



Electrochemical performance of polypyrrole/silver vanadium oxide composite cathodes in lithium primary batteries

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ABSTRACT

Polypyrrole (PPy)/silver vanadium oxide (SVO) composite cathode materials were synthesized by polymerizing pyrrole onto the surface of pure SVO particles. Electrochemical characterization was carried out by performing galvanostatic discharge, pulse discharge and ac-impedance experiments. The composite electrode exhibited better performance than pristine SVO in all the experiments. The composite electrodes yielded a higher discharge capacity and a better pulse discharge capability when compared to the pristine SVO electrode. The pulse discharge and ac-impedance studies indicated that PPy forms an effective conductive network on the SVO surface and thereby reduces the particle-to-particle contact resistance and facilitates the interfacial charge transfer kinetics. To determine the thermal stability of the composite cathode, galvanostatic discharge and ac-impedance experiments were performed at different temperatures. The capacity increased with temperature due to enhanced charge transfer kinetics and low mass transfer limitations. The peak capacity was obtained at 60 °C, after which the performance degraded with any further increase in temperature.

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1. Introduction

Implantable cardioverter defibrillators (ICDs) are electronic devices to treat life-threatening irregularities in heart beat. The battery that powers an ICD should be capable of delivering energy at high rate discharges on demand and at low rate discharge for monitoring and pacing [1]. A primary lithium battery used for ICDs performs most of the time at low power and occasionally delivers one or more high power pulses [2]. The battery requirements for ICDs are as follows: (i) it should be capable of delivering approximately 50J within 5–10 s with a continuous current drain in the order of microamperes for at least 5 years, (ii) the performance of the battery should be predictable so that there are adequate time for warnings before it is completely discharged, and (iii) the battery should be small enough to be implanted inside a human body.

ICDs were initially powered by Li/V₂O₅ system. Later silver vanadium oxide (SVO) of composition Ag₂V₄O₁₁ was used as the standard cathode material in the ICD industry [3] due to its high gravimetric and volumetric energy densities [4]. Seven moles of lithium can be theoretically inserted into SVO, yielding a discharge capacity of approximately 315 mAh g⁻¹ [5]. Practical utilization of

SVO is lower, especially during pulse discharges at high rates. The internal cell resistance drastically increases with progress in discharge, resulting in a poor rate capability of a Li/SVO cell [2].

In our previous work [5] a hybrid composite of polypyrrole (PPy) and SVO was synthesized for lithium primary batteries. The PPy/SVO composite electrodes were prepared using an oxidative polymerization of pyrrole monomer on the SVO surface in an acidic medium. The composite electrode exhibited higher discharge capacity and better rate capability as compared with the pristine SVO electrode. The improvement in electrochemical performance of the composite electrode was due to PPy which accommodates lithium ions and also enhances the SVO utilization. Chronoamperometric and ac-impedance measurements indicated that lithium intercalation proceeds under the mixed control by interfacial charge transfer and diffusion. The enhanced SVO utilization in the composite electrode results from the kinetics of interfacial charge transfer facilitated in the presence of PPy.

Our present work encompasses the performance study of PPy/SVO cathode materials. The discharge characteristics of the composite electrodes were studied using several electrochemical techniques such as galvanostatic potential transient technique, pulse discharge technique and ac-impedance spectroscopy. For extending the applicability of these composite electrodes for non-medical applications and also for studying the thermal stability characteristics, the electrochemical experiments were carried out at different temperatures.

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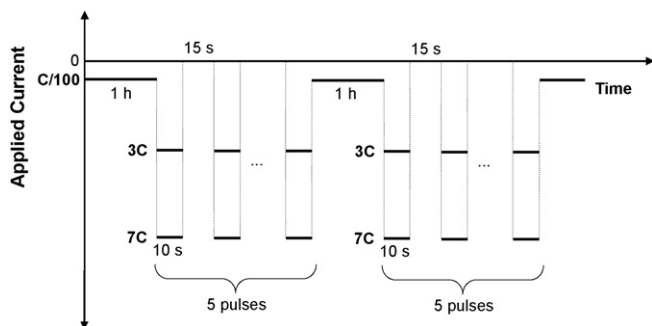


Fig. 1. Current profiles used for pulse discharge experiments.

2. Experimental

2.1. Preparation of PPy/SVO composites

SVO was prepared from a mixture of Ag_2O and V_2O_5 in a molar ratio of 1:2, which was heat-treated in air at 520°C for 24 h. The as treated sample with a dark brown color was grinded into fine powders. Then, the SVO powder was dispersed in a 1 M HClO_4 solution, and liquid pyrrole in various concentrations was slowly injected into the SVO-containing solution. The resulting PPy/SVO composite powder with a black color was collected by filtration, and they were thoroughly rinsed with a 1 M HClO_4 solution and deionized water, followed by drying under vacuum at 80°C for 12 h [6].

2.2. Electrochemical experiments

The active material powder was mixed with 5 wt% carbon black and 5 wt% polytetrafluoroethylene (PTFE) to prepare a pellet with a diameter of 1 cm. A three-electrode electrochemical cell was used for the electrochemical experiments. Both the reference and counter electrodes were constructed from lithium foil, and a 1 M LiPF_6 -DME/PC (50:50 vol%) solution was used as the electrolyte. The assembly of cells was performed in a glove box filled with purified argon gas. After assembling the cells, they were allowed to equilibrate at the OCV for 24 h, to ensure that the electrolyte diffused into the porous electrode.

Galvanostatic discharge was carried out using an Arbin BT-2043 battery test station at various current densities with the cut-off

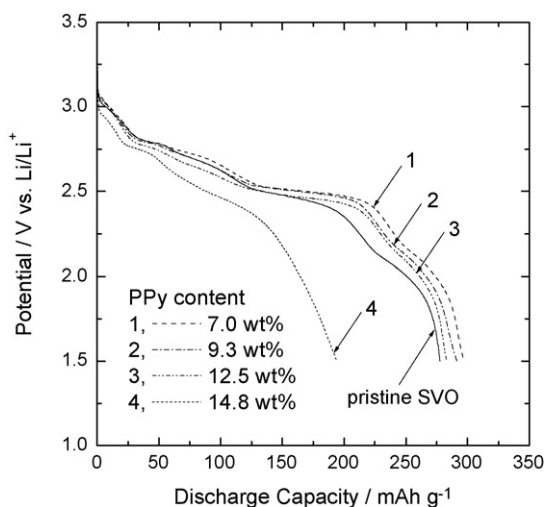


Fig. 2. Galvanostatic discharge curves of the PPy/SVO composite electrodes. The electrodes were discharged at the $C/25$ rate.

potential being 1.5 V vs. Li/Li^+ . Pulse discharge experiment was performed using the current profiles illustrated in Fig. 1. The cell was initially discharged at a rate of $C/100$ for 1 h. In the next step, the cell was discharged using 3C or 7C rates for 10 s, followed by a 15 s rest step. Each discharge step comprised of 5 pulse strings, followed by a $C/100$ rate discharge for 1 h. Electrochemical impedance spectroscopy (EIS) measurements were conducted using an EG&G PAR model 273 potentiostat combined with a Solartron 1255 frequency response analyzer. The impedance measurements were obtained by applying an ac-amplitude of 5 mV peak-to-peak over the frequency range from 10 mHz to 100 kHz. The morphology of the electrodes was studied using Quanta 200 ESEM.

3. Results and discussion

3.1. Electrochemical performance of PPy/SVO composite electrodes

Fig. 2 presents the galvanostatic discharge curves of the PPy/SVO composite electrodes for various values of PPy concentration obtained at the $C/25$ rate. The value of the specific discharge capac-

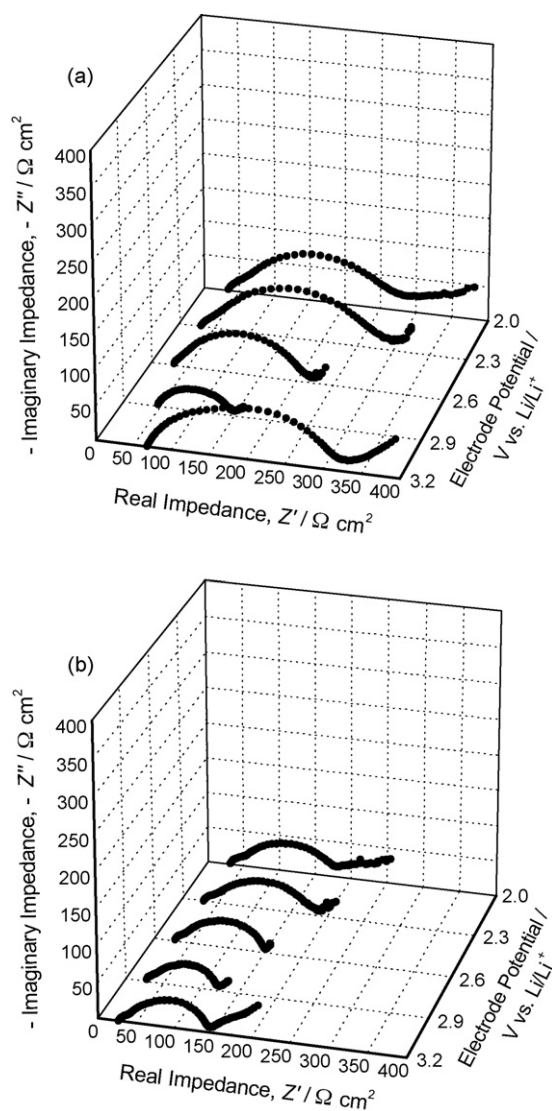


Fig. 3. Nyquist plots of ac-impedance spectra for (a) pristine SVO and (b) PPy/SVO composite electrodes measured at different potentials.

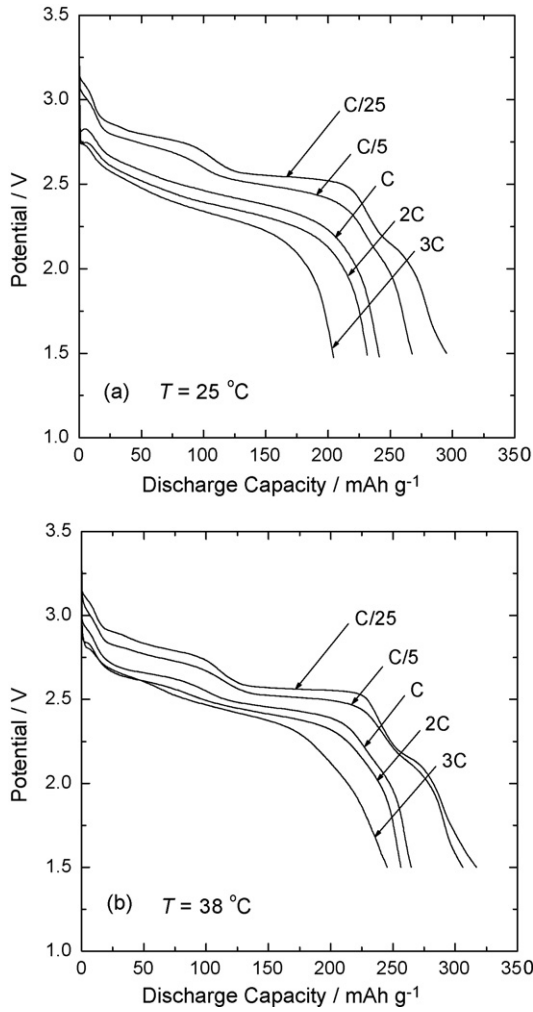


Fig. 4. Galvanostatic discharge curves of the PPy/SVO composite electrodes at (a) 25 °C and (b) 38 °C.

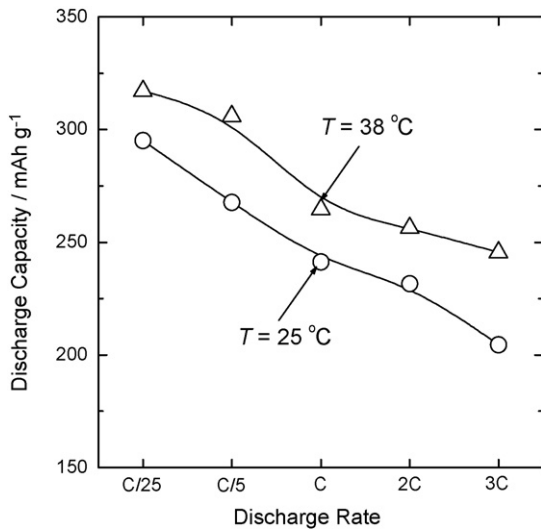


Fig. 5. Discharge capacities of the PPy/SVO composite electrodes at 25 °C and 80 °C as a function of the discharge rate.

ity was calculated based on the weight of the active material rather than the total weight of pellet with conductive carbon and organic binder. In Fig. 2, three distinct potential plateaus are observed at 2.8, 2.5 and 2.1 V vs. Li/Li⁺, which correspond to the reduction reactions of (i) Ag⁺ to Ag, (ii) V⁵⁺ to V⁴⁺ (and V⁴⁺ to V³⁺) and (iii) V⁴⁺ to V³⁺, respectively [4–6]. As shown in Fig. 2, the composite electrodes with 7.0–12.5 wt% PPy yield higher discharge capacity when compared to the pristine SVO electrode. This result indicates that the synergic electrochemical performance is obtained for the PPy/SVO composite electrodes, i.e., PPy is electrochemically active. It possesses a capacity of ca. 72 mAh g⁻¹ to intercalate lithium ions [7], facilitates lithium intercalation into SVO and increases the utilization of the active material by acting as a binder. When the PPy content in the composite is in the range of 7.0–12.5 wt%, it causes SVO to be fully utilized during the discharge process. The rest of the experiments involving the composite electrodes were carried out with 7 wt% PPy/SVO, for which discharge capacity of 297 mAh g⁻¹ was obtained.

Fig. 3(a) and (b) demonstrates Nyquist plots of the EIS spectrum obtained for pristine SVO and PPy/SVO composite. The electrode was potentiostatically polarized at different potentials until a low steady-state current was attained. The EIS response consists of a depressed arc in the high frequency range and a straight line inclined at constant angle to the real axis in the low frequency range. The high-frequency arc is ascribed to the interfacial charge

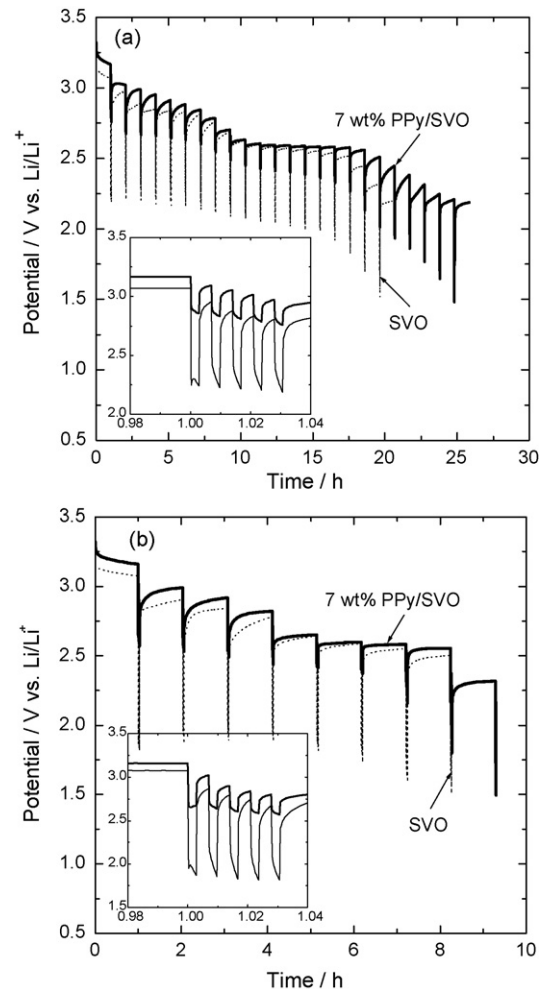


Fig. 6. Pulse discharge characteristics of pristine SVO and PPy/SVO composite measured at pulse rates of (a) 3C and (b) 7C.

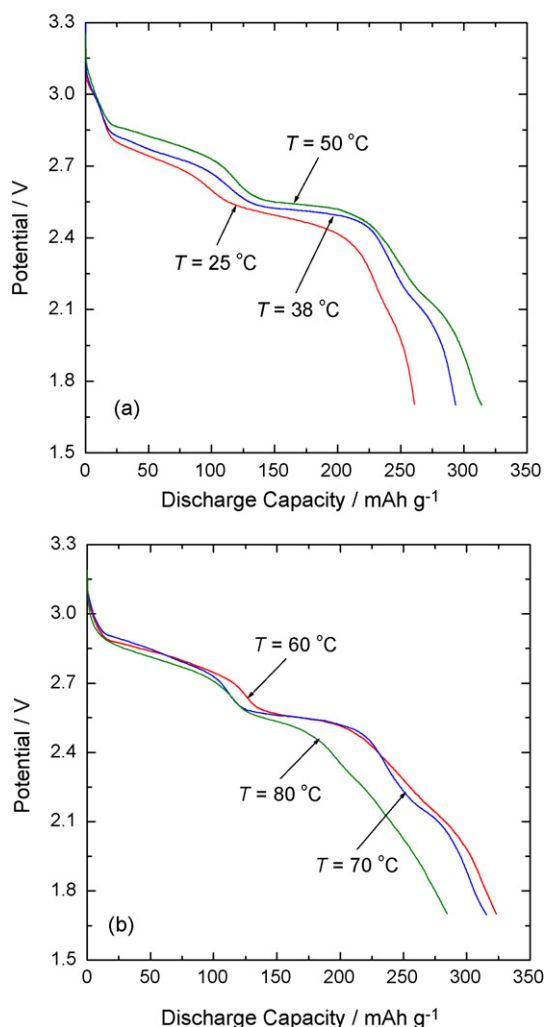


Fig. 7. Galvanostatic discharge curves of PPy/SVO composite at different temperatures. The electrodes were discharged at the C/5 rate.

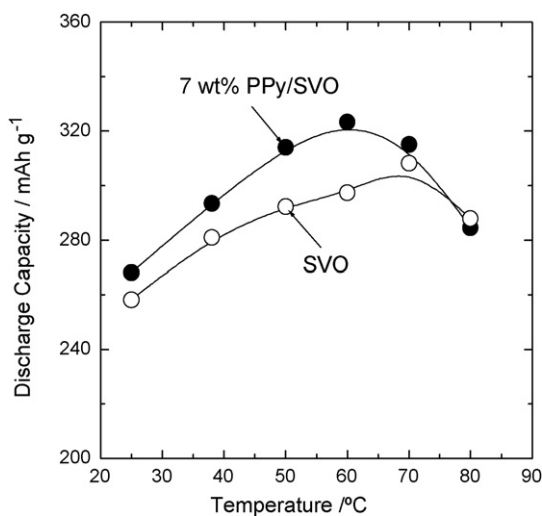


Fig. 8. Plot of discharge capacity vs. temperature obtained for the PPy/SVO composite and SVO electrodes.

transfer reaction, and a straight line at low frequencies is associated with the semi-infinite diffusion of lithium into the electrode (Warburg impedance) [8]. It should be noted that both the ohmic resistance and the charge transfer resistance of PPy/SVO composite decreases drastically when compared to the pristine SVO over the whole potential range. The results indicated that PPy not only decreases the particle-to-particle contact resistance, but also facilitates the interfacial charge transfer kinetics, by forming an effective conductive network on the SVO surface.

3.2. Electrochemical behavior of PPy/SVO composite at 38 °C

In order to demonstrate the feasibility of the PPy/SVO composite system in an implantable cardioverter defibrillator (ICD), the discharge characteristics was investigated at 38 °C (near human body temperature). Fig. 4(a) and (b) compares the galvanostatic discharge curves of PPy/SVO composite measured at 25 and 38 °C at different discharge rates. The discharge curves coincide well in shape with each other. The discharge capacities at 25 and 38 °C are plotted in Fig. 5 as a function of the discharge rate. The discharge capacity at 38 °C is higher than that at 25 °C over the whole range of discharge rates, indicating that the PPy/SVO-based electrochemical cell can be successfully used to power an ICD in the human body. The observed higher discharge capacity at 38 °C may result from better utilization of the active material due to lower mass transfer limitations at higher temperatures.

3.3. Pulse discharge characteristics

The batteries for ICDs undergo intermittent pulse loads, when abnormal heart beats are detected. Fig. 6(a) and (b) illustrates the pulse discharge curves at pulse rates of 3C and 7C, respectively, measured for pristine SVO and for the PPy/SVO composite. As shown in the insets of Fig. 6, the potential profile during each pulse consists of four parts. The initial potential drop is due to the internal ohmic resistance of the cell. This drop is proportional to the applied pulse current, and is determined by the total electronic resistance of the system. The second potential drop results from lithium intercalation into the electrode. This region is controlled by interfacial (Butler–Volmer) kinetics and lithium diffusion in the electrode. During current interruption, the potential profile regains the ohmic drop. Finally, due to a slow relaxation which occurs at the electrode/electrolyte interface the cell potential reaches an equilibrium value. The cut-off potential for pulse discharge experiments was 1.5 V vs. Li/Li⁺.

The results indicated that the ohmic potential drop for PPy/SVO composite is much smaller than that for pristine SVO during the pulse discharge experiments. This indicates that PPy forms a conductive network on the SVO surface, thereby decreasing the particle-to-particle contact resistance. Fig. 6 shows that the PPy/SVO composite electrode survived 24 pulse discharge steps when a 3C rate was used to discharge the battery. Note that the pristine SVO electrode withstood only 18 pulse discharge steps under the same conditions. SVO is being used as the cathode material in ICDs [3]. Under identical experimental conditions, PPy/SVO composite produces better pulse discharge results than the SVO electrode. Hence PPy/SVO composite cathodes could be a potential cathode material for ICDs.

3.4. Performance and stability of PPy/SVO composite at elevated temperatures

In order to address the stability of organic PPy on the SVO surface, the discharge capacities of pristine SVO and PPy/SVO composite were measured as a function of discharging tempera-

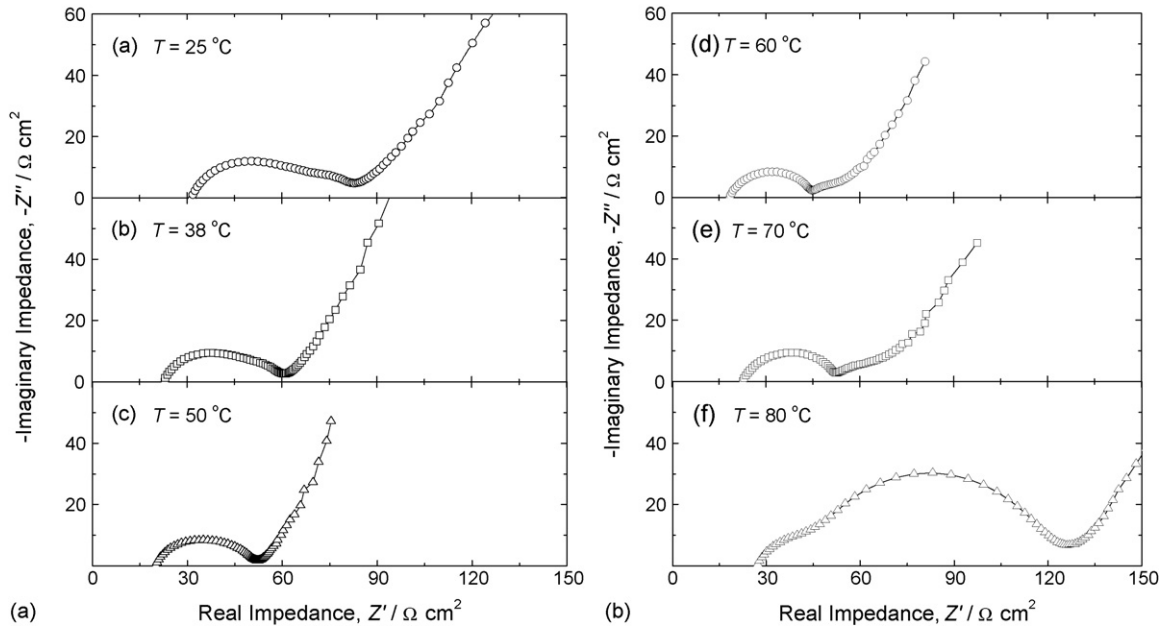


Fig. 9. Nyquist plots of the ac-impedance spectra measured for PPy/SVO composite at (a) 25 °C, (b) 38 °C, (c) 50 °C, (d) 60 °C, (e) 70 °C and (f) 80 °C. The measurements were performed at 3.0 V vs. Li⁺/Li.

ture. Fig. 7(a) and (b) shows the galvanostatic discharge curves of PPy/SVO composite at temperatures in the range from 25 to 80 °C. The cells were discharged with a C/5 rate. The discharge curves conform well in shape implying that no alternate discharge reaction mechanism exists at different temperatures.

The discharge capacity is presented in Fig. 8 as a function of temperature. The discharge capacity increases gradually with increase in the temperature, then reaches a maximum at 60 °C and finally decreases with further increase in temperature up to 80 °C. This behavior is observed for both the SVO and PPy/SVO composite electrodes and indicates that PPy remains stable and induces no significant degradation of the composite electrode at elevated temperatures.

To elucidate the reason for degradation in the performance at elevated temperatures ac-impedance spectra was measured

at these temperatures and the results are shown in Fig. 9. The impedance spectrum consists of a highly depressed arc (charge transfer resistance) observed in the high frequency range and a straight line incline at constant angle to the real axis (diffusion impedance) in the low frequency region. Fig. 10 plots the ohmic resistance R_{Ω} , charge transfer resistance R_{ct} and total cell resistance R_{total} for PPy/SVO composite as a function of temperature. The data were obtained by complex non-linear least squares (CNLS) fitting of the ac-impedance spectra shown in Fig. 9. As shown in Fig. 10, R_{total} has a minimum value at 60 °C and then it increases rapidly with an increase in the temperature. Hence the observed improvement in capacity can be attributed to enhanced charge transfer kinetics at high temperatures (38–60 °C). The high cell resistances at temperatures above 60 °C may result from a parasitic chemical reaction at the electrode/electrolyte interface.

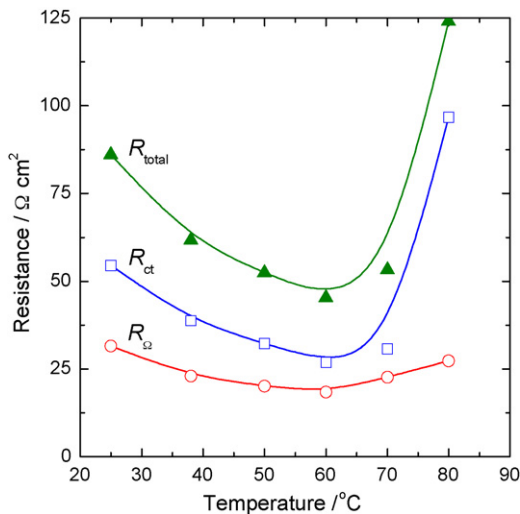


Fig. 10. The ohmic resistance R_{Ω} , charge transfer resistance R_{ct} and total cell resistance R_{total} for PPy/SVO composite as a function of temperature. The data were obtained by using CNLS fitting of the ac-impedance spectra shown.

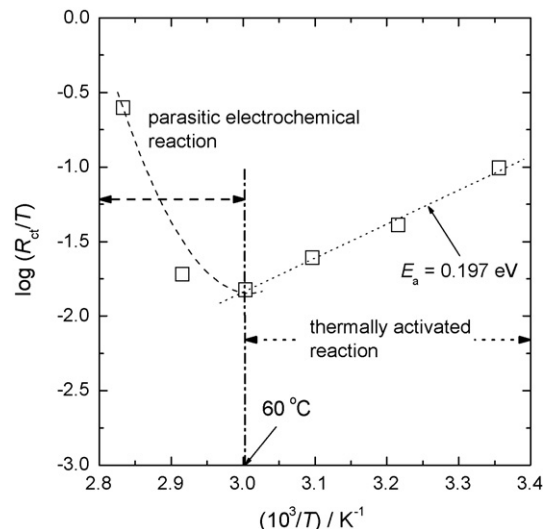


Fig. 11. Temperature-dependence of R_{ct} for PPy/SVO(A) composite. R_{ct} exhibits an Arrhenius behavior at temperatures lower than 60 °C.

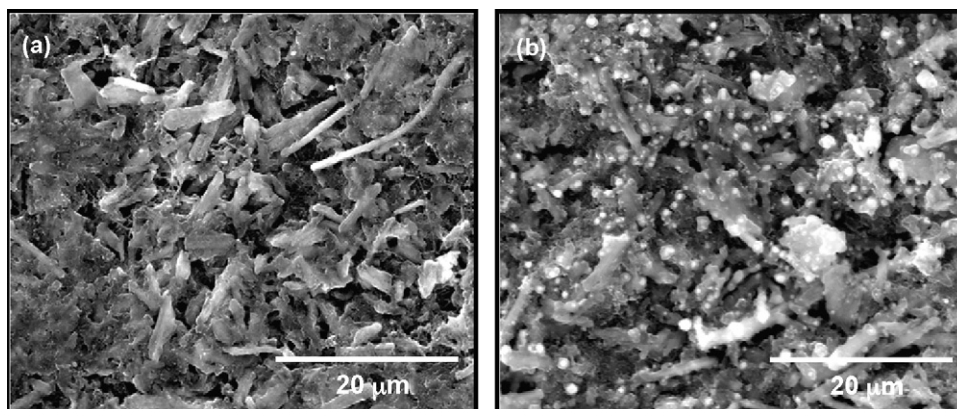


Fig. 12. Scanning electron microscopic images obtained from the surfaces of PPy/SVO composite discharged at (a) 25 °C and (b) 80 °C.

Since the kinetics of a thermally activated process is generally described by the Arrhenius expression, the charge transfer resistance R_{ct} can be written as

$$R_{ct} = aT \exp\left(\frac{E_a}{k_B T}\right) \quad (1)$$

where a is the pre-exponential factor, T the absolute temperature, E_a the activation energy of the charge transfer reaction, and k_B represents the Boltzmann constant. Fig. 11 presents the plot of $\ln(R_{ct}/T)$ vs. $1/T$ for PPy/SVO composite. R_{ct} exhibits an Arrhenius behavior below 60 °C, and the value of E_a was determined to be 0.197 eV from the slope of the plot. However, the plot of $\ln(R_{ct}/T)$ vs. $1/T$ deviates significantly from linearity at high temperatures, which suggests that the composite material undergoes parasitic chemical/electrochemical reaction at the electrode/electrolyte interface. The parasitic reaction could be the decomposition of the electrolyte. The thermal dissociation of the electrolyte at elevated temperature could have been accelerated by the catalytic effect of the active materials [9]. The products of this reaction could have resulted in the passivation of the electrode surface, thereby blocking the active sites for lithium intercalation and resulting in high increase of charge transfer resistance as exhibited in Nyquist plot. The surface morphology of the electrodes discharged at different temperatures was studied using scanning electron microscopy. As shown in Fig. 12(a) and (b), organic products were formed on the electrode surface discharged at 80 °C, possibly from the deposits arising from the decomposition of the electrolyte. No such deposits are found on the surface of the electrode discharged at 25 °C.

4. Conclusions

The PPy/SVO composite materials were synthesized by polymerizing pyrrole on to the surface of SVO in an acidic media. The composite electrodes with 7.0–12.5 wt% PPy yielded a higher

discharge capacity and better pulse discharge capability compared to the pristine SVO electrode. The optimized PPy/SVO composite electrode showed a discharge capacity of approximately 297 mAh g⁻¹. The pulse discharge and ac-impedance studies indicated that PPy forms an effective conductive network on the SVO surface that reduces the particle-to-particle contact resistance, facilitates the interfacial charge transfer kinetics and increases the utilization of the active material. Thermal stability experiments indicated an increase in the capacity with temperature. Peak performance was obtained at 60 °C. Further increase in temperature resulted in degradation of the performance. Impedance results and SEM micrographs suggest the possibility of composite material undergoing parasitic electrolyte dissociation at the electrode/electrolyte interface resulting in poor performance at 80 °C.

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