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SOLID STATE ELECTROCHEMICAL ALKALI SOURCES FOR COLD ATOM SENSING

Jonathan J. Bernstein^{*1}, Alison Whale², Justin Brown^{1,4}, Cort Johnson¹, Eugene Cook¹, Laurent Calvez³, Xianghua Zhang³ and Steve W. Martin²

¹Draper, Massachusetts, USA

²Iowa State University, USA

³University of Rennes, France

⁴Currently at PSI Corp, Massachusetts, USA

ABSTRACT

Alkali sources are used as getters, to coat thermionic emission electrodes and to provide alkali atoms for precision quantum sensors such as clocks, magnetometers, accelerometers and gyroscopes. Commercial alkali sources are electrically heated to 400 - 700°C, driving a chemical reaction which produces the alkali. These sources use high current, high power, operate at high temperatures, turn on and off slowly, and evolve impurities. We report here on solid state electrolytic sources for the production of cesium and rubidium at temperatures of 80°C to 170°C. The advantages of electrolytic sources over thermally driven sources are reduced current and power consumption, faster turn-on and turn-off, the ability to monitor the quantity of generated alkali by current integration, and reduced temperature of operation. Resistivity and activation energy of the solid ionic conductors was measured vs. temperature. Alkali vapor pressure was detected by optical absorption in a custom vacuum system. Strong alkali signals (comparable to commercial sources) were measured when current was passed through the samples. Reversing the polarity of the applied voltage results in ambient alkali absorption. These Solid State Ambipolar Alkali Sources (SSAAS) show potential as high purity, precision alkali sources for cold atom sensors where size, weight and power must be reduced.

INTRODUCTION

Alkali sources have been used for decades to coat thermionic emission electrodes and as vacuum getters. Recently, laser-interrogated atomic sensors such as highly accurate clocks [1], magnetometers [2] and inertial sensors [3] have been developed. The most accurate of these sensors operate in a high vacuum, using alkali atoms trapped by magneto-optical traps (MOT's) prior to performing an optical or microwave based measurement of time, magnetic field or acceleration. For these sensors, clouds of $\sim 10^7$ atoms are needed. The alkali partial-pressure must be maintained at an acceptable level ($\sim 10^{-8}$ to $< 10^{-9}$ Torr) over a potentially wide environmental temperature range. The vapor pressure of the pure metals are too high for a solid Cs or Rb source to be used. Maintaining the correct background pressure of alkali is further complicated by the kinetics of absorption, adsorption and desorption from the vacuum chamber walls, particularly with glass which can absorb substantial quantities of alkali [4]. An ideal source would be low-power, fast, well-controlled and could also act as a sink to regulate alkali vapor pressure.

Commercial alkali sources from SAES [5] and Alvatec [6] use thermally driven chemical reactions to liberate alkali, and may produce contaminant gasses as well. Typically 4-8 amps is used to resistively heat the device to its operating temperature of 400-700°C [7], producing unwanted light, heat and magnetic fields which can interfere with sensor operation.

It has long been known that alkali can be produced by solid state electrolysis of glass [8, 9]. Gong et al. [10] demonstrated the

formation of Cs vapor cells by building a CsBO₃ glass piece into a vapor cell wall, and driving Cs into the cell using a molten salt anode at 325°C. Later, Cs generation was demonstrated with CsBO₃ glass as an independent source (not part of a vapor cell wall) and using a solid metal anode at 170°C [11].

Chalcogenide glasses based on S, Se or Te doped with alkali-halides have been extensively developed for infra-red optics, and are known to have higher ionic mobility than most oxide glasses [12]. Chalcogenide glass is also less hygroscopic than oxide glasses with high alkali content. Na-β'-alumina is a ceramic phase of Al₂O₃ and Na with high ionic mobility, which can be substituted for other alkali through a high temperature diffusion process [13].

We report here for the first time chalcogenide (sulfide and selenide) glasses doped with Cs and Rb and Rb-β-alumina which produce high purity alkali by electrolysis when small currents (μA-mA) are passed through them.

Figure 1 shows a cartoon of an electrochemical source, with Rb ions drifting from anode to cathode under a bias voltage. We have also demonstrated for the first time absorption of alkali by reversing the bias voltage of a Rb β-alumina source, allowing both emission and absorption of alkali with the same device. A silver anode provides charge compensating ions for the migrating Rb ions.

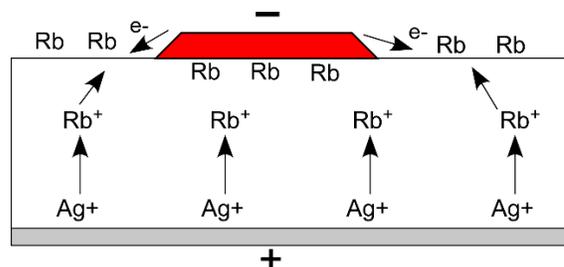


Figure 1. Cross-sectional diagram showing Rb ion migration through source from anode to cathode.

GLASS FABRICATION

Selenide glass (GeSe₂ + Ga₂Se₃) samples containing 30% or 40% CsI, and sulfide glass containing CsCl were produced at Iowa State University (ISU). Selenide glass with 25% or 30% RbI was produced at the University of Rennes. Rb-substituted β-alumina was obtained from Ionotec.

The glass samples from ISU were prepared from appropriate amounts of 99.99%+ purity constituent elements (Ge, Ga, Se, CsCl or CsI) then sealed in evacuated silica ampules. The silica glass ampules were placed in a rocking furnace and heated at 1°C/min to 850-950°C and then held for 12 hours. Different soaking temperatures were used to determine the optimum temperature. It was found that 950°C provided a high enough temperature to ensure complete reaction among the elements and yet not so high that vapor pressure would break the sealed glass tube. After soaking for 12 hours, the ampule was immediately transferred to a furnace that was

preheated to the glass annealing temperature of 250 to 270°C for four hours.

ELECTRODING

Anode: The back anode needs to inject mobile ions into the glass to avoid building up space charge as the alkali ions migrate up towards the cathode. This has proved a problem in previous work. In [10] a molten NaNO_3 salt anode was used as a source of compensating ions. Developers of high temperature alkali ion guns [14] using ion-exchanged Cs-mordenite electrolyte found that current flow was limited by anodic processes causing oxidation of the host lattice. Space charge formation led to a rise in voltage necessary to drive current through their device.

It is well known that metals such as Ag and Cu form non-blocking electrodes which inject ions into glass and have high ionic mobility [15]. For this reason continuous Ag electrodes were chosen for our anodes. The use of solid ion-injecting electrodes prevents development of space charge regions or oxidation of the host lattice anions.



Figure 2. $\text{CsI-GeSe}_2\text{-Ga}_2\text{Se}_3$ glass source with Al front electrodes.

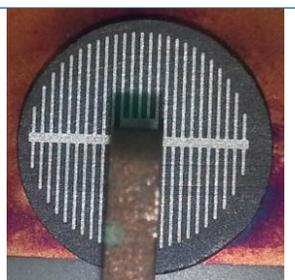


Figure 3. $\text{RbI-GeSe}_2\text{-Ga}_2\text{Se}_3$ glass source and spring contact.

Cathode: Cathodes were applied by evaporation of Al through an etched Invar shadow mask, held in place by magnets. The role of the cathode is to supply electrons to neutralize the alkali ions migrating to the surface. To allow the alkali atoms to evaporate without being blocked by the metal fingers, it is desirable to make these fingers narrow and to cover a small fraction of the front surface. Figures 2, 3 and 5 shows samples after application of the cathode finger array. These samples are 10-14 mm diameter and 1-3 mm thick. The shadow mask has finger widths resulting in 160 μm wide metal lines with 400 μm spacing, or about 60% open area.

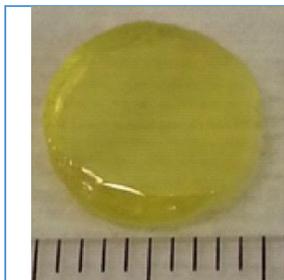


Figure 4. CsCl-sulfide glass without electrodes. Ruler markings are mm.



Figure 5. $\text{Rb } \beta'' \text{ alumina}$ source and spring contact.

EXPERIMENTAL METHODS

A vacuum chamber was constructed from a 6 port stainless steel cube for the measurement of alkali generation. A mechanically

backed turbo-pump was used for evacuation to the low 10^{-7} Torr range after bake-out. This pump could be valved off and an ion pump used to maintain vacuum.

A multi-pin electrical feedthrough to the chamber has connections for a small ceramic heater with built-in thermocouple, high voltage and ground to drive the solid state source, and driving a commercial source from SAES or Alvatec, used for demonstrating alkali absorption.

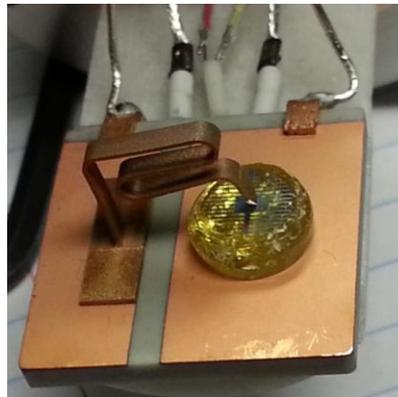


Figure 6. 25 mm X 25 mm heater, CsCl-sulfide glass sample and Be-Cu spring clip.

Alkali Measurement: A diode laser tuned to an optical transition of the alkali species of interest is passed through the chamber just above the sample to measure the concentration of each alkali [Cs] or [Rb]. To detect small absorption signals we used a lock-in detection method, the block diagram of which is shown in Figure 7. Phase modulation is applied using an electro-optic modulator (EOM) to put 2 GHz sidebands on laser light locked to an atomic transition. The EOM is driven almost to carrier suppression such that most of the optical power is in the sidebands. These sidebands are sufficiently detuned from the Doppler broadened atomic transition (~ 1 GHz) to pass through the vapor with minimal absorption. An RF switch driven with a 32 kHz square wave gates between light on-resonance and (modulated) light off-resonance.

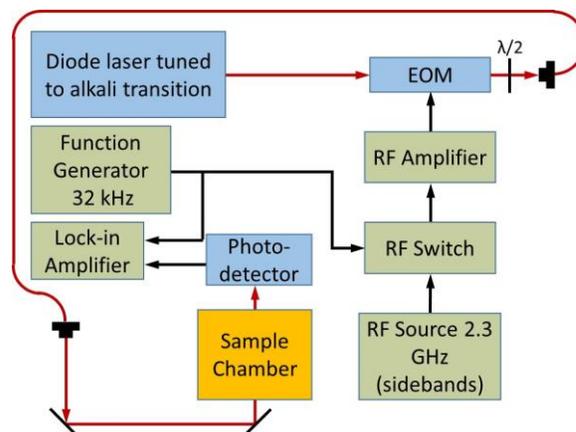


Figure 7. Electro-optical detection block diagram.

A lock-in amplifier referenced to the 10 kHz modulation provides the change in amplitude due to the absorption. The sensitivity of the measurement is currently limited by residual amplitude modulation of the EOM to Cs vapor densities of

$\sim 1 \times 10^8 / \text{cm}^3$. The detected alkali density is calibrated using standard alkali vapor cells (e.g. Thorlabs GC25075-CS).

CONDUCTIVITY MEASUREMENTS

The alkali ion conductivity vs. temperature was measured at ISU by small signal AC impedance techniques extrapolated to DC, after applying and baking silver paint electrodes on both sides. Results for 6 samples (5 material compositions) are shown in Figure 8. The β'' alumina has the highest conductivity. The Rb and Cs doped selenide glasses have a conductivity which depends strongly on the concentration of alkali [12], although activation energy for the various glass samples is similar at ~ 0.77 eV. High conductivity is an advantage as it allows operation at lower voltages and temperatures.

DC current-voltage vs. temperature measurements were made using evaporated Al finger electrodes on the front, and continuous silver electrodes on the back. Due to various effects including current crowding, space charge and electrode interfacial reactions, the ionic conductivity measured this way is typically 100X lower than the small signal AC measurements. A plot of current-voltage vs. temperature for a CsCl-sulfide glass is shown in Figure 9.

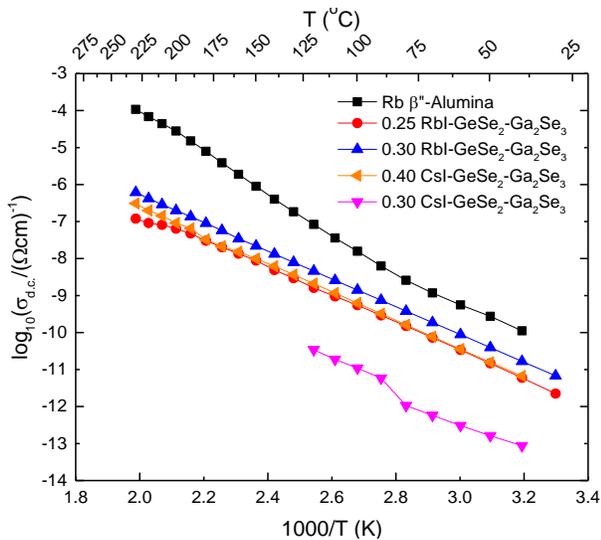


Figure 8. Log_{10} conductivity (AC impedance technique) vs. $1000/T(K)$ for 5 materials.

ALKALI EMISSION

Samples were placed on the ceramic heater in the vacuum system, held in place by a Be-Cu spring which also connects electrically to the top finger array. The resonant laser was directed over the top surface of the glass sample and its absorption was measured to determine the alkali vapor concentration. Alkali density was calibrated by comparison with the absorption of standard Cs or Rb vapor cells maintained at a known temperature.

CsCl-Sulfide Glass: A sample of CsCl-GeSe₂-Ga₂Se₃ glass from ISU was metallized with Ag on the back and Al fingers on the front. Current-voltage curves with temperature as a parameter were measured, shown in Figure 9. The current roughly doubles for every 10°C increase in temperature.

Cs vapor emission from this sulfide glass as measured by laser absorption is shown in Figure 10, held at 130°C with a bias voltage of 1200 V and current of 5 μA , cycled on and off twice. Cs losses are primarily to the chamber walls and (much less) to the pumps.

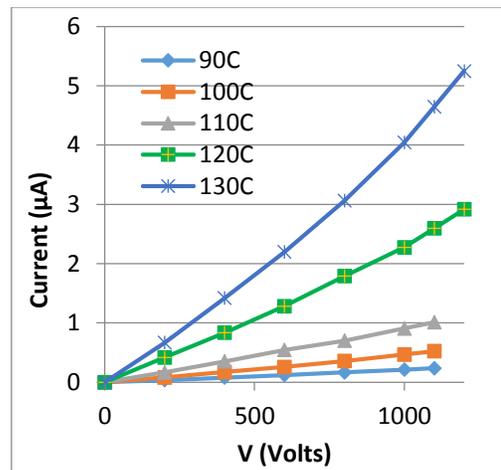


Figure 9. DC current-voltage-temperature plot for CsCl- Ge-Ga-sulfide glass shown in Figure 4.

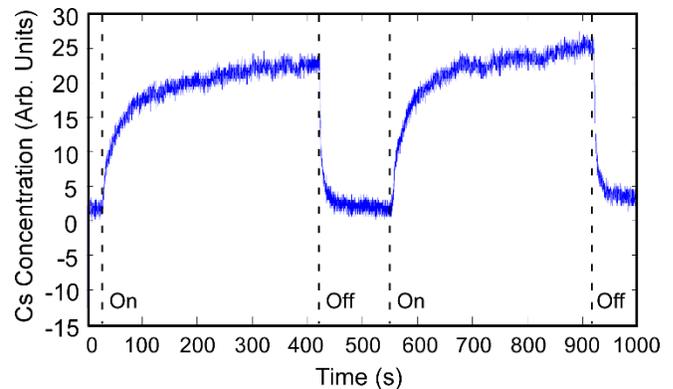


Figure 10. Optical absorption signal for Cs emission from sulfide glass sample at 130°C. Current through sample is 5 μA .

CsI-GeSe₂-Ga₂Se₃ Glass: A 40% CsI doped selenide glass supplied by ISU was electroded with Al fingers (cathode) and continuous Ag or Cu (anode). Strong Cs generation signals were measured after biasing to 1 kV at 170°C and 44-50 μA (Figure 11).

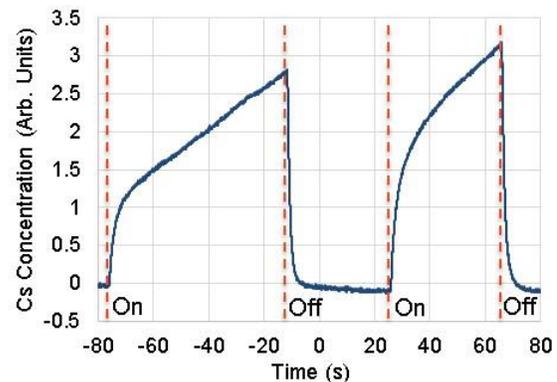


Figure 11. Cs generation from CsI-GeSe₂-Ga₂Se₃ glass.

Kinetics of alkali absorption and desorption from the chamber walls largely determine the concentrations and rate of change of the measured alkali in vacuum. Curve fitting the decay time of the Cs concentration shown in (e.g. Figure 11) gave a value of 1.25 s regardless of whether the chamber is sealed or actively pumped,

because at low pressure the chamber walls dominate the alkali partial pressure kinetics. Due to chamber wall effects, we do not yet know how fast the solid state sources can be turned on and off, but it is likely much faster than the present generation of thermally driven sources [16].

RbI GeSe₂-Ga₂Se₃ Glass: A RbI doped glass supplied by the University of Rennes was electroded in a similar manner to the previous samples (Al cathode fingers and continuous Ag back anode). Strong Rb absorption signals were seen when the glass was forward biased at 170°C and 1 kV, (Figure 12). Current through the sample increased from 80 μ A to 250 μ A at constant voltage, which is most likely due to sample self-heating. A constant current drive would provide improved stability compared to constant voltage.

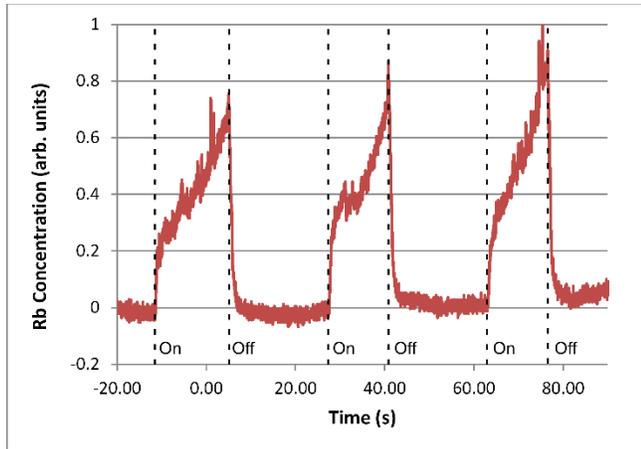


Figure 12. Rb generation signal from 30% RbI doped selenide glass.

β'' Alumina Ceramic: Figure 13 shows Rb emission from a Rb β'' alumina sample biased at 50 volts and a current of 0.7 mA at 120°C. Calibration of the atom density was performed by comparison with a standard Rb filled ampule. The strength of the Rb signal from this source was comparable to that from a SAES Rb source driven at 5 amps. The higher mobility of Rb in the β'' alumina allows this source to operate at reduced temperature and voltage.

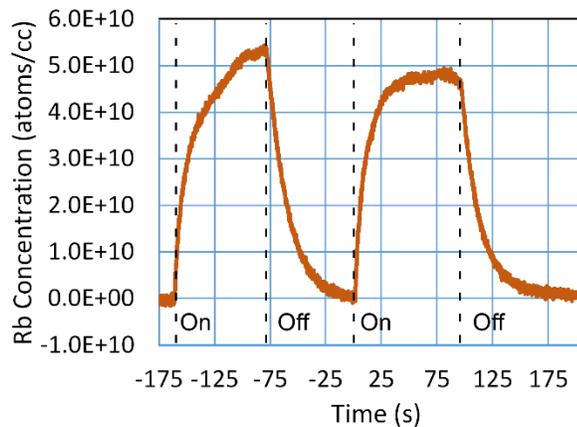


Figure 13. Rb generation from Rb doped β'' alumina.

Alkali Absorption: By reverse biasing the device, a surface region depleted of alkali ions is created. This ion-depletion region

is capable of absorbing incident alkali atoms, ionizing them and driving ions into the bulk. To demonstrate absorption, a Rb SAES source was mounted in the chamber and run at 4.88 amps for several minutes to establish a constant background Rb pressure. A Rb doped β'' alumina source was then reverse biased at -130 V (-0.21 mA) and 130°C, creating a Rb depleted surface while the SAES source was left on. The measured Rb concentration was reduced by 30-50%, as shown in Figure 14. Considering the small size of the SSAAS device ($\sim 1.1\text{cm}^2$) compared to the chamber walls ($> 280\text{cm}^2$), this demonstrates remarkably efficient absorption.

The measured Rb concentration is an integral over the path of the laser through the vacuum system. At each point in the path, the vapor pressure is proportional to an average over the entire 4π steradians solid angle of the incident flux of alkali atoms emitted from the surrounding surfaces. The laser passes close to the surface of the SSAAS device, and for that part of the integral, the SSAAS device is almost half the solid angle.

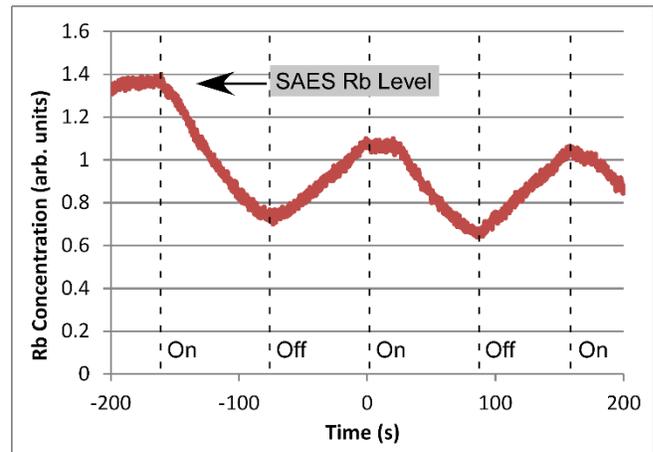


Figure 14. SSAAS device reverse biased as absorber. Background level set by SAES source at 4.88 A. SSAAS absorber turned on and off several times is able to absorb 50% of the Rb produced by the SAES source.

CONCLUSIONS

We have demonstrated solid state electrochemical alkali sources which, when compared to commercial thermally driven chemical sources, require greatly reduced current and power, operate at lower temperatures (70-170°C, compared to 400-700°C), exhibit faster turn-on and turn-off, and can both source and sink alkali using direct current control. The output of alkali was demonstrated to be comparable in magnitude to commercial SAES alkali sources consuming 5 amps.

Cold atom clouds formed in Magneto-Optical Traps (MOT's) used in high precision atomic clocks, magnetometers and inertial sensors require only about 10^6 to 10^8 atoms in a typical measurement. Solid state electrochemical sources will reduce the power, current and temperature required to produce alkali atoms by orders of magnitude. As cold-atom sensors enter the marketplace they will benefit from the high purity, small size and low power offered by these novel solid state atom sources.

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are those of the authors and do not reflect the official policy or position of the Department of Defense or the U.S. Government.

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CONTACT

J. J. Bernstein, tel: +1 617-258-2513, jbernstein@draper.com