

Research Article

Endah R. Dyartanti*, Agus Purwanto, Arif Jumari and Tika Paramitha

Optimization type of filler on electrochemical and thermal properties of gel polymer electrolytes membranes for safety lithium-ion batteries

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Abstract: Gel polymer electrolyte (GPE) membranes of polyvinylidene fluoride-based polymer matrix of different filler types such as nano-clay, ZnO, and SiO₂ extracted from fly ash is produced using the non-solvent induced phase separation method. Moreover, the electrochemical properties, electrode compatibility, and the batteries performance are investigated using these gel electrolyte membranes. It is observed that gel electrolytes with nano-clay filler exhibited more stable ionic conductivity and charge-discharge performance than those containing ZnO and SiO₂ extracted from fly ash. A maximum ionic conductivity of $5.62 \times 10^{-3} \text{ S cm}^{-1}$ was obtained with the addition of 8 wt% nano-clay filler at room temperature. The LiFePO₄ performance assembled with these membranes is examined using coin cells (LiFePO₄/GPE/graphite). After 50 cycles with a rate of 0.2 C, the battery with a different filler retained 97.7% of its initial capacity. It should be noted that this type of filler influences the electrolyte absorption, electrochemical properties, and performance of the LiFePO₄.

Keywords: PVDF, polymer gels electrolyte, filler, lithium-ion battery

1 Introduction

In the last two decades, there is increasing demand for portable and lightweight electronic devices, thereby creating a need for energy storage compatible with the design of these devices. The lithium ion battery (LIB) is an energy storage device adequately suitable for mobile systems applications. Additionally, lithium ion has an advantage over existing energy storage systems because they have a fast-charging design, long life cycle, and a higher power density in a simple battery pack module [1]. However, the battery system disadvantages include high cost, low compaction density, and battery safety, mainly when utilized in high-powered electric motors such as electric vehicles that require high energy density. The most critical safety factor is the generation of internal heat during electrochemical reactions in the battery cell [2]. Thus, the resulting heat includes a reversible heat generated from electrochemical reactions during the charging/discharging process, irreversible heat from internal ohmic resistance, polarization heat production, and side reaction heat [3,4]. To ensure batteries are kept safe, the rate of heat build-up and the use of solid or semi-solid electrolytes must be maintained.

Properties of polymer electrolytes such as safety factors, design flexibility, and suitability make them a suitable replacement for liquid electrolytes used in energy storage devices [5]. Generally, there are two types of electrolyte polymers, namely solid electrolyte polymer (SPE) and gel polymer electrolyte (GPE). The SPE is a salt of Lithium (Li) dissolved by a high molecular weight polymer chain. In addition, polymers serve as hosts for ion transfer through the movement of polymer segments [6]. However, practical use of the SPE is limited because its ionic conductivity is lower than the conductivity required in battery applications ($10^{-3} \text{ S cm}^{-1}$), while the GPE has advantages compared to SPE such as the ionic conductivity of GPE is higher than the SPE. The GPE also mitigates the risk of leakage since it entraps liquid electrolytes of

* **Corresponding author: Endah R. Dyartanti**, Department of Chemical Engineering, Universitas Sebelas Maret, Surakarta, Indonesia; Centre of Excellence for Electrical Energy Storage Technology, Universitas Sebelas Maret, Surakarta, Indonesia, e-mail: endah_rd@staff.uns.ac.id, tel: +62-271-632112

Agus Purwanto, Arif Jumari, Tika Paramitha: Department of Chemical Engineering, Universitas Sebelas Maret, Surakarta, Indonesia; Centre of Excellence for Electrical Energy Storage Technology, Universitas Sebelas Maret, Surakarta, Indonesia

polymer structures and performs a dual role of acting as a separator between the electrodes of the battery and electrolyte storage.

Furthermore, the GPE consists of a gel system and a heterogeneous phase, the heterogeneous phase is the polymer host matrix with interrelated pores filled with an electrolyte solution. In heterogeneous GPE, lithium-ion transport occurs in the quasi-solid state electrolyte phase. The common GPEs exhibit excellent conductivity of Li^+ in the order of $10^{-3} \text{ S cm}^{-1}$, this has made GPE one of the most attractive alternatives amongst various electrolyte systems with enhanced safety and flexibility.

The ionic conductivity and a stable porous structure of the membrane can be improved by combining the phase inversion process and the presence of filler in the membrane [7]. The Montmorillonite filler addition has the effect of increasing the charge and mobility for Li-ion battery applications [8]. The crystallinity of the polymer material can be reduced by the incorporation of several types of filler. In this case, the filler acts as a solid plasticizer and will increase the ion transfer characteristics and also interface characteristics to the anode [9]. Wachtler *et al.*, [10] showed that the PVDF-based GPE membrane with the addition of SiO_2 had the same electrochemical capacity when compared to that without filler. Costa *et al.* [11] reported that the best ionic conductivity is obtained by adding MgO , ZnO , and MCM-41 filler. ZnO particles are inert oxide ceramics that can alter polymer chain dynamics and increase the lithium transference number.

This research examines the influence of filler on the characterization and performance of the polymer electrolyte for LIB for PVDF-based polymer matrix. Additionally, this complements previous work carried out on GPEs using pore-forming materials and filler additives based on PVDF polymer matrix [12,13]. The results showed that fillers play a significant role in increasing the ionic conductivity and the life cycle of the battery in order to achieve optimum performance.

2 Materials and methods

2.1 Materials

Polyvinylidene fluoride (PVDF) powder (MW 534000, Sigma-Aldrich) and polyvinylpyrrolidone (PVP) (MW 25,000 g mol^{-1} , Merck) were dried at 60°C under a vacuum for 24 h. *N,N*-Dimethylacetamide (DMAc, Merck) was used as received. Also, surface modification of nano-clay (Sigma

Aldrich Nanomer[®] I.31PS, Nanomer[®] clay), nano zinc oxide, ZnO (20–30 nm, MTI Corporation, USA), and silicon oxide, SiO_2 , were extracted from fly ash waste. The electrolyte solution was 1.0 M LiPF₆ lithium hexafluorophosphate (LiPF₆) in EC/DMC/DEC = 4/2/4 (v/v/v) (MTI Corporation, USA).

2.2 Methodology

2.2.1 Preparation of gel polymer electrolyte (GPE) membranes

Different membranes were prepared by modifying the previously used procedure for nano-clay [13] and ZnO [12]. Modifications were made by allowing the nascent membrane to be in contact with air for 10 min and then immersed in demin water for 24 h with a water replacement process of 2 h periodically. The types of filler added were nano-clay, ZnO , and SiO_2 from fly ash with concentrations of 6, 8, and 10 wt%, respectively. Each filler was dispersed in *n,n*-dimethylacetamide solvent at 35°C for 2 h using an ultrasonic sonicator. After that, 10wt% of PVDF polymer was added to the membranes solution and continued to be mixed at 45°C (20 h). Then, PVP pore-forming agent was added and stirred again until completely mixed (4 h). The next step is a membrane degassing process for 4 h to remove bubbles in the casting solution. The solution is then printed on flat glass using a casting machine with a membrane thickness of 150 μm . The wet membranes were then immersed in a non-solvent (deionized water) at 25°C for 24 h. The membrane formed was dried under air for 24 h. Finally, to remove the remaining water and solvent still in the membrane matrix, a final drying process was carried out at 70°C under vacuum for 12 h. The membrane obtained will be ready to be activated with an electrolyte solution.

2.2.2 Characterization method

The Fourier Transform Infrared Spectroscopy (FTIR) was used to analyze the surface chemistry of the membrane. The characterization was done on a Shimadzu Prestige-21. The porosity (P) of membranes was evaluated using equation (1).

$$P (\%) = \frac{M_{\text{BuOH}}/\rho_{\text{BuOH}}}{M_{\text{BuOH}}/\rho_{\text{BuOH}} + M_p/\rho_p}, \quad (1)$$

where M_m is the membrane mass in dry condition and M_{BuOH} is the membrane mass after membranes were

immersed in *n*-butanol solution. ρ_{BuOH} and ρ_P are the density of *n*-butanol and membranes, respectively. The amount of electrolyte trapped in the membrane pores is determined according to:

$$\delta = \frac{M - M_0}{M_0} \times 100\%, \quad (2)$$

where M_0 is the membrane mass in dry condition and M is the membrane mass in the wet condition, respectively. Degree of crystallinity of the polymer membrane is determined using the differential scanning calorimetry (DSC) analysis. Equation (3) is used to estimate the value of the degree of crystallinity of membranes:

$$X_C (\%) = \frac{\Delta H_{\text{sample}}^m}{\Delta H_m^*} \times 100, \quad (3)$$

where X_C is the degree of crystallinity, $\Delta H_{\text{sample}}^m$ is the heat of fusion (fusion) per gram weight of the sample, ΔH_m^* = The enthalpy of the polymer PVDF (104.7 J g^{-1}) [14].

2.2.3 Electrochemical properties and battery performance

Ionic conductivity measurements were performed by Hi-Tester Model HIOKI LCR 3532. The characterization were done on the range of frequency of 42–5 MHz with an amplitude of 10 mV [15]. The membrane sample was immersed in electrolyte (1M LiPF₆) and then sandwiched with stainless steel (SS) electrodes (SS/GPEs/SS) in CR2032 coin battery cell. The ionic conductivity (σ) expression described by equation (4).

$$\sigma = \frac{d}{R_b S}. \quad (4)$$

In this study, R_b is the bulk resistance (Ω), d is the thickness of the membranes after swelling, and S is the contact area with SS electrode. The battery with a cell configuration consisting of LiFePO₄/GPE/graphite was used in the electrochemical performance test of the battery, and battery analyzer (0.02–10 mA, MTI corp.) was CT-1008-S1(Neware), in the voltage range between 2.5 and 3.65 V, with current densities 0.2 C for 50 cycles.

3 Results and discussion

3.1 Thermal stability

The functions of GPE membrane are an electrolyte for ion transfer media and a separator between the electrodes in

the battery cell. In the battery cell, an exothermic reaction takes place which releases heat during charging or discharging process. This thermal effect can cause deformation of the GPEs, which will result in reduced efficiency during the charging and discharging processes, and can cause short circuits in the battery cells. The thermal fusion ratio of PVDF obtained from the DSC analysis with thermal the fusion of pure PVDF critical materials is the value of the degree of crystallinity of the PVDF membranes [16]. The characteristics of the melting point and degree of crystallinity of PVDF membranes with PVP additives on different types of fillers are summarized in Table 1.

The crystallinity values (Table 1) range from 14.71 to 37.26% for various types of fillers. The inhibition of crystallization during the membrane solidification process due to the presence of filler reduces the volume of the crystal fraction in the membrane, resulting in a decreased degree of crystallinity [17]. In the polymer, the increase in amorphous phase correlates with the increase in the rate of nucleation during the membrane solidification as reported by ref. [18]. The degree of crystallinity (X_C) of this modified membrane was lower than the PVDF membrane when graphene/PVP (44%) was added [19].

3.2 Surface chemistry

Qualitative analysis of the chemical properties of a substance identified through specific absorption peaks for certain groups is achieved using infrared (IR) spectroscopy. The chemical bonds formed in the GPE membrane were used to determine the appearance of β -PVDF. Furthermore, the data in Figure 1 show the surface chemistry of PVDF GPE-modified membranes. Vibrational spectroscopy is the most important tool for studying the interactions between the different components of polymer electrolytes. FTIR Spectroscopy on the PVDF membrane was also used to determine the PVDF polymer's beta phase (β -phase). The

Table 1: Thermal Properties and Crystallinity of PVDF membranes

Composition				Degree of crystallinity, X_c (%)	Melting point, T_m (°C)
PVDF	PVP	Filler (wt%)			
10	0	—		37.26	162.71
10	7	Clay	8	14.71	163.2
10	7	ZnO	8	31.26	164.12
10	7	SiO2	8	34.23	164.97

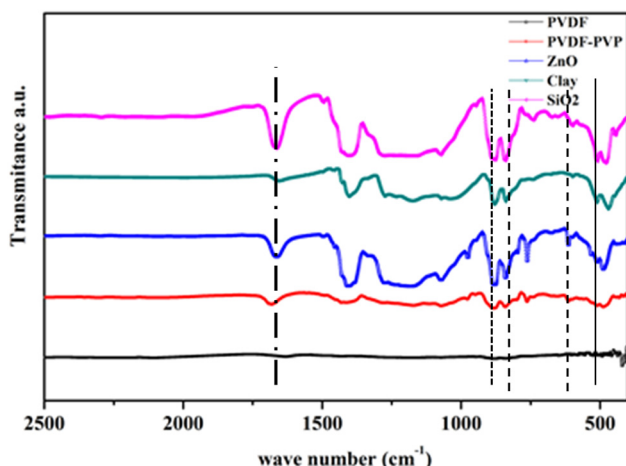


Figure 1: FTIR spectrum of PVDF GPE membranes with different fillers (nano-clay, ZnO, and SiO₂ from fly ash waste).

FTIR spectrum for the PVDF membrane is shown in Figure 1. The peak characteristics of pure PVDF membrane were identified at wavelengths of 1,414 cm⁻¹ (CH₂ functional group), 1,233 cm⁻¹ (–CF–stretching), 1,176 cm⁻¹ (–CF₂–stretching), and 881 cm⁻¹ (the vinylidene functional group of PVDF). The results of Dekka and Kumar's research showed that the peak characteristics of α -phase PVDF were 615 cm⁻¹ (–CF₂–bending and CCC skeletal bending) and 763 cm⁻¹ (–CH₂–rocking), while β -phase PVDF was observed at wavelengths of 840 and 510 cm⁻¹ [20]. The wavelength of 840 cm⁻¹ represents –CF₂–stretching and –CH₂–rocking, while the wavelength of 510 cm⁻¹ represents the CF₂ group. From the FTIR spectrum analysis of the PVDF/nano-clay/PVP membrane, the combined contribution of the nano-clay and carbonyl groups of PVP was observed at a wavelength of 1,661 cm⁻¹ (C=O) due to the formation of hydrogen bonds (C=O...H=O). In the phase inversion process, the synergy between PVP and nano-clay influences the separation rate [21].

The effect of the addition of the filler particles is shown in Figure 1. The visible peaks at wavelengths of 763 and 615 cm⁻¹, which are the characteristics of the α -phase polymer PVDF, decreased, while the peaks at wavelengths of 834 and 512 cm⁻¹, which are the characteristics of the β -phase PVDF, increased. The characteristics of the crystalline phase after the addition of filler exhibited the same tendency as the addition of nano-clay. Therefore, the accumulation of filler particles affects the change in the crystalline phase of the PVDF polymer from both α -phase and β -phase. This result is in line with Thakur's research, which reported that adding clay particles into PVDF polymer can alter the phase's crystalline properties, thereby changing the phase and increasing its concentration [22]. The addition of PVP did not show any

significant difference in the characteristics of the α -phase and β -phase. From Figure 1, it is shown that adding any filler will change the PVDF to a crystal phase. These changes are observed in the increased $F(\beta)$ value on the membrane. In addition, the change in the crystalline phase of PVDF decreased the degree of crystallinity of the PVDF polymer (Table 1). Therefore, the lower the crystallinity, the more the amorphous phases in the polymer increase the absorption of the membrane electrolyte.

3.3 Electrolyte uptake and ionic conductivity of gel polymer electrolyte

The porous membrane, activated with liquid electrolyte, has three phases: solid, gel, and adsorbed electrolyte liquid. The solid phase gives the structural membrane mechanical strength. Ion conductivity was significantly affected by the other two phases. The value of electrolyte absorption in the membrane is strongly influenced by the porosity and pore structure of the membrane [23]. Therefore, the design of pore structure of the membrane is the main factor in improving the ionic conductivity characteristics of GPEs. The type and concentration of fillers used to modify the membrane influence the porosity and absorption of ionic conductivity. In addition, the use of certain types of fillers enhances some specific characteristics of the separator [24–26]. Figures 2 and 3 show the relationship between the value of porosity (%), electrolyte uptake (%), and the ionic conductivity (mS cm⁻¹) of GPEs in different filler types.

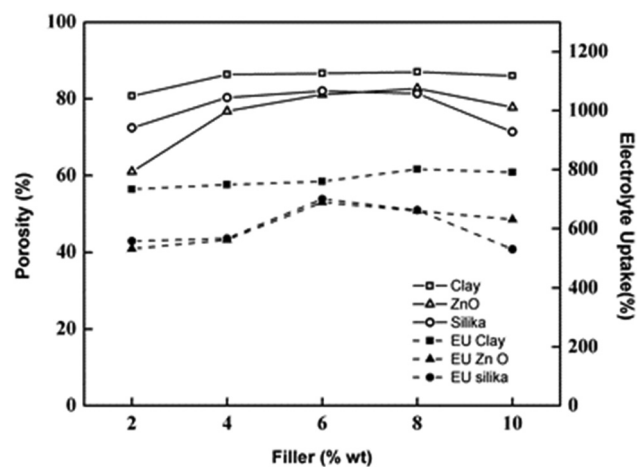


Figure 2: Porosity (%) and electrolyte uptake (%) of PVDF membrane with various types of filler.

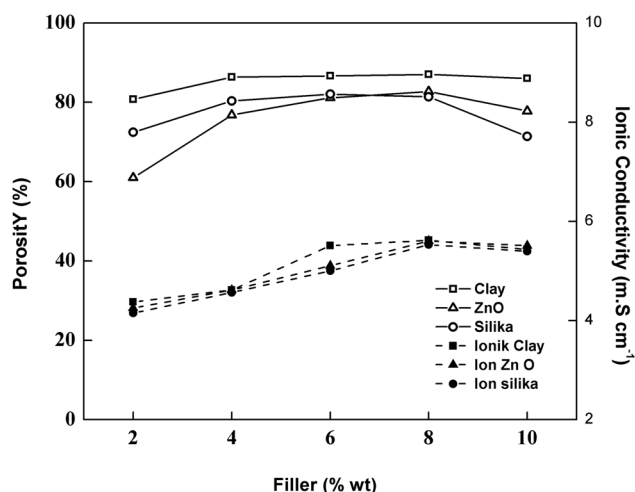


Figure 3: Porosity (%) and ionic conductivity (mS cm^{-1}) of PVDF membrane with various types of filler.

The GPEs with nano-clay filler particles have the porosity (87.03%), electrolyte uptake (801.69%), and ionic conductivity (5.62 mS cm^{-1}) and showed the best at the addition of 8% by weight of nano-clay. When compared with nano-zinc oxide (ZnO) particles with the same concentration, it gave porosity value (82.74%), electrolyte absorption value (660.00%), and ionic conductivity (5.60 mS cm^{-1}).

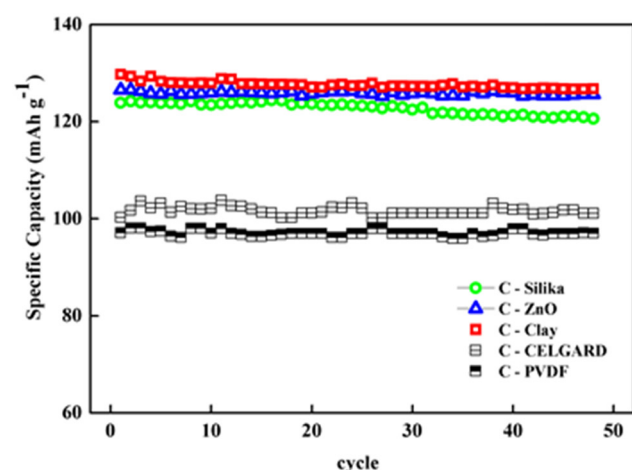
The addition of silicon oxide (SiO_2) filler extracted from coal fly ash waste with the co-precipitation process in the same concentration (8 wt%) resulted in a porosity value of 82.74%, electrolyte uptake value of 660.00%, and ionic conductivity of 5.53 mS cm^{-1} , which are lower than the results obtained with the other filler types. The superior properties of nano-clay particles are due to their layered structure.

The layered particle structure, which causes polymeric chain intercalation between the layers, is suitable for battery electrodes because it reduces the crystallinity of the membrane and increases its mechanical strength and heat resistance [27]. Furthermore, Meneghetti et al. found that nano-clay, which is well distributed in a polymer matrix, acts as a Lewis acid-base center because nano-clay forms complexes with lithium ions due to the negative charges on the surface [28]. Hence, the ion conductivity of lithium is increased due to the large number of free charge carriers generated from the interaction between lithium cations and polymer anions [29–31].

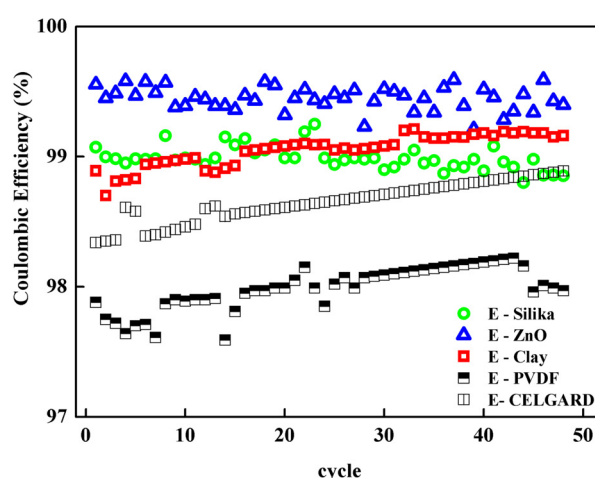
3.4 The electrochemical performance of the LiFePO_4 batteries

A CR2032-type coin cell battery determined the effect of filler types and concentration on the electrochemical performance of the electrolytic separator membrane. Figure 4 shows the charge–discharge cycle of PVDF/PVP membranes of different filler types (nano-clay, ZnO, and SiO_2) in $\text{LiFePO}_4/\text{GPE}/\text{graphite}$ batteries with a (C-rate) 0.2 C (0.4 mA). The flat second cycle charge–discharge graph shows the active cathode material's reversible charge/discharge cycle.

The specific discharge capacities at 0.2 C for the different filler types are nano-clay: $127.9094 \text{ mA h g}^{-1}$; ZnO: $126.0627 \text{ mA h g}^{-1}$; SiO_2 : $122.85 \text{ mA h g}^{-1}$; celgard: $97.4256 \text{ mA h g}^{-1}$, and for pure PVDF: $90.2056 \text{ mA h g}^{-1}$. The specific discharge capacity is proportional to the ionic conductivity and electrolyte uptake of the membrane of



(a)



(b)

Figure 4: (a) Specific capacity and (b) Coulombic efficiency of $\text{LiFePO}_4/\text{GPE}/\text{graphite}$ full cells at a charge–discharge rate 0.2 C (0.4 mA).

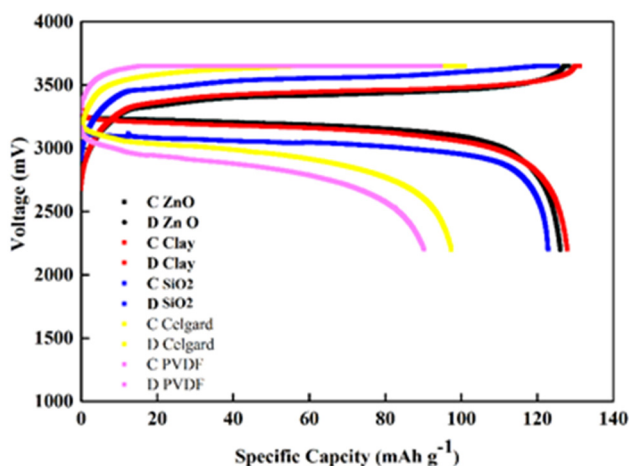


Figure 5: The charge–discharge profiles of $\text{LiFePO}_4/\text{GPE}/\text{graphite}$ with current densities at a charge rate of 0.2 C and discharge rate of 0.2 C.

different filler types. Out of the three fillers (nano clay, ZnO , and SiO_2), the nano-clay has the best lithium-ion transfer rate between electrodes and the lowest interface resistance value, resulting in the highest discharge rate. Thus, indicating that GPEs with nano-clay fillers have better compatibility with electrodes and lower reactivity with lithium metal electrolytes [32,33].

Figures 5 and 6 show performance test results of the specific discharge capacity of the battery for different filler types at different discharge rates between 0.2 and 4 C. The figure demonstrates the cyclical behavior of recoverable charge and discharge rates of the LiFePO_4 (LFP) cathode material for battery cells displayed in the following order: graphite-anode/separator/LFP-cathode. As depicted in the graph, the progressive decrease in potential discharge

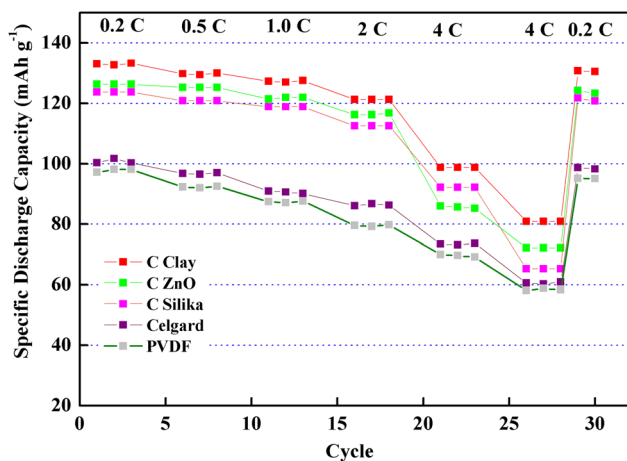


Figure 6: The discharge profiles of $\text{LiFePO}_4/\text{GPE}/\text{graphite}$ full cells at a different discharge rate condition.

voltage results from the polarization of the battery electrode material. This behavior is due to the electrode's increased resistance, which causes a slow lithium ion transfer rate [34].

4 Conclusion

GPE-based PVDF electrolyte membranes of different filler types have been fabricated with the phase inversion process of the non-solvent induced phase separation method. Different filler types were used in investigating the morphological characteristics, thermal structure, surface chemistry, membrane ionic conductivity, and electrochemical performance of GPE. The degree of porosity of GPEs with the addition of SiO_2 , ZnO , and nano-clay fillers was 82.05, 82.74, and 87.03%, respectively. The best porosity was with the addition of nano-clay filler (8 wt%). Furthermore, the PVDF/PVP membrane produced the highest ionic conductivity value of 5.62 mS cm^{-1} with the addition of a nano-clay filler. The full battery cell composed of graphite/separator/ LiFePO_4 provided the best performance using GPEs. The addition of nano-clay (8 wt%) resulted in a specific capacity of $127.9094 \text{ mA h g}^{-1}$ at a rate of 0.2 C. Similarly, using celgard and PVDF as separators resulted in specific capacities of 97.4256 and $90.2056 \text{ mA h g}^{-1}$, respectively.

GPE PVDF membranes with the different filler types showed good speed and cycle stability after 50 cycles. Therefore, all filler types used led to a targeted increase in the performance of GPE. The thermal characteristics, good ionic conductivity values, and high specific capacity performance results make nano-clay powder the best choice for filler in GPEs for lithium-ion batteries compared to ZnO and SiO_2 .

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Data availability statement: The datasets of this study are available on reasonable request from corresponding author.

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