



Electronic conductivity of vanadium-tellurite glass-ceramics



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ABSTRACT

In this paper, we investigate the electronic conductivity of $2\text{TeO}_2\text{-V}_2\text{O}_5$ glass-ceramics with crystallinity ranging from 0 to 100 wt.%, i.e., from entirely amorphous to completely crystalline. The glass is prepared by the melt quenching technique, and the crystal is prepared by subsequent heat treatment thereof. Glass-ceramics are prepared by mixing glass and crystal powder, followed by a sintering procedure. Activation energies for electronic conduction in the glass and in the crystal are determined by fitting the Mott–Austin equation to the electronic conductivity data obtained by impedance spectroscopy. We find similar activation energies for both glass and crystal, implying that they have similar conduction mechanisms, i.e., thermally activated hopping. The electronic conductivity of $2\text{TeO}_2\text{-V}_2\text{O}_5$ glass is about one order of magnitude higher than that of the corresponding crystal, and a percolation phenomenon occurs at a glass fraction of 61 wt.%, increasing from a lower conductivity in the crystal to a higher conductivity in the glass. We explain the behavior of electronic conduction in the $2\text{TeO}_2\text{-V}_2\text{O}_5$ glass-ceramics by considering constriction effects between particles as well as percolation theory. This work implies that, based on its electronic conductivity, vitreous $2\text{TeO}_2\text{-V}_2\text{O}_5$ is more suitable as a cathode material in secondary batteries compared to a $2\text{TeO}_2\text{-V}_2\text{O}_5$ glass-ceramic.

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1. Introduction

Batteries are essential in modern society to sustain our high-tech lifestyles. Since a large segment of the world's population utilizes electronics powered by batteries every day, both available technologies for batteries and prospects for future technology are objects of extensive research. As an excellent source of mobile energy, batteries are receiving a large amount of attention compared to other available technologies.

Lithium is both the most electro-positive (-3.04 V vs. a standard hydrogen electrode) as well as the lightest metal and therefore has the strongest potential for designing batteries with a high energy density [1]. For high power electrochemical cells, it is important that the electronic conductivity in the electrodes is high and that there is a rapid change in charge carriers at the electrolyte/electrode interface (transfer from lithium ions in the electrolyte to electrons in the electrodes) [2]. Considering these requirements, the use of an amorphous mixed conductive electrode material has been proposed [2], i.e., an amorphous material that is able to conduct a current by both electrons and ions. Since $\text{V}_2\text{O}_5\text{-TeO}_2$ glass may intercalate lithium ions [3], the use of lithium-intercalated $\text{V}_2\text{O}_5\text{-TeO}_2$ may present several advantages: First, the change in charge carriers is not confined to the surface of the electrode but can extend through the material,

which increases the number of sites available for transfer. Second, in an amorphous electrode, the electro-active species is separated from the electron and occupies well-defined cationic sites. When dissolved in this manner, the electro-active species is considered to be intercalated, and its chemical potential is far less than that of the pure species [2]. This difference in chemical potential is the driving force for current flow in a battery and is therefore highly important for the design of highly energy dense electrochemical cells. Third, when comparing amorphous and crystalline structures, degradation during consecutive lithiation cycles (repetitions of charging and discharging) is lowest in an amorphous material [2]. Compared to a crystalline material, the structural units in a glass are easier to rearrange, and thus, the glass is more resistant to the degradation caused by expansion during lithiation cycles.

The most common cathode material in secondary lithium batteries is LiCoO_2 . However, LiCoO_2 only has a moderate energy density (measured in kWh/kg), and the CoO_2 layers created during delithiation (charging) are sheared from the electrode surface, which reduces the energy density because fewer lithium sites are available for lithiation [4]. Cobalt, which is both expensive and toxic, is also dissolved in the electrolyte during delithiation [5]. Due to the listed limitations of the current cathode material, it is of interest to find another material with superior properties. Lithium vanadotellurite is a mixed conductor that previously has been suggested for use as a cathode material [2,3,6,7]. Vanadium tellurite is able to intercalate lithium ions and experiences high electronic conductivity compared to other binary or ternary vanadium compounds [2,8–21]. Because electronic conduction

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occurs by electron hopping from one vanadium ion to another, theoretically, the highest electronic conductivity is achieved in pure vanadium oxide, simply because the distance between adjacent vanadium ions is minimized. Hirashima et al. [22] postulate that the conductivity of a vanadium tellurite crystal might be as high as that of a divanadium pentoxide crystal and that both are 2 orders of magnitude larger than that of the corresponding glass. The synthesis of congruent $2\text{TeO}_2\text{-V}_2\text{O}_5$ crystals has been reported [6,23–31], but to the best of our knowledge, the electronic conductivity of either the crystal or the mixtures between glassy and crystalline $2\text{TeO}_2\text{-V}_2\text{O}_5$ has not been measured. Therefore, in this paper, we investigate the dependence of the electronic conductivity on the weight % of glass in different mixtures of congruent $2\text{TeO}_2\text{-V}_2\text{O}_5$ crystal and glass.

2. Experimental

Glass samples were prepared via the normal melt quenching technique using reagent grade $\geq 99.6\%$ V_2O_5 and $\geq 99.5\%$ TeO_2 . Appropriate amounts for obtaining $2\text{TeO}_2\text{-V}_2\text{O}_5$ were mortared, and 12 g was melted in a gold crucible at 700°C for 1 h. The melt was quenched on a brass block and annealed for 2 h at 250°C . Differential scanning calorimetry (DSC) (Netsch, DSC404) at 1 K/min was performed up to 400°C on a solid sample using gold crucibles. Heat treatment was conducted at 400°C for 2 h in order to crystallize the glass, and both crystalline and glassy samples were examined with a scanning electron microscope (SEM) (Phenom). Images were taken on the surface of the samples and in fractures (the interior of the samples). Different ratios of glass and crystal were mixed to obtain nine samples with a glass fraction ranging from 0 to 100 wt.%. Each sample was pressed under 20.6 MPa and sintered for 2 h at 270°C . All samples were disc shaped with a diameter of 1.8 mm and a height of 1 mm. The temperature of sintering (T_s) was obtained with an optical dilatometer (Misura, HSM-ODHT) measuring 2-dimensional shrinkage during scans from 298 to 673 K with scanning rates of 2, 5 and 10 K/min. T_s is then defined as the temperature where the largest volume shrinkage occurs. SEM images were taken of these glass-ceramic samples. The samples were polished, and gold was sputtered on the parallel surfaces before the electronic conductivity was measured by impedance spectroscopy (IS) (Solartron, SI1260). The electrical measurements were performed in air with a two-point sample holder from 303 to 523 K and with an applied voltage of 100 mV in the frequency range from 10^6 to 1 Hz. X-ray diffraction (XRD) (Rigaku, Ultima IV) using $\text{Cu K}\alpha$ -radiation was applied at room temperature on all samples in order to confirm their amorphous or crystalline states. Scans were conducted at $0.02^\circ/\text{s}$ from 10 to 90° .

3. Results & discussion

Fig. 1 shows the DSC curve of the $2\text{TeO}_2\text{-V}_2\text{O}_5$ glass, from which the glass transition temperature (T_g) and the crystallization temperature (T_c) are determined to be 251 and 400°C , respectively. T_c is determined from the crystallization peak position, whereas T_g is determined from the onset temperature of the glass transition [32,33]. The $2\text{TeO}_2\text{-V}_2\text{O}_5$ glass crystallizes around a single distinctive temperature, indicating the formation of one single crystalline phase. The T_g and T_c values agree well with those reported in the literature [13,25,30]. Figs. 2 and 3 show the XRD patterns and scanning electron microscopy images of both glassy and crystalline $2\text{TeO}_2\text{-V}_2\text{O}_5$ (the crystalline phase was obtained by heat treatment at 400°C for 2 h). The XRD pattern confirms the amorphous nature of the sample before heat treatment due to the lack of Bragg peaks [34]. Fig. 2(b) and (c) shows that the XRD pattern of the analyzed sample coincides with the pattern of $2\text{TeO}_2\text{-V}_2\text{O}_5$ from the Joint Committee on Powder Diffraction Standards (card no. 71-0719) [25,29], indicating that the crystal obtained in this work is $2\text{TeO}_2\text{-V}_2\text{O}_5$. SEM images were taken of both glass and crystal (Fig. 3). As shown in Fig. 3, the glassy sample contains no

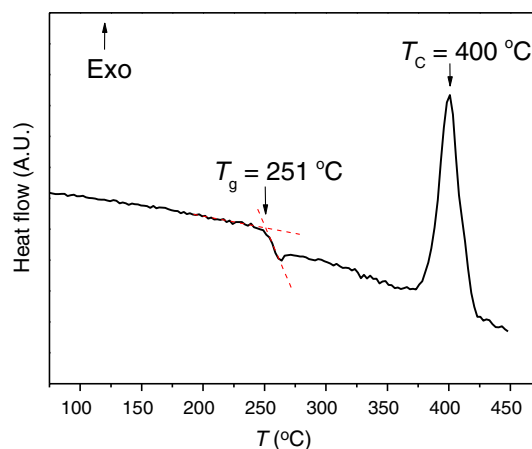


Fig. 1. A DSC scan of $2\text{TeO}_2\text{-V}_2\text{O}_5$ glass at a scanning rate of 1 K/min. Glass transition temperature (T_g) and crystallization temperature (T_c) are marked on the figure.

detectable crystals (Fig. 3(a)), and the crystalline sample contains no detectable vitreous phase either on the surface (Fig. 3(b)) or in the bulk (Fig. 3(c)); thus, the vitreous sample is fully amorphous, and the crystalline sample is completely crystallized.

The mixed glassy and crystalline samples are sintered at $T_s = 543\text{ K}$. As shown in Fig. 4, this temperature corresponds to that of the largest volume shrinkage and, hence, the highest sintering rate. Moreover, T_s is independent of the heating rate, and sintering starts almost immediately after the temperature is raised above T_g . Sintering, which is driven by a diffusion of atoms, occurs immediately after the temperature exceeds T_g due to a fast drop in viscosity upon heating, which indicates a fragile liquid. Fig. 4 shows that an expansion occurs at temperatures higher than T_s , which is attributed to the release of trapped air. At high heating rates, the time for the trapped air to be released is so short that the expansion becomes more pronounced (Fig. 4).

We analyzed a vitreous bulk sample and a vitreous sintered sample, i.e., a sample made by sintering glass powder following the sintering conditions described above, and found identical electronic conductivity for the two samples. XRD data confirm that both the bulk and the sintered powder samples are amorphous. Both samples present the same electrical conductivity, so the applied sintering process does not induce crystallization (which was expected based on Fig. 1.) and does not change the electronic conductivity. In Fig. 5, the electronic conductivity of a vitreous and a crystalline bulk sample is plotted against the inverse temperature. Earlier measurements combined with those presented in this paper show that by increasing the melting temperature, the electronic conductivity can be increased by 2 orders of magnitude [13–15]. Since an increase in melting temperature reduces the valence state of the vanadium in the melt, the

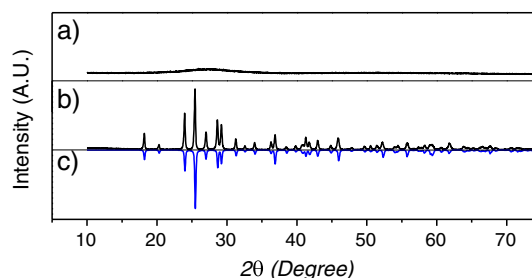


Fig. 2. X-ray diffraction patterns of (a) $2\text{TeO}_2\text{-V}_2\text{O}_5$ glass produced in this work, (b) $2\text{TeO}_2\text{-V}_2\text{O}_5$ crystal produced in this work, and (c) $2\text{TeO}_2\text{-V}_2\text{O}_5$ crystal from [29]. For better comparison between the crystal produced in this work and the crystal presented in [29], their pattern has been inverted (Fig. 2(c)).

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