Preparation of polymer electrolyte hydrogels using poly(vinyl alcohol) and tetraethylorthosilicate for battery applications

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Abstract. Hybrid polymer electrolyte hydrogels were developed from poly(vinyl alcohol) (PVA) and tetraethyleorthosilicate (TEOS) through hydrolysis and condensation reaction. The ratio of TEOS to PVA was varied at 10, 20, 30, and 40 mass% and the resulting hydrogels were designated as S-1, S-2, S-3 and S-4 respectively. The chemical reaction between PVA and TEOS was confirmed using FTIR. After studying the specific gravity of polymer electrolyte hydrogels, efficiency of battery containing polymer electrolyte hydrogels was studied using custom made battery testing unit. The experimental values demonstrated that polymer electrolyte containing 40% tetraethyleorthosilicate showed better charge holding and retention capacity.

1. Introduction

The acute need for renewable, eco-friendly, alternative energy sources is because of the growing demands for energy, swift depletion of fossil fuels and the negative effects by the use of fossil fuel on the environment [1]. Therefore, the energy produced from wind and solar power which are renewable sources are seen to be increasing in demand [2], because of this renewable energy production generating capacity is greatly increased in past few years. However, renewable energy sources are intermittent in nature [3,4], due to this, need for energy storage systems to store the energy generated by this renewable source arises. In order to take full advantage of renewable energy sources, energy storage technologies are required and hence electrochemical cells offer best liberty in the design of energy systems [5].

Electrochemical energy storage in batteries is attractive because it is compact, easy to deploy, economical and provides virtually instant response both to input from the battery and output from the network to the battery. There are a range of battery chemistries that can be used but lead batteries offer a reliable, cost-effective solution which can be adapted for different types of energy storage applications [6,7].
Flooded lead-acid battery means electrodes are freely suspended in the battery case and mobile electrolyte. Due to their loosely design, the oxygen and hydrogen gases formed while charging are lost to the atmosphere through a vent, so it is essential to maintain electrolyte level and sulphuric acid concentration by refilling it by distilled water. Consequently, they require maintenance. To overcome this drawback, “Valve-regulated lead-acid (VRLA) batteries” were developed [8]. These batteries are sealed, which allows gases generated to escape to the atmosphere when the internal pressure reaches set limit through pressure-release valves. These batteries are developed in which electrolyte is immobilized so that the oxygen generated in charge cycle is trapped and recombined in the battery, viz “Oxygen recombination cycle”, resulting in lower or no water loss [9]. Usually, two different immobile electrolyte batteries have been used. One is the valve regulated lead-acid battery with an absorbptive glass mat(AGM)separator and starved electrolyte [10]. The other one is VRLA battery with gelled electrolyte [11, 12].

The gel VRLA batteries have edge over AGM batteries because their service life is long and deep discharge cycles provide high reliability, acid stratification does not take place and installation can be done in any orientation. Besides they exhibit long service life under deep discharge cycles, there is no leakage of acid mist, charge stability is good, and operation is maintenance free, long service life, small self-discharge, deep-cycle performance and so on [13,14]. The gelled electrolyte has lower corrosion rate of positive grid compared to AGM battery technology and higher over-potential of the evolution of hydrogen on negative plate, because of this VRLA batteries are having better performance. [12]

Properties of polymer gelled electrolyte have great influence on working of Gel-VRLA batteries [15]. Different gelling agents are used in Gel-VRLA batteries [16,17], fumed silica is usually used as gelling agents. In this research work, an attempt is made to enhance performance of lead acid battery by customizing the gel electrolyte with different PVA and TEOS ingredients rather than using conventional sulfuric acid and distilled water combination. Polymer electrolyte hydrogels developed were characterized using FTIR and hydrometer. Battery is tested using custom made battery testing unit.

2. Experimental section

2.1. Materials

Poly (vinyl alcohol) ($M_w \sim 124,000$, degree of hydrolysis 86-89 %) was purchased from s.d. fine Chemicals Ltd., Mumbai, India. Tetraethyorthosilicate ($M_w \sim 208.33$, 99% purity) was procured from Sigma-Aldrich Chemicals, USA. Sulphuric acid was supplied from Spectrum reagent and chemicals Pvt. Ltd., Cochin, India. Chemicals used were of reagent grade. Distilled water was used throughout research work.

2.2. Preparation of polymer electrolytehydrogels

The PVA solution (4 mass%) was prepared by dissolving in the distilled water with constant stirring for 12 hours. Solution was filtered and the filtrate is designated as S, a required amount of TEOS and 1 ml of concentrated H$_2$SO$_4$ as a catalyst were added to prepared PVA solution for the sol-gel reaction and resulting reaction solution was agitated overnight at 60°C. Quantity of TEOS with respect to PVA was varied as 10, 20, 30, 40 mass% and resulting hydrogels were designated as S-1, S-2, S-3 and S-4 respectively. The reaction route and chemical structure of the PVA-TEOS polymer hydro gels are illustrated in Figures 1 and 2.
2.3 FTIR studies

Fourier transform infrared spectrometer (Nicolet, Impact-410, USA) is used to confirm the reactions of PVA and TEOS. Samples were mixed with KBr pellets and grounded at 400 kg/cm² using hydraulic pressure and the range of spectra recorded was from 500–4000 cm⁻¹.

2.4 Battery testing studies

Custom made block diagram of battery testing unit is shown in Fig. 3, once the battery is assembled, voltage is continuously sampled at an interval of every half second with the help of voltage sensor based on voltage divider principle which reduce the high voltage DC to a lower range which can be fed to 8-Bit analog to digital converter, further the digitally converted signal from A to D converter is processed by the microcontroller (ATMEGA 328) to calculate the actual voltage across the battery terminals. These calculated values are picked up from serial USB port of the computer for graphical representation of the voltage values. The values obtained at the serial port of the computer are used to study the battery charging and discharging characteristics.
3 Results and discussion

3.1 FTIR studies

Figure 4 illustrates the FTIR spectra of TEOS cross-linked PVA hydrogels. A characteristic strong and broad band was present at around 3400 cm⁻¹ and multiple peaks appeared between 1000 and 1100 cm⁻¹ are respectively assigned to O-H stretching of hydroxyl groups and C-O stretching which proves the presence of PVA.
The band for Si-O stretching also appears around 1100 cm\(^{-1}\) which is overlapping with the band for C-O. Further the increase in the intensity of the bands around 1000 and 1100 cm\(^{-1}\) suggest the formation of Si-O-C bond which is the evidence for cross linking between PVA and TEOS [18]. Intensity of O-H band decreased marginally from plain PVA to PVA-40% TEOS hydrogel which is due to crosslinking between O-H group of PVA and TEOS and also due to free O-H groups of PVA involving intermolecular hydrogen bonding [19]. Small peaks near 1430 cm\(^{-1}\) is due to S=O stretching. The peak area increased around 1130 cm\(^{-1}\) which is due to presence of S-OH groups of H\(_2\)SO\(_4\) in hydrogels.

### 3.2 Specific gravity studies

Hydrometer was used to test specific gravity of prepared polymer electrolyte hydrogels. The results are given in the table 1.

| S. No | Electrolyte     | Specific gravity |
|-------|-----------------|------------------|
| 1     | PVA             | 1.05             |
| 2     | PVA-10% TEOS    | 1.08             |
| 3     | PVA-20% TEOS    | 1.12             |
| 4     | PVA-30% TEOS    | 1.18             |
| 5     | PVA-40% TEOS    | 1.23             |

From the table 1, we can observe that the value of specific gravity goes on increasing as we increase TEOS content in PVA solution. Among all the above polymer electrolytes, we can see that electrolyte S-4 (PVA-40% TEOS) has highest specific gravity value, therefore we can say that S-4 is best suited as polymer electrolyte hydrogel, hence battery testing was carried out using PVA-40% TEOS polymer electrolyte hydrogels.

### 3.3 Battery testing studies

For battery characteristic study, by using custom made battery testing unit in which test was carried out for battery with customized PVA-40% TEOS polymer electrolyte hydrogels. The specific gravity of testing electrolyte was made 1.27 by adding additional concentrated H\(_2\)SO\(_4\). The electrodes used were of standard lead acid battery electrodes, in which prepared electrolyte was added till it has covered its 1/4\(^{th}\) portion of electrodes.
Battery charging: the chemical energy of the battery can be restored by utilizing the electrical energy from the external source. In this work, 2.5 V was applied to the battery for charging at 70 minutes. Figure 5 demonstrates the variation of voltage with time in minutes. The voltage of the battery increases and reaches to 2.25 V at minimum period (70 minutes), which indicates that battery has undergone charging at minimum time.

Battery discharging: during the discharge process of a battery, the free energy change of the redox reaction is converted into electrical work. To study the discharge characteristics, 100 Ω load was applied to the battery with time. Figure 6 and 7 shows the variation of voltage and current with time in minutes. The voltage and current of the battery decreases very slowly with time. From this, it is clear that, battery requires less time for charging and more time for discharging, this is due to high ionic conductivity of the polymer electrolyte and also presence of silicon content in the polymer electrolyte hydrogels.
In polymer electrolyte hydrogel lead acid battery, the sulfuric acid was captured in the cross-linked polymer network structure. At the end of charging process oxygen was evolved at the positive plate and hydrogen liberation at the negative plate is slower because of presence of hydroxyl groups. Recombination reaction of oxygen occurs by rapid diffusion of oxygen from the positive to the negative plate through polymer network to retain water in the cell. Therefore, this battery can operate in a sealed manner.

4. Conclusion

TEOS cross-linked poly (vinyl alcohol) hydrogels were prepared by so-gel technique and reaction was confirmed using FTIR. These hydrogels were used as electrolyte for the lead acid battery. The voltage of the charged battery is 2.25 V. Battery voltage during discharging varies from 2.25 V to 1.86 V in 165 min. The average discharge rate was 0.0023 V/min. It can be concluded that the charge holding and retention capacity of the battery is better, and discharge rate is slow and hence battery can operate in a sealed manner.

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References

[1] Anish R K, Sourav B, Amian R, Urbi P, Sagar M, 2012, Battery technology for energy storage, Encyclopaedia of sustainable technologies, 469-486.

[2] Hedegaard K, Meibom P, 2012, Wind power impacts and electricity storage – a time scale perspective, Renew Energy, 37, 318–324.

[3] González I, Ramiro A, Calderón M, Calderón A J, González J F, 2012, Estimation of the state-of-charge of gel lead-acid batteries and application to the control of a stand-alone wind-solar test-bed with hydrogen support, J. Hydrogen energy, 37, 11090-11103.
[4] Zhou W, Lou C, Li Z, Lu L, Yang H, 2010, Current status of research on optimum sizing of stand-alone hybrid solar-wind power generation systems, Appl Energy, 87, 380-389.

[5] Posada J O Get.al, 2017, Aqueousbatteriesasgridscaleenergystoragesolutions, Renewable and Sustainable Energy Reviews, 68, 1174-1182

[6] May G J, Davidson A, Monahov B, 2018, Lead batteries for utility energy storage: A review, J. Energy Storage, 15, 145-157.

[7] Tan X, Li Q, Wang H, 2013, Advances and trends of energy storage technology in Microgrid, Journal of Electrical Power & Energy Systems, 44, 179–191.

[8] Moseley P T, Rand D A J, The valve-regulated battery – a paradigm shift in lead acid technology, in: Moseley P T, Rand D A J, Garche, Parker C D (Eds.), Valve- Regulated Lead-Acid Batteries, (Amsterdam: Elsevier BV), 2004, p. 1.

[9] Tantichanakul T, Chailapakul O, Tantavichet N, 2013, Influence of fumed silica and additives on the gel formation and performance of gel valve-regulated lead-acid batteries, J. Industrial and Engineering Chemistry, 19, 2085-2091.

[10] Papazov G, Pavlov D, Monahov B, 2003, Influence of temperature on expander stability and on the cycle life negative plates, J Power Sources, 113, 335-344.

[11] Lambert D W H, Greenwood P H J, Reed M C, 2002, Advances in gelled-electrolyte technology for valve-regulated lead- acid batteries, J Power Sources, 107, 173-179.

[12] Guo Y, Hu J, Huang M, 2006, Investigations on self-discharge of gel valve-regulated lead-acid batteries, J Power Sources, 158, 991-996.

[13] Tang L, Li A, Chen H, Li H, Chen Q, Zhou H, Wei W, Zhang W, Hu J, Dou C, Wang H, Finlow D, 2011, The electrochemical performances of a novel lead–sodium binary grid alloy for lead-acid batteries, Electrochim Acta, 56, 4566-4570.

[14] Li H, Liua H, Wang Q, Chen H, Ren A, Hu J, 2010, Effects of covalently bonded siloxane on the electrochemical and physical behaviour of GEL-VRLA battery, ElectrochimicaActa, 56, 663-666.

[15] Toniazzo V, 2006, The key to success: Gelled-electrolyte and optimized separators for stationary lead-acid batteries, J. Power Sources, 158, 1124-1132.

[16] Tang Z, Wang J M, Mao X X, Shao H B, Chen Q Q, Xu Z H, Zhang J Q, 2007, Investigation and application of polysiloxane-based gel electrolyte in valve-regulated lead-acid battery, J. Power Sources, 168, 49-57.

[17] Pan K, Shi G, Li A J, Zhao R R, Wang F Q, Zhang W Q, Chen Q, Chen H Y, Xiong Z L, Finlow D, 2012, The performance of a silica-based mixed gel electrolyte in lead acid batteries, J. Power Sources, 209, 262-268.

[18] Kulkarni S S, Tambe S M, Kittur A A, Kariduraganavar M Y, 2006, Modification of Tetraethylorthosilicate Crosslinked Poly(vinyl alcohol) Membrane Using Chitosan and Its Application to the Pervaporation Separation of Water–Isopropanol Mixtures, Journal of Applied Polymer Science, 99, 1380-1389.

[19] Kariduraganavar M Y, Kulkarni S S, Kittur A A, 2005, Pervaporation separation of water–acetic acid mixtures through poly(vinylalcohol)-silicone based hybrid membranes, Journal of Membrane Science, 246, 83–93.