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Specific heat capacity of lithium polymer battery components

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Abstract

The specific heat capacities of a polymer electrolyte and a polymer-containing composite cathode have been determined by differential scanning calorimetry in the range from 70 to 140 °C. This range well includes the operating temperature range of the devices incorporating these materials (lithium polymer batteries). The determination of the specific heat capacities of the battery polymeric components was driven by the need of designing high performance devices.

Keywords: Specific heat capacity; Polymer electrolyte; Composite electrode; Lithium battery; LPB

1. Introduction

Lithium polymer batteries (LPBs) have recently attracted the interest of researcher in the field of environmentally compatible vehicles. In particular, polymer electrolytes based on polyethyleneoxide (PEO) have evoked widespread attention as replacement of liquid organic electrolytes to realise all-solid-state, solvent-free, electrochemical power sources [1]. However, PEO-based polymer electrolytes show an appreciable conductivity only at temperatures above 65 °C, which corresponds to the melting point of the pure polymer. Typically, the operating temperature of polymer electrolyte batteries ranges from 80 to 120 °C even if some complexes ($P(EO)_n$LiBETI) exhibit a good ionic conductivity already at 60 °C [2]. Thus, LPBs would require a careful control of temperature in order to optimise the performance. Therefore, the study of thermal characteristics of the polymer electrolytes and the cathodic materials plays a key role for the realisation of LPBs.

The aim of this work is the analysis of the thermal characteristics of both PEO-based polymer electrolyte and composite cathode proposed for the realisation of $Li/P(EO)_{20}LiBETI/V_2O_5$ batteries for electric vehicle applications at ENEA. All the electrochemical tests devoted to asses the performance of such LPBs and to investigate the interfacial properties of PEO-based electrolytes with metallic lithium have been described in previous papers [2–4].

2. Experimental

PEO–LiBETI polymer electrolyte tapes with an ethylene oxide (EO)/LiBETI molar ratio of 20:1 were synthesised through a solvent-free procedure [2]. The components PEO (MW = 4 ML, Polyox WSR301, Union Carbide) and LiBETI salt (3 M) were dried under vacuum for 48 h at 50 and 150 °C, respectively. After drying, the materials were sieved, gently mixed by ball milling and hot-pressed at 90 °C using an ATS FAAR hydraulic press to form thin tapes.

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The composite cathode was prepared by following a procedure developed at ENEA and industrially scaled up at Ferrania S.p.A. [4]. It involves the deposition of a slurry onto an aluminium foil current collector (battery grade, 0.02 mm thick) by doctor-blade technique. The slurry had the following dry composition: V_2O_5 (Pechiney) 60%, carbon (Super P, MMM carbon) 10%, PEG (Carbowax, Union Carbide) 27%, and PEO (Polyox WSR301, Union Carbide) 3%. A mixture of chloromethane and methanol (2:1 in weight) with traces of acetone was used as solvent. The solvent was allowed to evaporate under a hood and then the coated films were dried under vacuum at 50 °C for 24 h to remove the adsorbed water. The absence of salt in the composite cathode favours the moisture and solvent removal. As a final step, the coated films were cold-calendered inside the dry room to remove the porosity left by the solvent evaporation. At the end of the process, the thickness of the composite cathode layer (excluding the aluminium substrate) was about 0.045 mm. Its geometric density (mass/volume) was about 1.8 g cm^{-3} corresponding to an active material (V_2O_5) surface loading of 5 mg cm^{-2}, approximately.

Thermal analysis and heat capacity measurements of the battery components were carried out using a differential scanning calorimeter of TA Instruments (DSC 2910). The instrument was calibrated with high-purity indium standard (from Aldrich, 99.999%) at a scanning rate of 5 °C min^{-1}. The transition temperature and enthalpy of indium standard are 156.6 °C and 28.5 J g^{-1}, respectively, as reported in [5]. All thermograms were achieved on 20–30 mg samples sealed into aluminium pans at a heating rate of 5 °C min^{-1}, and using dry nitrogen as purge gas.

Thermogravimetrical analysis (TGA) was performed on the $P(EO)_{20}LiBETI$ and V_2O_5-based cathode material using a simultaneous DTA/TGA (TA Instruments—SDT 2960). Samples, averaging 4–6 mg, were loaded into aluminium pans and then heated in air at 10 °C min^{-1} from 40 to 220 °C.

The preparation of the materials, the sample handling, and the whole procedure of DSC pans assembly

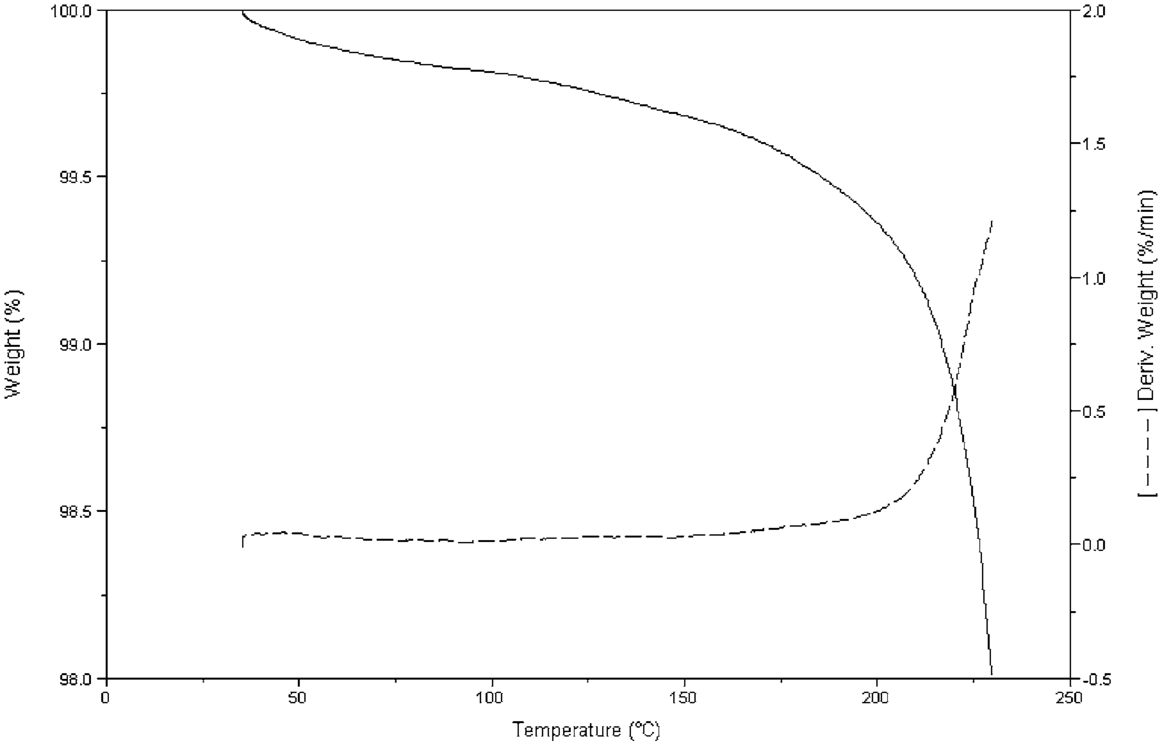

Fig. 1. Weight loss (TGA) and derivative weight loss (DTA) vs. temperature curves of V_2O_5–C–PEG–PEO composite cathode.

were carried out in a controlled environment dry room (Corridi S.r.l., RH $< 0.2\%$).

3. Results and discussion

Figs. 1 and 2 show the thermogravimetric curve of the composite cathode and the polymer electrolyte. The measurements were taken in the temperature range from 40 to 250 °C under a flux of dry air in order to investigate the thermal stability of the materials in low-moisture environment (dry room).

In Fig. 1 are reported the weight loss and derivative weight loss curves of the cathodic material. From the shape of the curves, it is observed that the cathodic material is very stable up to 200 °C. The weight loss was only 0.25% at 130 °C and 0.59% at 195 °C. The degradation process of the composite cathode initiates at temperature higher than 200 °C, as indicated by the steep change of the two curves illustrated in Fig. 1.

In Fig. 2 are reported the same curves for the polymer electrolyte that showed a somewhat lower thermal stability in air. Apart from a smooth weight loss below 100 °C, likely due to the water absorbed during handling, the polymer electrolyte showed a good stability up to 150 °C, where a first sharp feature is seen. The lithium salt clearly catalyses the reaction since the salt-free composite cathode did not show any feature at such a temperature. Nevertheless, the major decomposition takes place above 200 °C as found for the composite cathode. However, both materials did not show any reaction in air below 150 °C, thus indicating that the thermal processing do not induce any deterioration in the materials.

Fig. 3 displays the thermogram of the V_2O_5-based cathode performed under N_2 flux from −70 to 150 °C with a 5 °C min^{-1} heating rate. The curve shows two endothermic transitions centred at around 40 and 60 °C, which correspond to the melting of the PEG and PEO crystalline polymeric matrices, respectively.

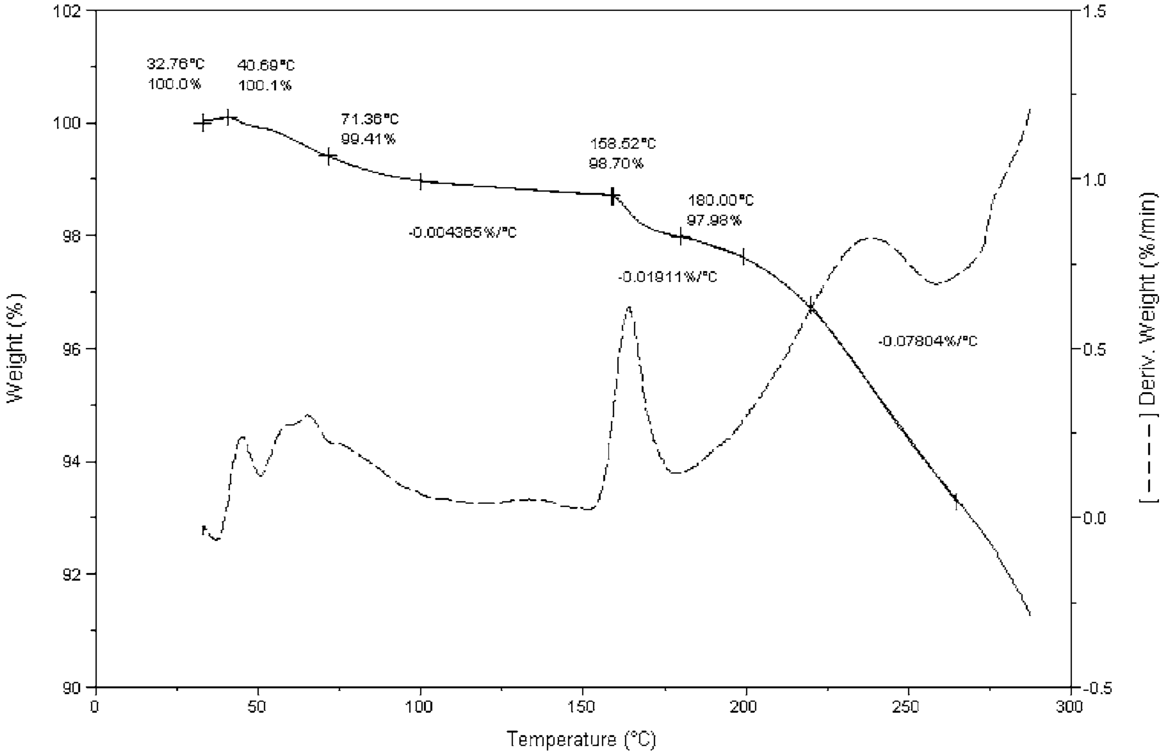

Fig. 2. Weight loss (TGA) and derivative weight loss (DTA) vs. temperature curves of $P(EO)_{20}LiBETI$ polymer electrolyte.

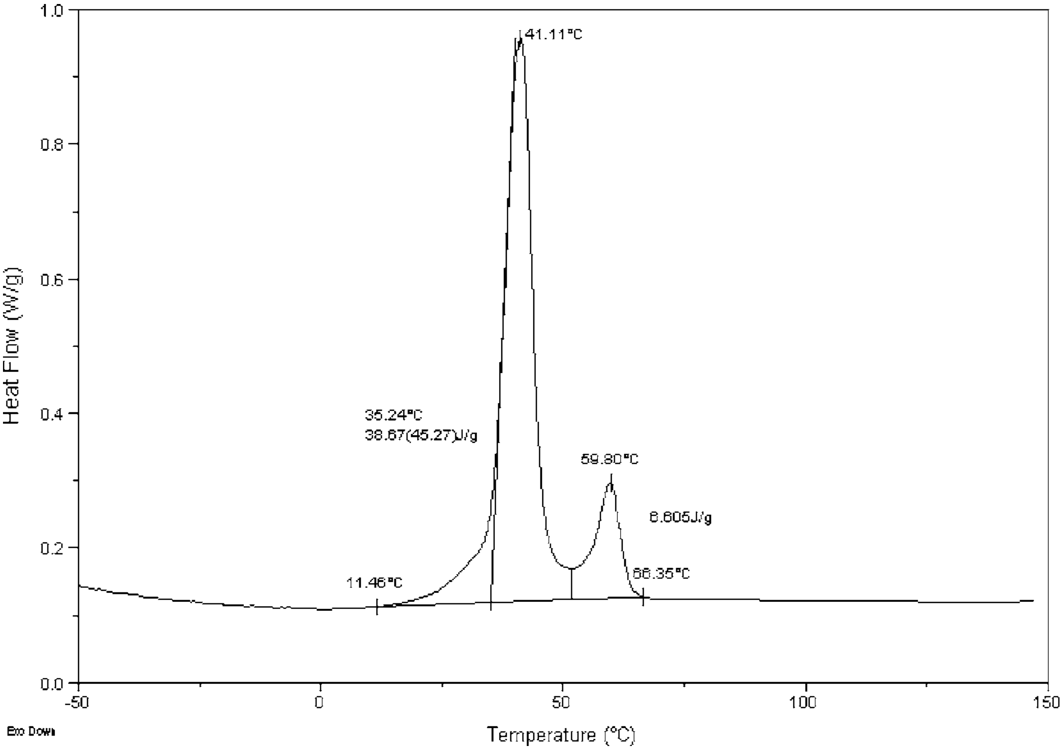

Fig. 3. DSC thermogram of the V_2O_5–C–PEG–PEO composite cathode.

In Fig. 4 is shown the thermogram of the polymer electrolyte (P(EO)$_{20}$LiBETI) performed under a nitrogen atmosphere from −70 to 170 °C with a 5 °C min^{-1} heating rate. In the figure are clearly visible three thermal transitions. The first and the third features are associated to the pure polymer. In particular, the first feature is detected as a step change around −23 °C and is due to the glass transition of the polymeric matrix. The broad peak centred at 67 °C is instead associated with the melting of the polymer. The intermediate feature is an endothermic transition related to the melting of the crystalline PEO–LiBETI complex which composition is not clearly identified yet [2]. PEO-based polymer electrolytes are well known to form crystalline complexes with lithium salts, which the most common are P(EO)$_3$LiX and P(EO)$_6$LiX [6,7]. However, to our knowledge this is the first evidence of a sub-ambient melting crystalline complex composed of PEO and a lithium salt.

Apart from the temperature regions at which material phase changes take place, the differential heat supplied by a DSC instrument to a sample is proportional to the specific heat capacity at constant pressure (C_p) of the latter. Therefore, the C_p of a sample in a defined temperature range can be determined by DSC measurements. This is done by comparing the ordinate displacement of the unknown sample (D_s) and that of a sample of known C_p (D^{ref}) with the baseline behaviour of the empty pan. A sapphire (Al_2O_3) disk can be used as standard specimen, whose C_p values (expressed in kJ kg^{-1} K^{-1}) are reported from 90 to 1650 K [8].

The specific heat of the sample can be calculated from the following expression:

$$C_p = \left(\frac{M^{\text{ref}}}{M_s}\right)\left(\frac{D_s}{D^{\text{ref}}}\right) C_p^{\text{ref}} \qquad (1)$$

where M^{ref} and M_s refer to the weight of the sapphire standard and test sample, D^{ref} and D_s to the baselines of the standard and sample, respectively.

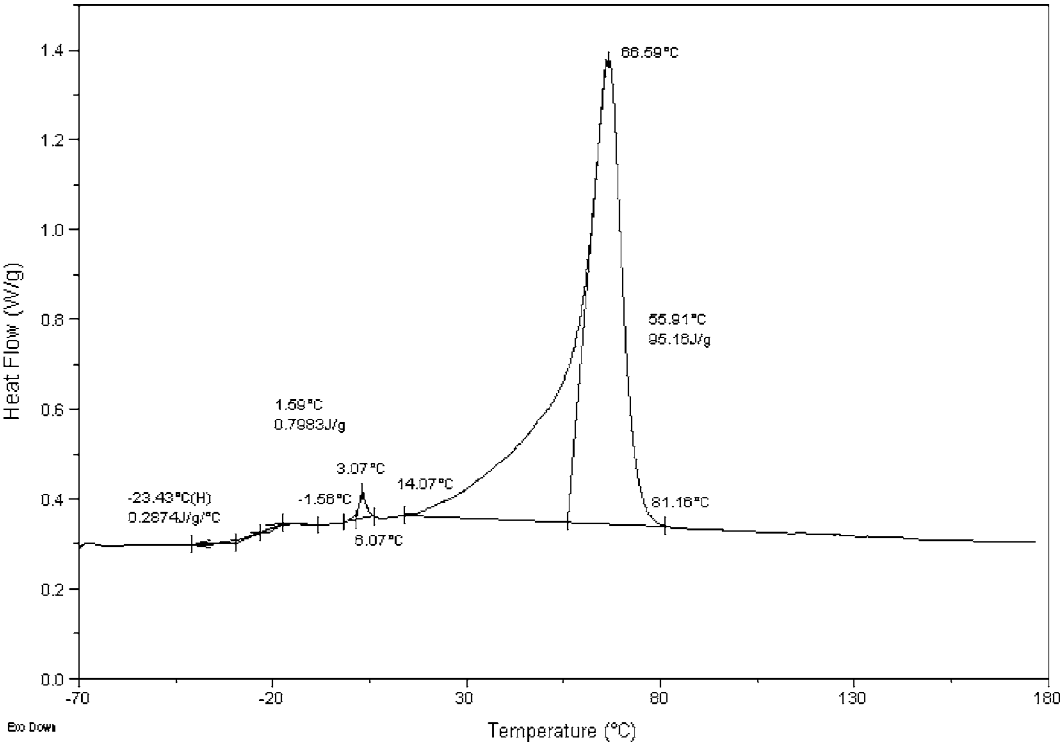

Fig. 4. DSC thermogram of the $P(EO)_{20}LiBETI$ polymer electrolyte.

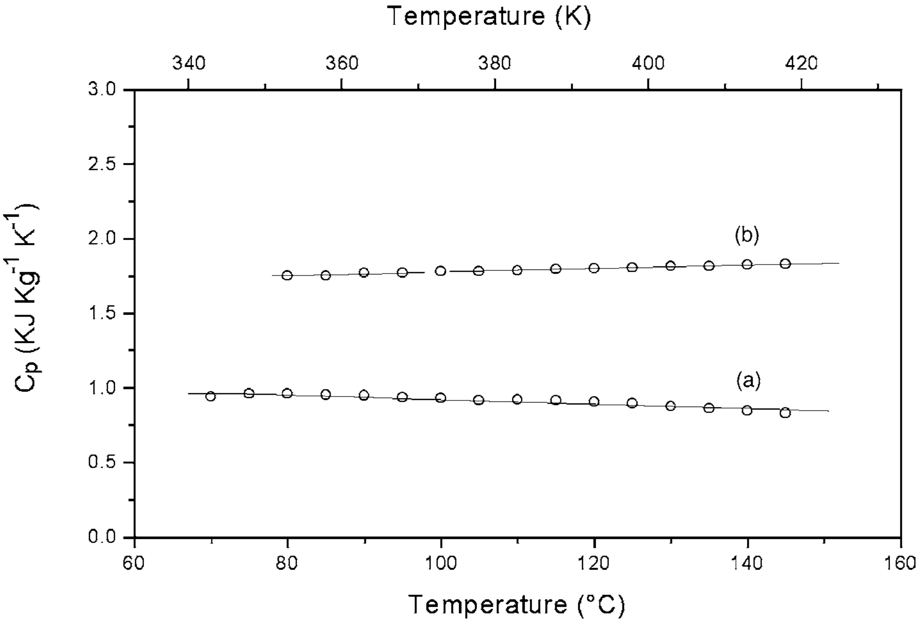

Fig. 5. Specific heat capacity curve of V_2O_5–C–PEG–PEO composite cathode (curve a) and $P(EO)_{20}LiBETI$ polymer electrolyte (curve b) as a function of temperature, expressed in °C (lower axis) and in K (upper axis).

Table 1
Specific heat capacity vs. temperature data of V_2O_5–C–PEG–PEO composite cathode and $P(EO)_{20}LiBETI$ polymer electrolyte

Temperature		C_p of composite cathode	C_p of polymer electrolyte
°C	K	(kJ kg^{-1} K^{-1})	(kJ kg^{-1} K^{-1})
70	343	0.941	–
75	348	0.957	–
80	353	0.959	1.76
85	358	0.952	1.75
90	363	0.947	1.77
95	368	0.936	1.77
100	373	0.931	1.78
105	378	0.916	1.78
110	383	0.920	1.79
115	388	0.913	1.79
120	393	0.904	1.80
125	398	0.894	1.81
130	403	0.877	1.81
135	408	0.859	1.82
140	413	0.845	1.83
145	418	0.829	1.83

Fig. 5 illustrates the specific heat profiles at constant pressure as a function of temperature for the two battery components investigated. The data points also reported in Table 1, were obtained by substituting in Eq. (1) the known values M^{ref} and M_{s}, the baselines assessments D^{ref} and D_{s} and the tabulated C_p^{ref} data.

The specific heat capacity of composite cathode approached a linear dependence by the temperature expressed by the following equation: $C_p(T) = 1.068 - 0.0015T$. The agreement between the experimental data and the C_p values, calculated from the linear fitting, was 0.98%.

The C_p experimental data of the polymer electrolyte in the temperature range 75–150 °C agree very well with the linear relation $C_p(T) = 1.660 - 0.0012T$.

4. Conclusions

The determination of the specific heat capacities of polymer battery components was driven by the need of designing high-performance lithium anode, polymer electrolyte batteries. The determination was performed by means of DSC in the operative range of such devices (80–120 °C). The heat capacities of the polymer electrolyte and the composite cathode have shown a linear correlation with the temperature.

Acknowledgements

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