present in potash alum is lost between 45 °C to 50 °C leading to a loss of the H^+ and OH^- ions that were responsible for the conductivity of the composite sample.

3.3 Scanning electron microscopy

Scanning electron microscopy (SEM) was used to check the surface morphology of composite electrolytes. We have recorded the SEM micrographs using a SEM instrument (SEM, Hitachi S-570) and the micrographs are shown in **Figure 4**.

It is clear from this figure that potash alum shows a needle-like morphology (**Figure 4a**) while fly ash (of an unknown purity) shows a more or less irregular structure when seen under SEM (**Figure 4c**). From the potash alum/fly ash composite SEM micrograph it is clear that the composite system shows a mixed morphology where the white-colored fly ash is uniformly mixed with the light-blackish potash-alum grains (**Figure 4b**).

3.4 Infrared spectroscopy

Infrared spectroscopy (Perkin Elmer 883) was carried out to study the composite nature and the functional groups present in the composite electrolyte. **Figure 5** shows the recorded IR spectra of pure potash alum, pure fly ash and the potash alum doped with fly ash (the maximum σ composition).

It is obvious that the IR spectrum of the composite material (**Figure 5c**) contains the peaks related to either pure potash alum (**Figure 5a**) or to alum (**Figure 5b**). An absence of any new peaks in the composite electrolyte other than those of the host materials clearly confirms the composite nature. The IR spectrum of potash alum (**Figure 4a**) based on one monovalent and one trivalent cation has been published.[18] Ross gave an interpretation of the infrared spectrum of potassium alum as (981, 1200, 1105, 618 and 600) $cm^{–1}$ for $(SO_4)^{2–}$. The water stretching modes were reported at 3400 $cm^{–1}$ and 3000 $cm^{–1}$, the bending modes at 1645 $cm^{–1}$ and the vibrational modes at 930 $cm^{–1}$ and 700 $cm^{–1}$.[19]

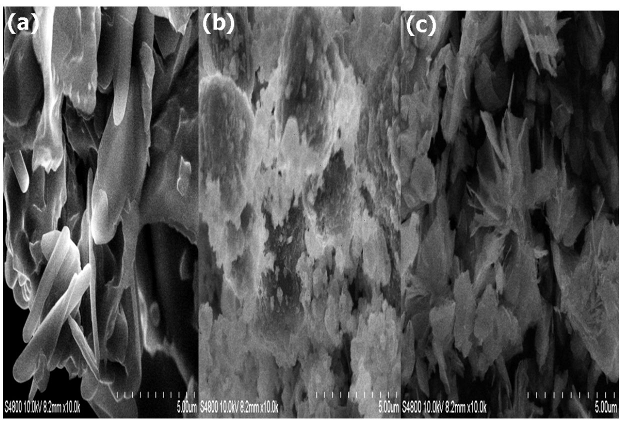

Figure 4: SEM micrographs of: a) pure potash alum, b) potash alum/fly ash composite and c) pure fly ash

Slika 4: SEM-posnetki: a) čisti kalijev galun, b) kompozit kalijev galun-leteči pepel in c) čisti leteči pepel

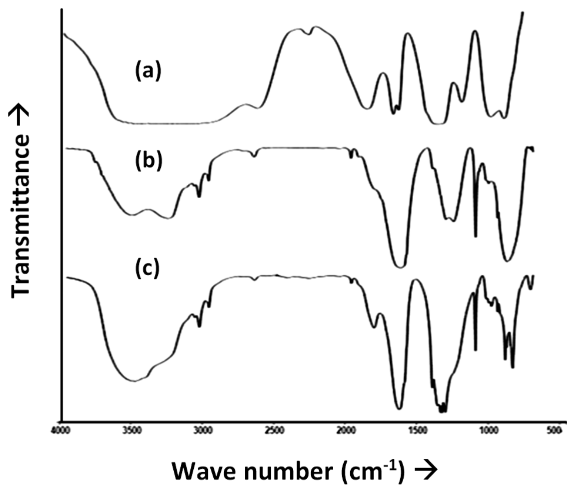

Figure 5: IR spectra of: a) pure potash alum, b) pure fly ash, c) potash alum/fly ash composite

Slika 5: IR-spektri: a) čisti kalijev galun, b) čisti leteči pepel, c) kompozit kalijev galun-leteči pepel

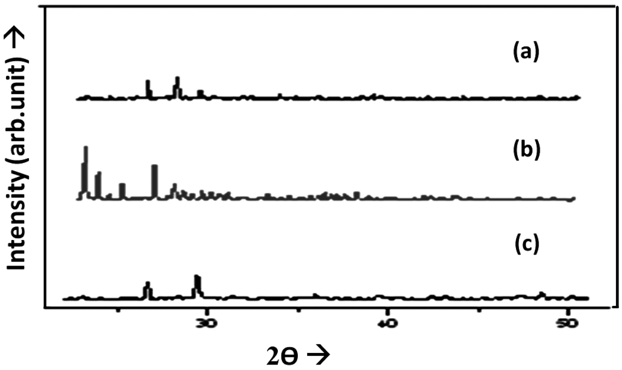

Figure 6: XRD patterns of: a) pure fly ash, b) potash alum and c) potash alum/fly ash composite
Slika 6: XRD-posnetki: a) čisti leteči pepel, b) kalijev galun in c) kompozit kalijev galun-leteči pepel

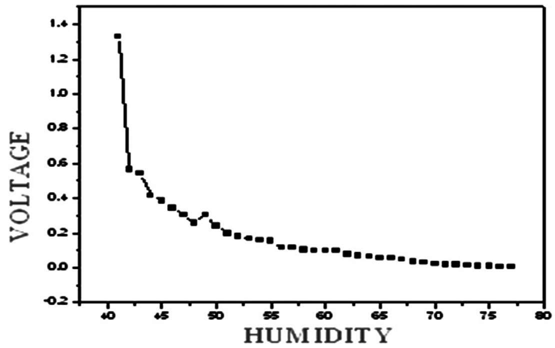

Figure 8: Response of the humidity sensor based on the potash alum/fly ash composite (the maximum conductivity sample)
Slika 8: Odziv na vlago senzorja na osnovi kompozita kalijev galun-leteči pepel

Figure 5b shows the IR spectrum of fly ash, in which the characteristic IR peak observed at 1094 cm^{-1} may be attributed to the presence of silica.[17] This peak confirms the highest % of silica in fly ash, which is confirmed by a chemical analysis.[8] Several absorption peaks are observed in the range from 1400 cm^{-1} to 1300 cm^{-1}, which correspond to the various metal oxides present in fly ash. A characteristic broad band at 3422 cm^{-1} in the spectrum of the composite is due to the N-H stretching of aniline (**Figure 4b**). The absorptions at (1297.49 ± 10, 1139.71 ± 10, 1089.48 ± 10 and 794.81 ± 20) cm^{-1} correspond to the fly-ash constituents in the potash alum/fly ash composite (**Figure 5c**).

3.5 X-ray diffraction

To further investigate the composite nature, we recorded the XRD patterns of the composite electrolytes along with the host materials and the recorded patterns are shown in **Figure 6**. It was noted that the peaks that appear in the XRD pattern of the composite material (**Figure 6c**) also appear in the XRD patterns of fly ash (**Figure 6a**) or potash alum (**Figure 6b**) affirming the composite nature that we have already found with the IR data.

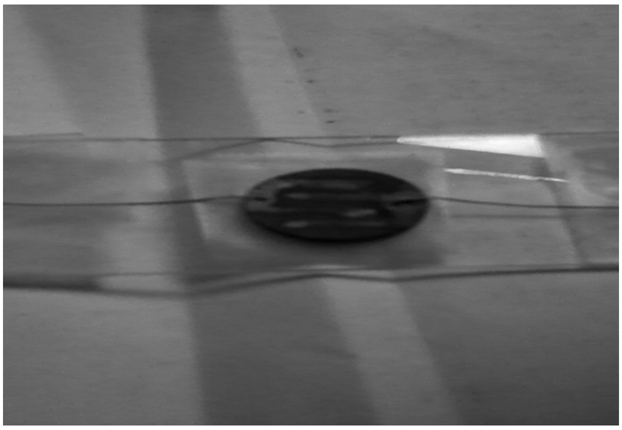

Figure 7: Photograph of developed humidity sensor based on the potash alum/fly ash composite
Slika 7: Posnetek razvitega senzorja vlage, ki temelji na kompozitu kalijev galun-leteči pepel

4 APPLICATIONS

4.1 Humidity sensor

On the basis of the maximum electrical conductivity sample we tried to fabricate a humidity sensor in our laboratory. The optical photograph of the sensor is shown in **Figure 7**. To develop it we made a finger-type electrode on the surface of the composite pellet using vacuum-coated silver paint as the electrode material and deposited the pattern using the vacuum coating unit (Hind High Vacuum, India) at a pressure of 1.33×10^{-3} mbar. A conducting copper wire was used for the contact and sensing behavior. To measure the response of the humidity sensor we also developed a constant-humidity chamber in our laboratory as designed by Chandra et al[20]. A very simple approach was adopted for creating different constant humidities for an in-situ measurement inside the chamber. It is known that the water-vapor pressure in over-saturated solutions of 'different salts' give different relative humidities. We applied different humidities inside the close chamber developed by us and measured the sensor response. The response of the sensor (voltage vs. humidities) is shown in **Figure 8**. It is clear from this figure that the developed sensor shows a good sensing behavior with a quick response. Within a short period the developed sensor shows an exponential decrease in the voltage with an increase in the humidity level.

5 CONCLUSION

A solid-state composite based on potash alum/fly ash has been developed and well characterized using various techniques. The electrical-conductivity measurement shows that by adding fly ash the electrical conductivity enhances the attained maxima at 65 % of fly ash in the composition to the conductivity value of 1.5×10^{-5} S/cm and this is followed by a decrease. IR as well as XRD confirmed the composite nature, while SEM affirmed the homogeneous mixing of potash alum/fly ash. A humidity sensor has been fabricated (with the maximum conductivity sample) and it shows a stable and good performance.

Acknowledgments

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