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Short Communication

# Internal resistance and cathode content in silver borovanadate batteries

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**Abstract**

Silver borovanadate (SBV) glass with the stoichiometric composition $60AgI–20Ag_2O–2B_2O_3–18V_2O_5$ is prepared by rapidly quenching a melt of the constituent chemicals at liquid-nitrogen temperature. The glassy nature of the sample is confirmed by X-ray diffraction. Infrared spectroscopy revealed bands attributed to V–O stretching at 1008 $cm^{-1}$, V=O vibrations at 920 $cm^{-1}$, B–O bond stretching of tetrahedral $BO_4$ units at 850 $cm^{-1}$, and B–O bond stretching of trigonal $BO_3$ units with a non-bridging oxygen (NBO) atom at 1230 $cm^{-1}$. The vibration of the boroxol ring is observed at 1400 $cm^{-1}$. The electrical conductivity of the sample is $1.2 \times 10^{-4}$ S $cm^{-1}$ at 300 K. The transference number, as determined by the electromotive force (e.m.f.) method, is at least 0.98. The glass was used to fabricate several $Ag/I_2$ batteries and the battery with a cathode composition that consists of five-parts iodine, five-parts carbon and one-part glass is the best in terms of a low internal resistance and a longer discharge lifetime.

*Keywords* Batteries; Silver; Boron; Vanadium, Internal resistance; Cathode

## 1. Introduction

There are many reports of $Ag/I_2$ batteries in which the cathode composition consists of five-parts iodine, five-parts glass or electrolyte (ionic conductor), and one-part carbon as the electron conductor [1]. The anode is usually silver mixed with the ionic conductor in a 1:1 weight ratio. The above-mentioned cathode mixture should be less electron conducting than if it contained a larger portion of carbon and a smaller portion of glass. There are hardly any data, to our knowledge, that relate the performance of the battery to different electrolyte–carbon compositions in the cathode. The internal resistance of a solid-state battery is considered to be composed of the electrolyte impedance and the contact between the electrodes and electrolyte [2]. In this work, an attempt is made to demonstrate that the internal resistance of solid-state batteries is also dependent on the cathode composition. The electrolyte used here is silver borovanadate (SBV).

## 2. Experimental

### 2.1. *Sample preparation*

Analar grade AgI, $Ag_2O$, $B_2O_3$ and $V_2O_5$ were mixed in the stoichiometric ratio of $60AgI–20Ag_2O–2B_2O_3–18V_2O_5$ in a silica crucible and then melted in a furnace at 600 °C for about 2 h. The melt was then stirred several times to form a homogeneous solution before quenching at liquid-nitrogen temperature.

Table 1
Weights (g) of battery components

| | Anode | | Electrolyte | Cathode | | |
|---|---|---|---|---|---|---|
| | Ag | SBV | SBV | C | SBV | $I_2$ |
| Cell 1 | 0.3 | 0.3 | 1.0 | 0.09 | 0.09 | 0.45 |
| Cell 2 | 0.3 | 0.3 | 1.0 | 0.06 | 0.30 | 0.30 |
| Cell 3 | 0.3 | 0.3 | 1.0 | 0.30 | 0.06 | 0.30 |

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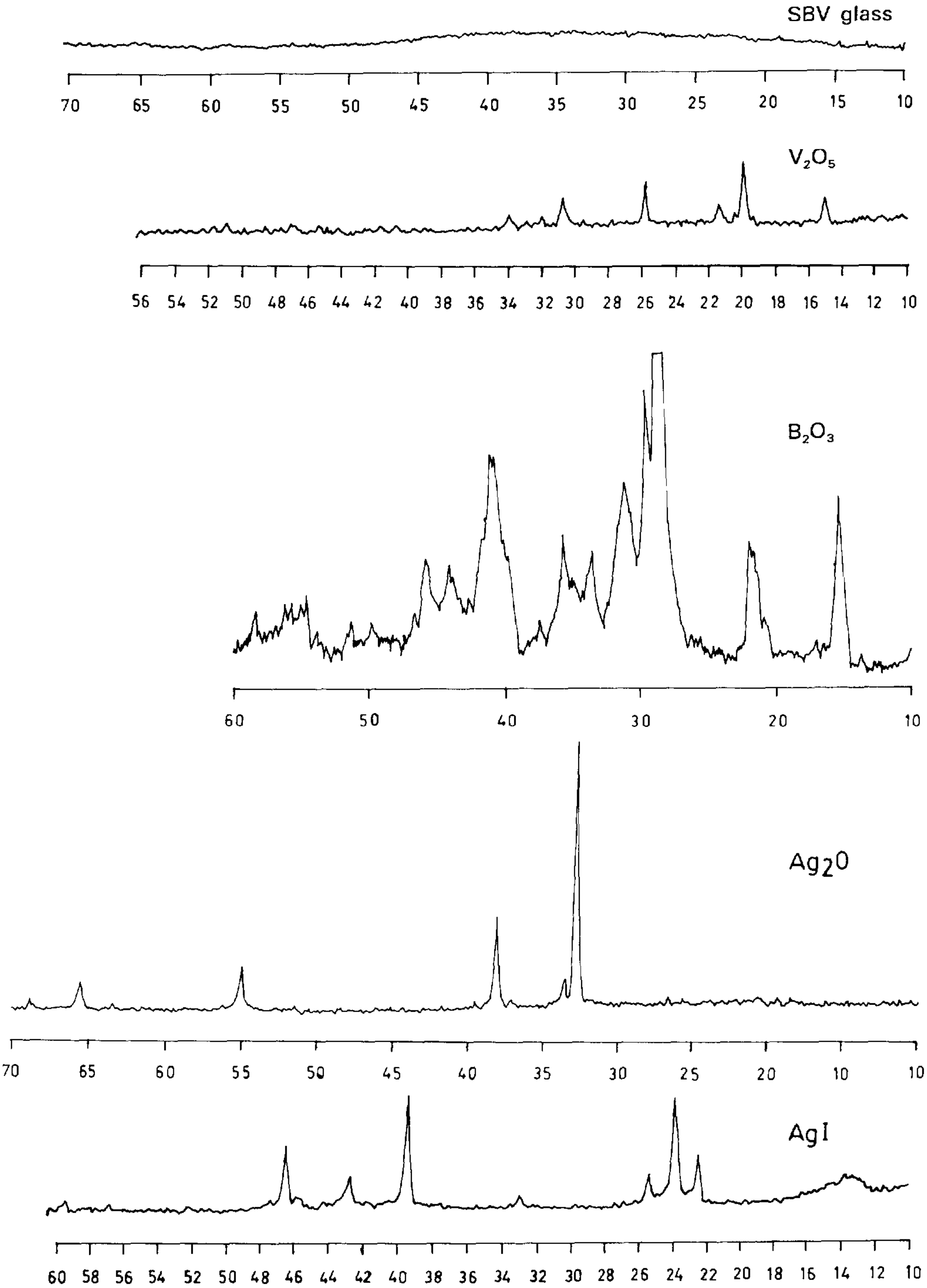

Fig. 1. X-ray diffractograms of constituent chemicals and silver borovanadate glass.

### 2.2. X-ray diffraction phase analysis

The solid phase obtained above was finely powdered and then subjected to X-ray analysis using a Shimadzu XD-5 diffractometer. This instrument employs a Cu K$\alpha$ radiation of wavelength 154.2 pm.

### 2.3. Infrared spectroscopy

The infrared spectrum was obtained with a Beckmann spectrophotometer in the wavenumber region 400 to 4000 cm$^{-1}$ by application of the KBr method. The glass and KBr powder were mixed in the ratio 1:10.

### 2.4. Electrical conductivity

The electrical conductivity was measured using a HIOKI 3520-01 LCR Hi tester which operates in the frequency region between 1 to 100 kHz. The bridge was interfaced to a microcomputer via an IEEE 488 multifunction card. Electrical wires were attached to

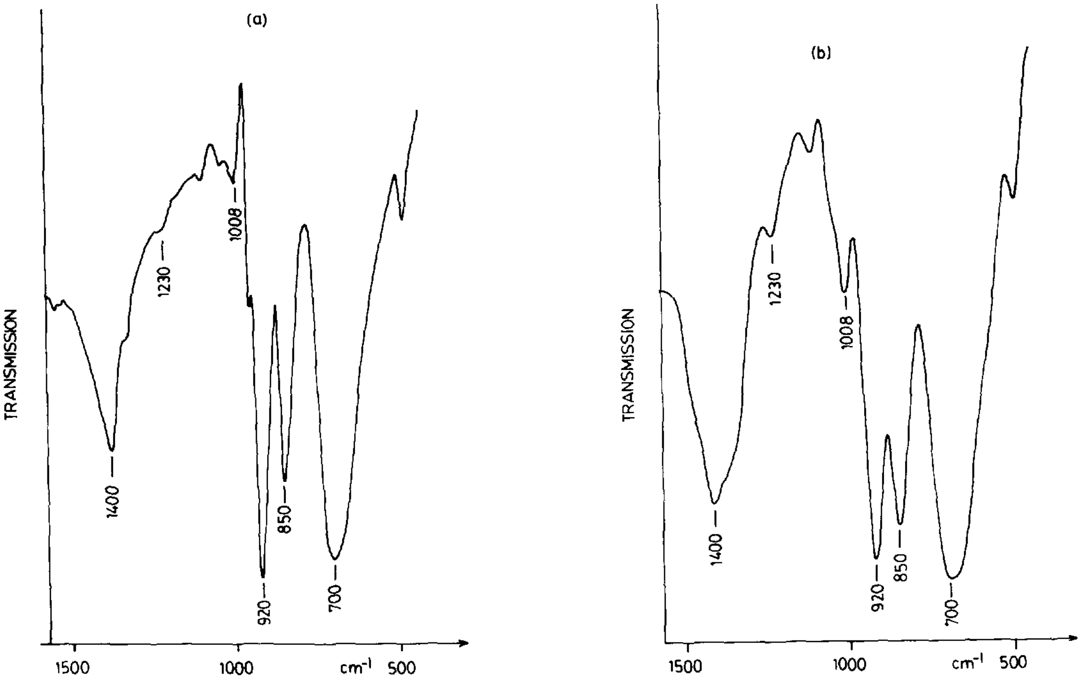

Fig. 2. Infrared spectra· (a) 2 mol% $B_2O_3$, and (b) 4 mol% $B_2O_3$.

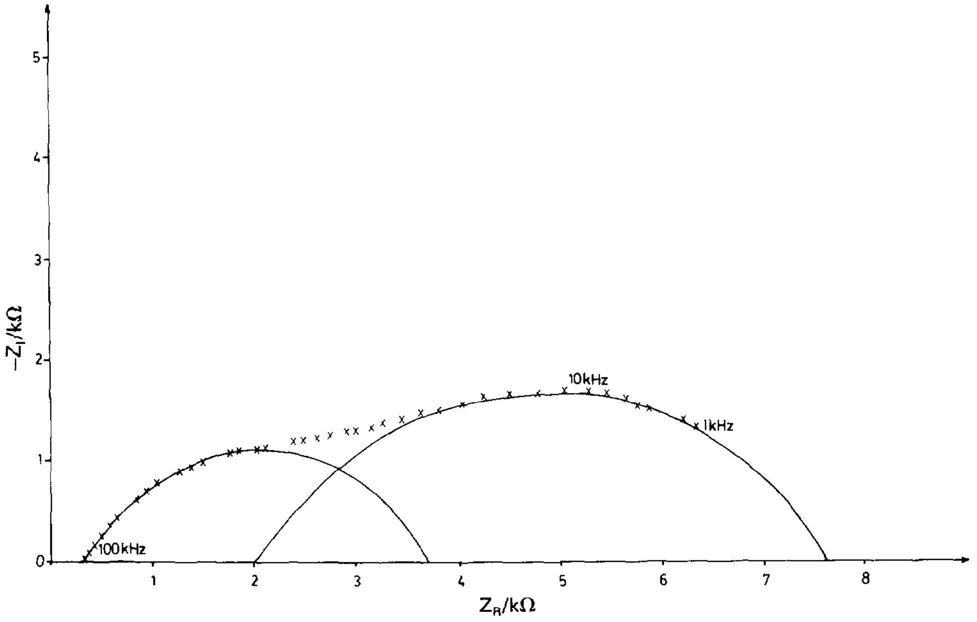

Fig. 3. Impedance plot of $60AgI–20Ag_2O–2B_2O_3–18V_2O_5$ glass

each circular side of the pellet with silver dag that covered the entire surface.

### 2.5. Battery fabrication

The anode of the batteries contains a mixture of silver powder size (2–3.5 μm) and glass in a weight ratio of 1:1. The weight of each component in the battery is given in Table 1.

The anode, electrolyte and cathode were pressed together into a three-layered disk at a compacting pressure of 14 MPa. This ensures that the contacts between the electrodes and the electrolyte is the same in all batteries. The diameter of each battery was 13 mm. The methods employed to measure the open-circuit voltage (OCV), internal resistance and discharge characteristics have been described elsewhere [3].

## 3. Results

The X-ray diffractograms of the glass and its chemical components are presented in Fig. 1. The infrared spec-

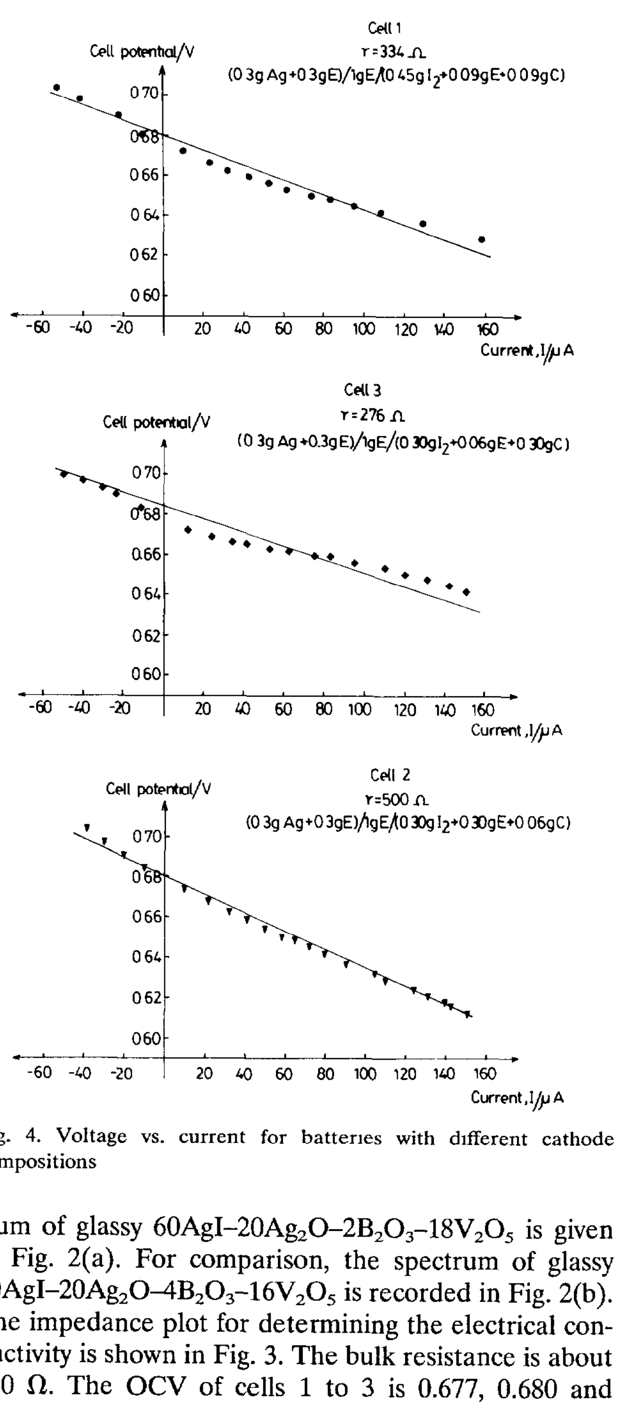

Fig. 4. Voltage vs. current for batteries with different cathode compositions

trum of glassy $60AgI–20Ag_2O–2B_2O_3–18V_2O_5$ is given in Fig. 2(a). For comparison, the spectrum of glassy $60AgI–20Ag_2O–4B_2O_3–16V_2O_5$ is recorded in Fig. 2(b). The impedance plot for determining the electrical conductivity is shown in Fig. 3. The bulk resistance is about 260 Ω. The OCV of cells 1 to 3 is 0.677, 0.680 and 0.676 V, respectively. By the e.m.f. method, the ionic transference number is at least 0.98. The internal resistance of cells 1 to 3 is 334, 500 and 276 Ω, respectively (Fig. 4). The discharge characteristics of the cells for a constant-current drawn of 100 μA are presented in Fig 5.

## 4. Discussion

The absence of peaks in the X-ray diffractograms confirms the glassy nature of the sample. The infrared spectra reveal bands at 1400, 1230, 1008, 920, 850 and 700 $cm^{-1}$. From infrared studies on silver borate glasses [4], the 1400 $cm^{-1}$ band is attributable to the vibration of the boroxol ring and the 1230 $cm^{-1}$ peak can be assigned to the B–O bond stretching of $(BO_3)^{3-}$ with a non-bridging oxygen (NBO) atom. This according to Ref. [4] is based on results from nuclear magnetic resonance (NMR) experiments of Ref. [3].

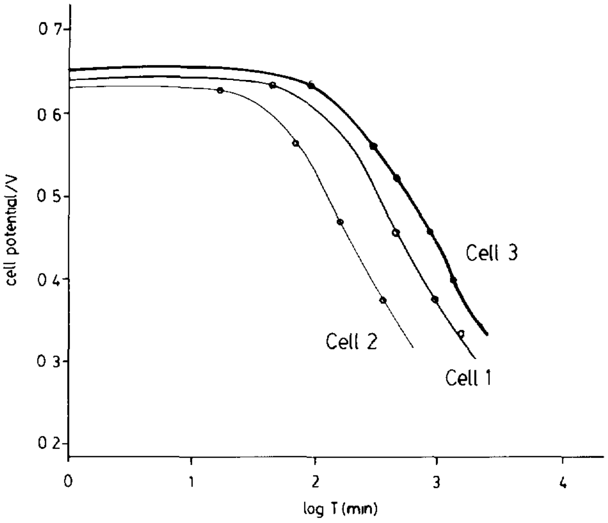

Fig. 5. Discharge characteristics of silver borovanadate batteries with different cathode compositions for a load current of 100 μA.

The bands in the region 850–1100 $cm^{-1}$ is due to B–O stretching of $(BO_4)^{5-}$ units [4]. Hence, the band observed at 850 $cm^{-1}$ in the present investigation is assigned to $(BO_4)^{5-}$ units.

The 700 $cm^{-1}$ band is the bond-bending vibration of B–O–B bridges of the boron network [4]. The bands attributable to vanadium oxide are located at 1008 and 920 $cm^{-1}$. The band at 1008 $cm^{-1}$ corresponds to the V–O stretching. Similar observations have been reported by Ghoneim [6]. The band at 920 $cm^{-1}$ corresponds to V=O vibrations. It has been reported [7,8] that, in vanadate glasses, this band occurs at 1020 $cm^{-1}$. Due to $Ag_2O$ interaction, this vibration no longer exists in the free state and is shifted to lower frequencies at 960 $cm^{-1}$ in $Ag_2O–V_2O_5$ glasses. With the introduction of $B_2O_3$ and the possible formation of other borate and vanadate complexes, this band could possibly shift further to lower frequencies, i.e., 920 $cm^{-1}$. We have also noted the possibility of this band occurring at 910 $cm^{-1}$ in silver vanadium molybdate $60AgI–20Ag_2O–4V_2O_5–16MoO_3$ glass [9]. The modifying effect of $Ag_2O$ on $V_2O_5$ has already been proposed [10].

The internal resistance for each battery can also be obtained from data at the beginning of the discharge characteristics. The voltage of cells 1 to 3 dropped to 0.640, 0.630 and 0.650 V, respectively, when a current of 100 μA was drawn from the cells. By definition, the internal resistance of cells 1 to 3 is 370, 500 and

260 Ω, respectively. These results are in reasonable agreement with those obtained from Fig. 4 and thus demonstrate the reliability of the internal resistance measurements.

The bulk resistance, as obtained from the impedance plot, appears to be in reasonable agreement with the internal resistance of the batteries. The difference can be attributed to the cathode composition since contact is assumed to be the same as the compacting pressure to form the battery disk is the same. Different carbon–electrolyte compositions could lead to different impedances, just as different electrolyte compositions result in different bulk resistances and conductivities. Hence, to improve the battery performance, the correct choice of cathode composition should be made.

## Conclusions

Internal-resistance measurements have shown that a mixture of five-parts active material, five-parts electron conductor, and one-part ionic conductor is an appropriate composition to use in solid-state batteries. With all other parameters except for the cathode composition kept constant, the battery with this cathode composition has the lowest internal resistance and longest discharge life.

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