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**"ELECTROCHROMIC + ANTI-FOG PERSONAL-PROTECTIVE
EYEWEAR (PPE) BASED ON UNIQUE,
VERY LOW POWER, CONDUCTIVE COATINGS AND LEVERAGING
UNIQUE, ANSI Z87.1-/MILITARY-QUALIFIED
ELECTROCHROMIC EYEWEAR TECHNOLOGY"**

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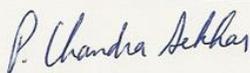
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LIST OF TERMS AND ABBREVIATIONS

CP Conducting Polymer

CV Cyclic Voltammogram

IR Infrared

ITO Indium Tin Oxide

NIH National Institutes of Health

NIOSH National Institute of Occupational Safety and Health (one of the NIH institutes)

OSHA (US) Occupational Safety and Health Administration

PPE Personal Protective Eyewear

UV-Vis Ultraviolet-Visible

ABSTRACT

This project sought to address the need for Personal Protective Eyewear (PPE) technologies in high risk industrial sectors such as manufacturing, mining, construction, environmental remediation and warehousing relating to the worker transitioning from very bright to dark areas, with fogging of protective eyewear exacerbating the situation [1-9]. Per recent OSHA statistics [1-2], the number of fatal accidents potentially caused by light/dark (L/D) plus fogging issues may be up to 30% of the total (3.2/100,000 workers, 2012), with non-fatal accidents having a similar proportion. In Ebola work, frequently in hot, humid, sunny environments, the suit wearer critically needs automated, hands-free L/D and antifogging control. Current PPE technologies for L/D control, e.g. photochromics, clip-on sunshades/-extra sunglasses, are inadequate. Similarly, PPE antifogging technologies, e.g. superhydrophilic/-oleophobic coatings, or double-pane polycarbonate, are also grossly inadequate, with the US Army Public Health Command even specifically prohibiting these.

Now in very recent work prior to this Phase I project, this firm developed and patented [82] a new, automated-function electrochromics technology, based on unique, matched-dual-polymer conducting polymer electrochromics (which change color with small, e.g. 5 VDC, applied voltage). This overcame drawbacks that heretofore prevented practical, commercial electrochromic eyewear. Fully functional, automated-operation electrochromic spectacles and goggles conforming to ANSI Z87.1-2010 and US military specifications were demonstrated. In separate, preliminary work, this firm also developed a new, unique, active anti-fogging technology, based on mild heating of specially designed, transparent, conductive electrodes; this direct defogging approach overcame the poor performance of indirect approaches such as superhydrophobic coatings.

The present Phase I project sought to combine these two unique technologies to yield PPE with *combined L/D control plus anti-fogging capabilities*.

The achievements of the present project can be briefly summarized as follows: **(1)** All objectives of the original Phase I project eminently achieved, and in many cases exceeded. **(2)** Fully functional, automated (photosensor-activated), PPE (spectacles as well as goggles) with combined (electrochromic + defogging) function developed, fabricated tested. **(3)** These showed **5 to 6 seconds** defogging times. **(4)** These prototypes used two types of conductive films, selected from seven evaluated in detail. **(5)** This firm's existing electrochromics Microcontroller was modified to accommodate electronics for driving the defog function. **(6)** Several humidity sensors were evaluated for automated function of the defog capability based on internal/external humidity parameters, and two selected for further use in potential Phase II work. Meanwhile, a simple On/Off operation of the defog function was demonstrated in the Phase I prototypes. **(7)** A refined CAD design was completed for the fully functional, automated (photosensor-activated), PPE spectacles with combined (electrochromic + defogging) function, to be used for pilot-plant manufacture in potential Phase II work. **(8)** Semi-automated and automated instrumentation was designed and developed for the key electrochemical polymerization ("electroplating") and processing steps for medium-scale manufacture of the PPE. **(9)** A clear pathway was demonstrated for potential Phase II work that would lead directly to a semi-automated, demonstration pilot plant for inexpensive manufacture of 1,000 PPE pieces per month (12,000 per year) with estimated cost of < \$60 per PPE piece.

1. SECTION 1

1.1 NEED, IN BRIEF

With regard to Personal Protective Eyewear (PPE) technologies, a major *occupational hazard* in high risk industrial sectors such as *manufacturing, mining, construction, environmental remediation and warehousing* (but one which has received very limited attention to date) is that associated with *the worker transitioning from very bright to dark areas; fogging* of protective eyewear exacerbates the situation [1-9]. This is especially amplified in, e.g., protective suits worn in **Ebola** work, which must generally be worn in hot, humid, sunny environments. Per recent OSHA statistics [1-2], the number of *fatal* accidents potentially caused by **light/dark (L/D)** plus **fogging** issues may be up to 30% of the total (4,383 in 2012, 3.2/100,000 workers), with non-fatal accidents having a similar proportion. In Ebola work, the suit wearer critically needs *automated, hands-free* L/D and antifogging control. Current PPE technologies for L/D control, e.g. photochromics (which change color with UV light and don't work indoors or in cars), clip-on sunshades or extra sunglasses, are inadequate. Similarly, PPE technologies for antifogging, e.g. superhydrophilic coatings or double-pane polycarbonate are also grossly inadequate. Indeed, the US Army Public Health Command specifically prohibits photochromics or clip-ons for military personnel in outdoor/indoor settings.

1.2 OBJECTIVES OF THE WORK, IN BRIEF

Now in very recent work prior to this Phase I project, this firm developed and patented [82, 31-46] a new, automated-function *electrochromics* technology, based on unique, *matched-dual-polymer* conducting polymer *electrochromics* (which change color with small, e.g. 5 VDC, applied voltage). This has excellent performance, and overcomes drawbacks that have heretofore prevented practical, commercial electrochromic eyewear. Typical performance: very high L/D contrast, 1% to 70% (vs. *air* reference); thin (< 0.4 mm), flexible, durable lens construction; unique applied-potential algorithm residing on an inexpensive (<\$8) Microcontroller yielding switching times of < 2 s L→D, ~instantaneous D→L; automated-function (photosensor-based, Li battery-powered), electrochromic spectacles/ goggles demonstrated; very low power (3 days operation before Li batteries need recharging; 15 μW/cm², +/- 3.0 VDC); demonstrated as retrofit to spectacles/goggles conforming to ANSI Z87.1-2010 and US military specifications. In separate, preliminary work, this firm also developed a new, unique, *active* anti-fogging technology, based on mild heating of specially designed, transparent, conductive electrodes; this direct defogging approach overcame the poor performance and many drawbacks of indirect approaches such as superhydrophobic coatings.

The present Phase I project sought to *combine these unique electrochromics and antifogging technologies to yield PPE with combined L/D control and anti-fogging capabilities*. The simple of combination of the two technologies was via deposition of the above-described defogging conductive coating on *one side* (the inner side) of the electrochromic lens, to use the same Li battery to power the defogging, and to incorporate the defogging function into the Microcontroller as well. The broad technical objectives were: (1) To clearly demonstrate the new anti-fogging technology. (2) To combine this with the electrochromics technology to produce proof-of-concept, prototype, (electrochromic + anti-fogging)-function eyewear.

1.3 SIGNIFICANT (KEY) FINDINGS

It should be mentioned at the outset that the key overall objectives of this project, *to clearly demonstrate the new anti-fogging technology and then to combine this with the electrochromics technology to produce proof-of-concept, prototype, electrochromic+anti-fogging PPE eyewear (as both sunglasses and goggles), were eminently achieved*.

Findings in summary: (1) A very large number and type of conductive, transparent coatings were fabricated and tested for defogging capabilities, and the best ones identified both in terms of performance and also compatibility with our electrochromics technology. (2) The final PPE eyewear developed as a

deliverable in the present project incorporated a single lens piece with the electrochromic function further refined for the present project, and with a specially designed conductive coating on the inside of the lens (facing the eye) with the antifogging capability. The electrochromic function was automated, via a photosensor and complex Microcontroller such that the light intensity falling on the wearer's eye was a constant, preselected value. The antifogging capability was triggered by a manual switch in this Phase I (to be automated in Phase II). (Insets at right show photos of the spectacles version of this final prototype deliverable, which combines the automated electrochromic and defogging functions; for detail, see Section 2 below.) (3) Defogging was shown to occur to a **within 6 seconds**. (4) It was shown that defogging could be accomplished via off-the-shelf Li batteries, with a full day's (8 hours) expected defogging use before recharging was necessary. (5) The existing Microcontroller for this firm's current electrochromic sunglasses was modified to accommodate the electronics for driver for the defog function (6) It was demonstrated that humidity sensors could be used in the control loop for auto-On/Off of the defogging function. (7) A CAD design for the final PPE sunglasses, including a single Microcontroller for both electrochromic and defogging functions, two separate Li batteries for each of these functions, and automated function of the defogging capability through combined use of a humidity sensor and the photosensor, were arrived at. (8) Semi-automated instrumentation was designed, developed for medium-scale manufacture of the PPE. (9) xx Clear pathway demonstrated for potential Phase II work that would lead directly to a semi-automated, demonstration pilot plant for inexpensive manufacture of 1,000 PPE pieces per month (12,000 per year) with estimated cost of < \$60 per PPE piece.



1.4 TRANSLATION OF FINDINGS

As noted above, a PPE technology that allows automated, independent (e.g. hands-free) function of persons in work environments that involve frequent and/or rapid transitions between L/D, and fogging up (due to the environment, to being heavily suited up, or both), is sorely lacking to date. A technology that combines rapid, high-contrast, automated electrochromic function and rapid, efficient, automated defogging, as successfully developed in the present project, would ideally and eminently address this need. The specific workplace environments or fields addressed include the *factory floor* (e.g. assembly-line workers), *warehousing* (e.g. forklift drivers heading in/out of L/D, low/high-humidity areas), *construction sites*, *environmental or hospital workers* (when suited up and/or wearing PPE), *military* (soldiers in the field, especially those in HazMat suits), and even *truck drivers*. Per the above-cited OSHA studies [1-2], up to 30% of the 4,383 workplace fatalities in 2012 may be ascribed to a combination of L/D and fogging issues. Furthermore, the extension to other markets such as sports (motorcycle visors, bicycling eyewear, extreme sports) and extreme environments would create a much larger market leading to lower prices for the NIOSH-addressed workplace market. The method of application to the workplace would be adoption of the combination electrochromic + defogging PPE as *required* safety gear for the above workplace categories.

1.5 OUTCOMES/IMPACT

Potential outcomes: A possible, future Phase II project would further develop the technology and demonstrate pilot commercial production. As described above, if commercially implemented, the technology would drastically reduce the OSHA-documented [1-2] workplace fatalities and injuries ascribed to L/D and fogging issues, impacting the following workplaces: *factory floor/industrial workers*; *warehousing*; *construction sites*; *environmental or hospital workers* *military (soldiers)*; *truck drivers*.

Intermediate and end outcomes: As this is a Phase I SBIR project, intermediate and end outcomes of this work have not yet been realized, but are expected to be realized at the end of potential Phase II work. These are expected to include drastic reduction of fatalities and injuries ascribed by recent OSHA studies to L/D and fogging issues.

2. SECTION 2

2.1 BACKGROUND, NEED, COMPETING TECHNOLOGIES

Background and Need: As briefly noted above, with regard to Personal Protective Eyewear (PPE) technologies, a major *occupational hazard* in high risk industrial sectors such as *manufacturing, mining, construction, environmental remediation* and *warehousing* (but one which has received very limited attention to date) is that associated with *the worker transitioning from very bright to dark areas* (typically indoors or in heavy shade to outdoors or brightly-lit indoor areas, but also between dark and well-lit areas of a factory floor). **Fogging** of protective eyewear exacerbates the situation [1-9]. This is especially amplified in, e.g., protective suits worn in *Ebola* work, which must generally be worn in hot, humid, sunny environments. Per recent OSHA statistics [1-2], the number of *fatal* accidents potentially caused by **light/dark (L/D) plus fogging issues** may be up to 30% of the total (4,383 in 2012, 3.2/100,000 workers). Non-fatal accidents are an even larger proportion; and although the proportion of these due solely to light/dark transition problems is unavailable, descriptions ("fall", "struck by object", "caught in/between") suggest they may play a strong part [1-9]. And in a recent study, 100% of construction, service and retail workers cited fogging as a factor for *not wearing* or *removing* required protective eyewear [6]. In *Ebola* work, the suit wearer critically needs *automated, hands-free* L/D and antifogging control. If an adequate, relatively inexpensive technology combining efficient electrochromic + defogging function could be made available, it would lead to a very significant improvement in safety in the workplaces and environments identified above (manufacturing, mining, construction, environmental remediation and warehousing).

Competing technologies: Current PPE technologies for L/D control are grossly inadequate. For example, *photochromics* (which lighten/darken with light) require UV light for operation and so don't work indoors or in cars. Clip-on sunshades or multiple, extra sunglasses, are inadequate and of course require the wearers constant input, i.e. are not automatic. Electrochromics based on metal oxides [15-17] or, more recently, *conducting polymers (CPs)* [18-30], have shown performance, in terms of parameters such as light/dark (L/D) contrast, L/D switching time, cyclability (number of switches), durability, and cost, that has been seriously inadequate (see also detail below). Similarly, PPE technologies for *antifogging*, e.g. superhydrophilic and oleophobic coatings [11-12] or double-pane polycarbonate, achieve inadequate defogging under extreme working conditions, e.g. in an *Ebola* suit. indeed, the US Army Public Health Command specifically prohibits photochromics for military personnel in outdoor/indoor settings [3-4], and OSHA strongly recommends against them [2, 8]. These agencies also view clip-on sunshades or extra sunglasses as very poor in addressing this risk [2-5].

2.2 BASIS OF TECHNOLOGY

Electrochromics component: With regard to the *electrochromics component* of our technology (see **Figs. 1, 2** below for a concise summary of its status *prior to the start of this Phase I project*), in very recent prior and ongoing work [31-41], this firm has developed and patented [36-41, 82] a new electrochromics technology based on unique, *matched-dual-polymer*, CP electrochromics with the following features (see <https://ashwin-ushas.com/electrochromic-sunglasses-goggles/>): **(1)** Nearly perfectly-matched, *new*, cathodically- and anodically-coloring CPs ("dual-polymer"), in contrast to all prior dual-polymer electrochromics [42-60] which have poor matching; this leads to very high L/D contrast (1% to 70% Transmission, integrated over the Visible spectrum, against *air* reference, "dialable" to any value in between), high cyclability (> 10 K cycles), long shelf life (> 2 years), desirable color change (near-transparent to dark-blue-black), high durability. **(2)** Very thin (< 0.4 mm), flexible durable lens construction

(base substrates 7 mil ITO/Mylar, which are *naturally UV-blocking*). **(3)** A unique applied-potential algorithm residing on an inexpensive (<\$8) Microcontroller that drastically reduces switching time (< 2 s L→D, ~instantaneous D→L). **(4)** Unique design with fully automated, photosensor-based control based on ambient light, rechargeable Li batteries. **(5)** Very low power consumption (72 hours continuous function with 12 L/D/L switches per hour before the Li batteries need recharging; 15 $\mu\text{W}/\text{cm}^2$, +/- 3.0 VDC). **(6)** Demonstrated as retrofit to Smith Optics safety spectacles and goggles conforming to *ANSI Z87.1-2010* and *GL-PD 10-12 (US military, APEL)* specifications [61-62]. **(7)** Initial prototype, *ab-initio* design of safety spectacles seamlessly and invisibly incorporating electrochromic lens, Li batteries, Microcontroller, photosensor, electrical conduits. **(8)** Initial issues of high-volume manufacture (e.g. electrodeposition of the CPs) addressed. **(9)** Estimated very low cost (<\$60 pair). **(10)** Established teaming with eyewear manufacturers (Smith Optics, Oakley, Tag-Heuer). **(11)** Well protected by patents [36-41], including patents that have issued during this Phase I project [82].

Our now-patented [82, 36-41] **electrochromics** technology is based on cathodically- and anodically-coloring polymers [42-60] which are nearly perfectly matched electrochromically and electrochemically [82, 31-41]. This near-perfect matching, achieved for the first time, means that at the applied potential (voltage) that one polymer is fully oxidized, the other polymer is fully reduced, and vice versa; it overcomes major drawbacks of extant dual-polymer electrochromics and leads to unequaled performance, as measured by parameters such as light/dark (L/D) contrast, L/D switching time, cyclability, shelf life and durability. The cathodically-coloring polymers used are newly synthesized Cl-, Br- and NH₂- substituted derivatives of poly(dibenzyl propylene dioxythiophene) (P(DiBz-ProDOT)) [63-74], used individually as well as as copolymers. The anodically-coloring polymers are copolymer poly(aromatic amines) [34, 75-82]. Importantly, *haze*, an important parameter in the industry that measures vision distortion, is < 2% for D and L states of all our lenses (desired <6%). Our electrochromic lenses have been *retrofitted* to ANSI-Z87.1-2010- MIL-PRF-32432- and GL-PD 10-12 (US military) qualified industrial- and military-safety spectacles and goggles [61-62], with incorporated Microcontroller, rechargeable Li battery/recharge port, and electrical wiring/connections. The result is functional, industrial-safety sunwear with automated (photosensor-based) operation that maintains a constant, user-selected light level at the eye. (See videos of these functioning at: <https://ashwin-ushas.com/electrochromic-sunglasses-goggles/>.) In further work, an *ab-initio* design has been arrived at for spectacles and goggles frames in which these components (Microcontroller etc.) are seamlessly and invisibly incorporated into the frame. This still uses an outer, polycarbonate lens with the ITO/Mylar (Mylar= poly(ethylene terephthalate), PET) based electrochromic lens now bonded to the polycarbonate with UV-cured, optically transparent adhesive. The inexpensive (<\$8) Microcontroller uses a unique, patented [82, 36-41] algorithm that applies overvoltages, for very short periods of time (order of ms), to drastically reduce switching times. The data/Figures below summarize some of the features of our technology.

Defogging component: This component of our technology is based on the premise that *simple heating of a surface, if available, still remains the best (and simplest) defogging method*, without the complications involved in such technologies as superhydrophilic or oleophobic coatings [11-12]. *Transparent, inert conductive coatings*, such as ITO/Mylar (ITO= indium tin oxide), exactly as used in our current electrochromic lenses, are put down on the *inside* surface of the eyewear, where fogging occurs, to serve as *very low-power resistive heaters*. (The surface resistivity (i.e. conductivity), determines heat generated, via $P=V^2/R$, where P = heat power generated, V =voltage applied, R =resistance.) Such heating uses low, DC voltages (< 9 VDC) and low power. That is to say, one of the two ITO/Mylar substrates used in our electrochromic lenses (cf. Fig. 1(a) below), specifically, the one closest to the user's eye, has an additional, conductive coating; i.e., it will be ITO/Mylar/ITO. (In the Phase I work, in addition to ITO, other transparent conductive coatings, such as Ag nanowire coatings, were tested and found seriously deficient.) With smart control (using an adaptation of our current electrochromics Microcontroller), power is turned on only when fogging is desired, drastically lowering power requirements. *Prior to this Phase I effort*, our defogging technology had been demonstrated to a very basic, proof-of-concept level (data in

Phase I proposal). This pre-Phase-I status is summarized in **Fig. 3** below. As the Phase I results below show, this defogging technology has been highly successful, beyond expectation.

Fig. 1: Status of our electrochromics technology prior to the start of this Phase I project: (a) Schematic of Ashwin dual-polymer **electrochromic lens** (CP= conducting polymer). (b) Typical lens edge-on, flexed showing exceptional thinness/durability. (c(1,2)) Typical light/dark (L/D) contrast of rectangular lens, hooked up to Microcontroller chip (see description further below). (d) Microcontroller (with cm-scale). (e) L/D spectra of typical standard electrochromic lens. *NOTE: Our spectra are against air reference, i.e. real-life.* In comparison, most published data of others use substrates (i.e. minus the active electrochromic) in the reference compartment of the spectrometer, thus yielding light-state %T of > 90% in many cases (whereas the %T of even clear glass is only ca. 90%!). (f) L/D spectra of typical "very dark" electrochromic lens. (g) L/D spectra of typical "high contrast" electrochromic lens. (h) Typical L/D switching data of "standard" lens. (i) Switching times with standard lab potentiostat applying ± 1.1 V to switch the lens vs. Microcontroller using Algorithms A and C (showing drastic reduction with Microcontroller). (j) Long term cyclability data: 0 and 10,000 cycles.

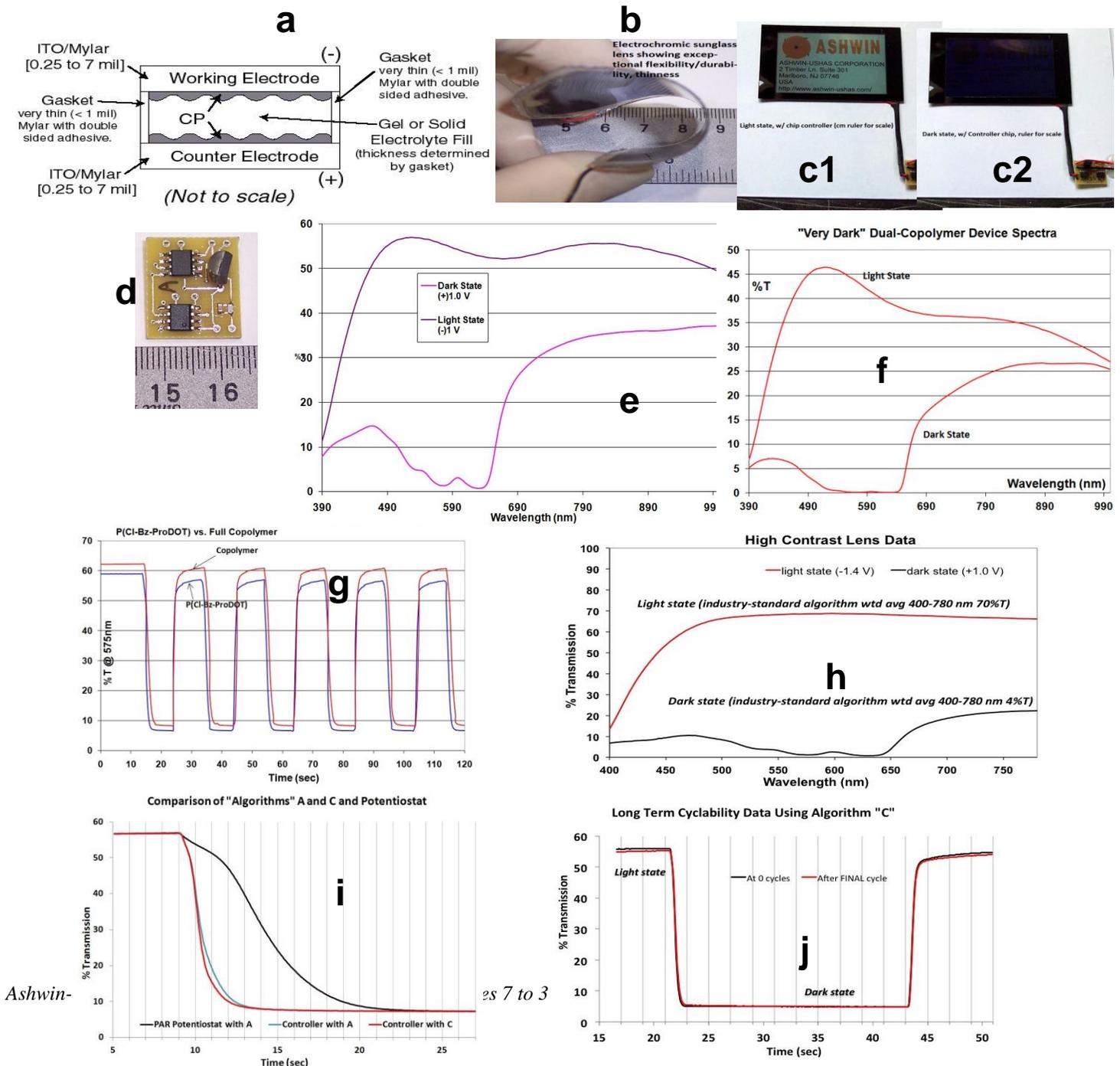


Fig. 2: Status of our electrochromics technology prior to the start of this Phase I project, cont.: Our electrochromic lenses retrofitted to existing safety eyewear: Retrofit of the Smith Optics Elite Model # AEGABK12-2R ("Aegis arc eyeshield") safety spectacles, and Smith Optics Elite Model # OTW01BK12-2R ("Outside-the-wire goggle") goggles, both of which conform to ANSI Z87.1 and GL-PD 10-12 (US military) specifications. **(a)** Electrochromic lens. **(b)** Elements of the spectacles frame, disassembled. **(c)** Schematic of the retrofit of spectacles. **(d)** Photo of actual, retrofitted spectacles. **(e(1,2))** Photos of a user wearing retrofitted spectacles, in light, dark state. (A video of their automated, photosensor-based operation is available elsewhere at: <http://www.youtube.com/watch?v=yDA-Z0YauM0>). **(f)** Schematic of retrofitted goggles. **(g)** Photo of actual, retrofitted goggles. **(h)** Schematic of *Ab-initio* spectacles frame and sunglasses (design completed December 2013), which seamlessly and invisibly incorporates all components, such as Li battery, photosensor, microcontroller, wiring, recharge port. A snap-in prescription-insert is also included for users wearing prescriptions. **(i(1,2))** Actual, first-iteration 3-D print of this design.

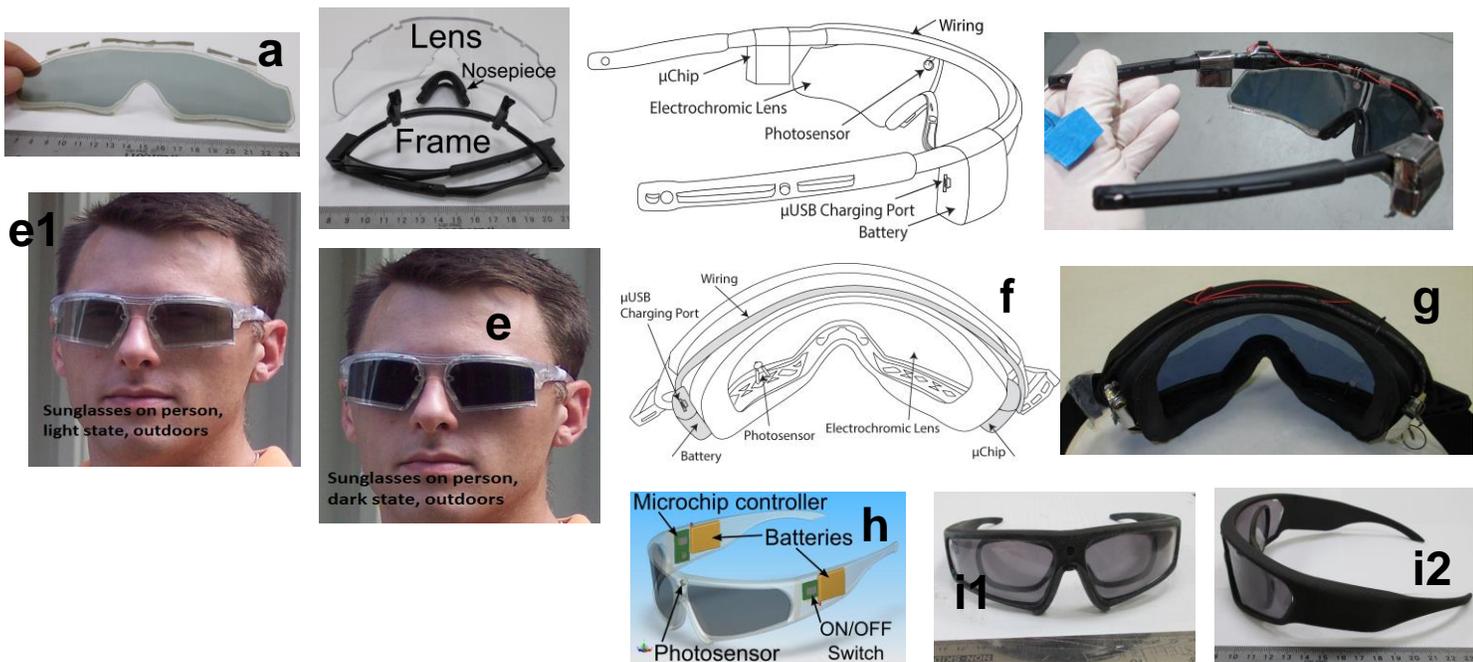
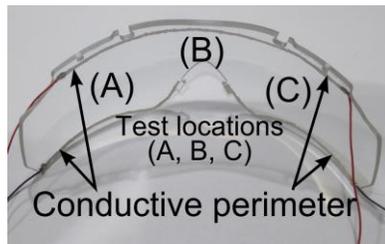


Fig. 3: Status of our defogging technology prior to the start of this Phase I project:



Temperature rise, °C, at 90 seconds, on application of 6 VDC, @ Region of Coated Lens (as Identified in Figure at left).			
A	B	C	Uncoated Lens (For Reference)
5.8 °C	5.8 °C	N/A	N/A

2.3 SPECIFIC AIMS

The overall Aim of the Phase I work was to ***combine the above-described electrochromics and anti-fogging (defogging) technologies, to yield a product addressing the serious workplace issues identified above.*** It also sought to also address high-volume-manufacture issues. The *Specific Aims* as outlined in the original Phase I proposal were: **(1)** Fabricate, extensively test, optimize the active anti-fog coatings. **(2)** Further optimize electrochromic lenses. **(3)** Demonstrate that modification of the existing electrochromics Microcontroller for anti-fog operation is possible. **(4)** Fabricate, test, full-function (***electrochromics + anti-fog***) eyewear prototypes. **(5)** Address specific, high-volume-manufacture issues.

Prior to this Phase I project, as described above, our current electrochromics technology was already developed to a level of maturity that, with further development as proposed herein, it would lead to a commercially viable, inexpensive (ca. \$60), high-volume-manufacturable *product. PPE* (both spectacles and goggles) with *combined electrochromics/anti-fog capability* (the first ever), automated function based on ambient light (via photosensor) and humidity/temperature (via sensors), and meeting ANSI Z87.1-2010 personal-protective specifications. Our ongoing collaborations or teaming relationships with Smith Optics, Oakley, Tag Heuer, and others, all established eyewear manufacturers, were planned to be further utilized in this respect.

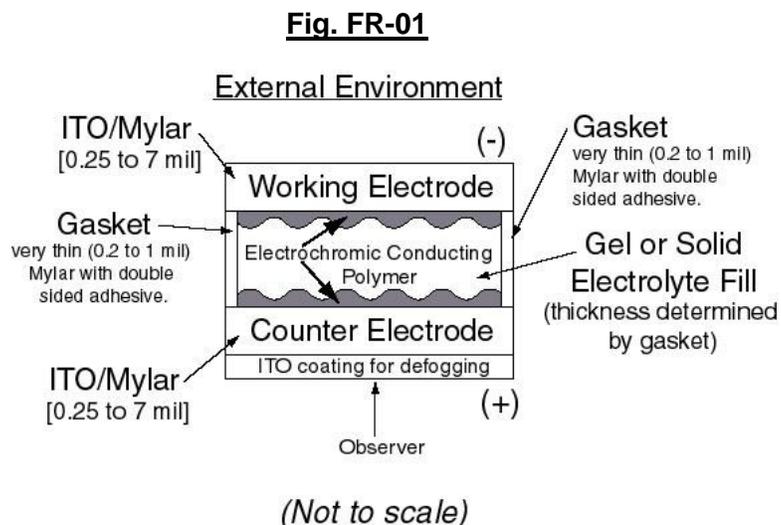
If successful, the inexpensive (<\$60) product resulting from this work would be the first commercially viable electrochromics eyewear product and also the first combining electrochromics + defogging functionalities. It would address a serious occupational hazard and workplace safety need, as described above, and drastically upgrade PPE. Ancillary markets (skiwear, motor sports, military) would be expected to further lower costs.

In consideration of the Specific Aims as described above, the **Tasks** as originally proposed in our Phase I proposal were as follows: **Task 1**: Fabrication, Extensive Testing and Optimization of the Anti-Fog Coatings. **Task 2**: Further Optimization of the Electrochromic Lenses. **Task 3**: Modification and Testing of Existing Microcontroller. **Task 4**: Fabrication of Full-Function (*Electrochromic + Antifog*) Spectacles and Goggles and Extensive Testing and Demonstration of Their Function. **Task 5**: Addressing of All Manufacturing Issues to Facilitate High-Volume (10,000 to 100,000 Pieces Per Year) Production. **Task 6**: Outline Future (e.g. Phase II) Work, Tie-Ups with Eyewear Manufacturers. **Task 7**: Final Report.

2.4 METHODOLOGY

2.4.1 Anti-fogging (Defogging) Coatings Fabricated

Anti-fog (defogging) conductive coatings and defogging tests: The anti-fog conductive coating is laid down on one surface of the *electrochromic lens* surface, the inside surface facing the eye of the wearer, as shown in **Fig. FR-01** (at right), which is a schematic of the full lens. The resistivity of the coating determines heat generated on application of a voltage, via $P=V^2/R$, where P = heat power generated, V =voltage applied, R =resistance. The %Transmission for the 60 Ohms/square ITO/Mylar used in our work is 77% to 83%, vs. the requirement for adequate function of about $\geq 65\%T$.



It should also be mentioned at the outset that conductive coatings other than ITO were also tested for initial function, as originally outlined in our Phase I proposal. These included the very new (2012-2013) technology of UV-cured *Ag-nanowire coatings*, which is claimed to have begun to replace ITO coatings for displays. Among claimed advantages of the Ag-nanowire coatings over ITO are that they can be put down from a spray or ink (rather than via PVD) and have higher conductivity/transparency than ITO. Major suppliers are Blue Nano, Cambrios and Toray (cf. <http://www.cambrios.com/>). All these other conductive coatings showed poor performance due to various reasons, and were thus not pursued further. Poor performance modes included very poor adhesion of the coatings, inadequate conductivity, and poor transparency.

As a first series of tests, conductive *defogging coatings with different surface resistivities (i.e. conductivities)* were laid down on a *single side (only)* of 7 mil (about 175 μm) Mylar (poly(ethylene terephthalate), PET) substrates, at our proprietary vendor (Vaculayer, Inc.). The resistivities varied from 15 to 202 Ohms/square, as shown in **Table FR-01**. Subsequently, these conductive coatings were laid down on the opposite side of one of the two ITO/Mylar films used in the

2.4.2 Defogging Tests

Defogging tests were carried out using two *methods*: **(1) Temperature rise as function of time upon application of voltage on conductive ITO/Mylar films** monitored using thermocouples. **(2) Actual, defogging tests on conductive ITO/Mylar films**, using a unique, specialized methodology, as described further below. **(3) Actual Actual, defogging tests on fully-assembled, fully-functional (electrochromic + defogging function) spectacles ("sunglasses")**.

In the **temperature-rise** tests, A 10cmX5cm portion of each conductive coating substrate to be tested was cut out and Ag epoxy was applied on the 10cm edges for electrical contact. After the specified 1-hour cure for the epoxy, these samples were hooked up to a DC power supply via copper clips. A voltage was applied and the temperature and current were monitored. The voltage was applied in a stepwise fashion and the temperature was recorded as a function of time. The current (in mA) and temperature for each film was recorded. The procedure is summarized in **Fig. FR-02**.

Fig. FR-02 (at right): Summary of procedure used for the *temperature-rise* test method for defogging capability. The ITO/Mylar (conductive coating) sample is cut out in a 10cmX5cm size, as shown. T1, T2 and T3 are the locations of the thermocouples. DC indicates application of a DC voltage for heating the conductive sample.

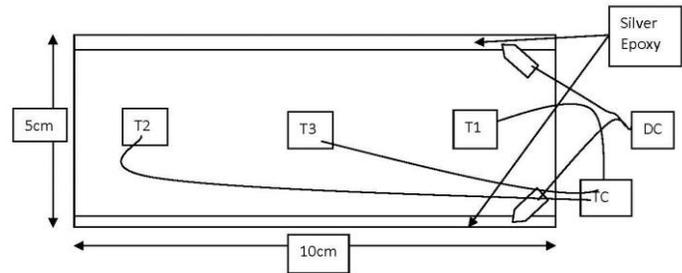


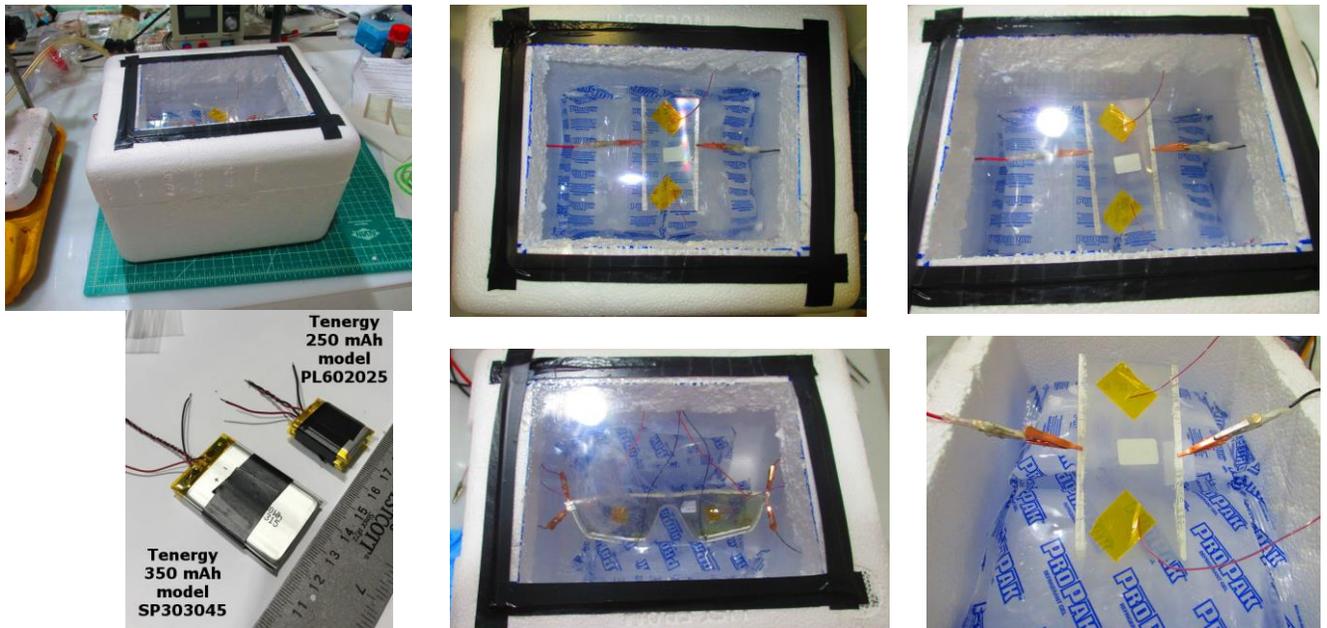
Table FR-01 (at right): Defogging conductive coatings fabricated for testing, and their properties.

Designation (ID)	Surface (sheet) Resistance (Ohms/square)	Thickness (nm)	%Transmission, Average of 3 points
LR-15	15	350	80.8%
LR-30	30	180	83.5%
C3130	48	150	76.6%
C3131	60	115	74.9%
C3132	105	70	76.4%
C3133	112	97	75.0%
C3134	143	60	76.4%
C3135	202	40	78.1%

For the **actual, defogging tests**, a custom test chamber was used (see **Figs. FR-02**). This consisted of a Styrofoam chamber with a polycarbonate, see-through window. Dry-ice packs were placed in this chamber to create a cold environment as low as -15°C . Once a conductive (ITO/Mylar) film was ready to be tested it was “incubated” in the chamber for about 1 min to allow the film to become cold. Initial incubation times were 90 s. subsequently, 60 s was found to be adequate for incubation, and gave better results. The setup used is shown in **Figs. FR-02**. Once the desired (low) temperature on film was reached, a handheld steamer was used to apply a water vapor that emulated a thick fog on the film. Once fog was stabilized on the film in the chamber, a voltage was applied and the time taken to defog was recorded. Initially, a using a DC power supply was used to apply the voltage, with voltages of, typically, 6.8 V to 7.4 V, being applied. Subsequently, two rechargeable Li batteries were used for more “practical” defogging tests. These batteries were down-selected from more than 10 different batteries initially tested. The specs of the two finally selected Li batteries used were: Model Nos. PL602025 (250 mAh) and SP303045 (350 mAh). It is noted that the 250 mAh battery *is the same battery as used in our current electrochromic sunglasses*, allowing for dual use in the composite electrochromic + defogging function. It was found that a single battery was not sufficient for efficient defogging. For this reason, two batteries in series, doubling the voltage to about 6.8 V, were used for defogging.

Two defog times were recorded: A “*practically defogged*” one, where the film was sufficiently clear to see well through and the fogging on it was discernible only on very close examination; and a “*fully defogged*” one, where there was no trace of any condensation on the film whatsoever, when examined through a 5X power magnifying class.

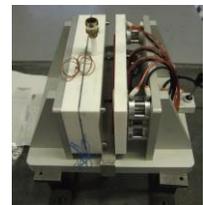
Figs. FR-02: Photos showing setup used for the **actual defogging tests**, and also the rechargeable Li batteries used for voltage application in the tests. **Clockwise from top left:** Full test chamber with see-through window; looking in through window to ITO/Mylar test sample with thermocouples (attached with yellow Kapton tape) and electrical contacts for applying voltage (alligator clips), prior to fogging; same after fogging; closeup of fogged film (lid removed); actual, fully-functional (electrochromic + defog) lens in same test, again through see-through window of chamber; batteries used, with cm-scale. (See text for detailed description).



2.4.3 Fabrication and Testing of Full (Electrochromic + Defogging) Lenses

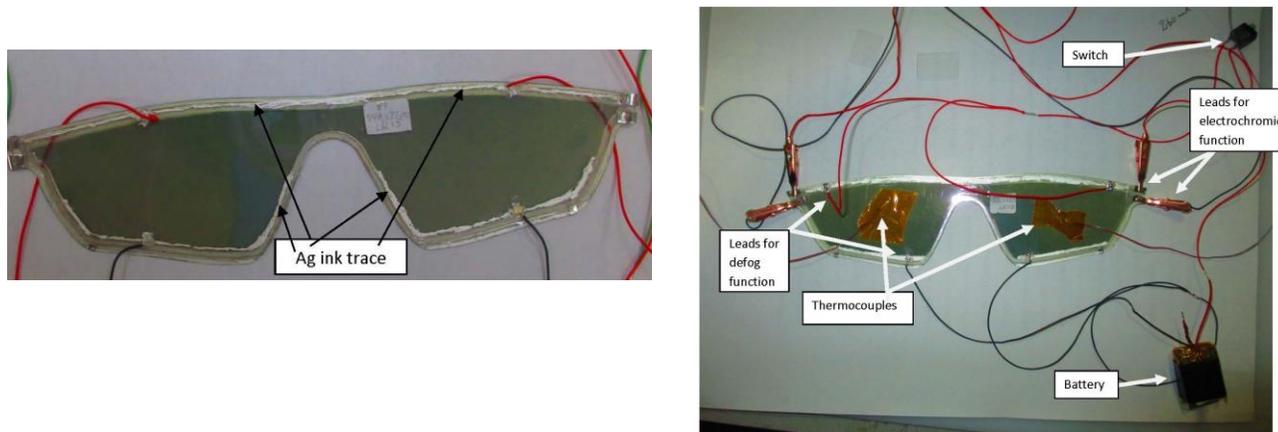
The electrochromic lenses were fabricated per our established, mature electrochromics technology, as described in some detail in the Basis of Technology section above. In brief, the two, unique Conducting Polymers comprising the dual-polymer pair are each electrochemically polymerized from monomer solutions onto ITO/Mylar substrates in a specially designed, semi-automated, pneumatically-controlled deposition (“electroplating”) tank, as shown in **Fig. FR-03**_(at right). After post-dep processing, the two individual electrochromic pieces are assembled into a full, hermetically-sealed lens, as described in our issued patents [82].

Fig. FR-03



For the combined electrochromic + defogging function, the inside (defogging) surface of the electrochromic lens had to be separately electrically-contacted. The same Ag-paste conductive perimeter method, as used the electrochromic part of the lens, was used for the defogging contact, with a minor variation. The defogging function also required a *separate electrical connection*. and a separate Li battery, of capacity slightly higher than that of the electrochromic lens battery. The detail of the defog test setup for the combined (electrochromic + defog) function lenses, with their separate electrical contacting and temperature monitoring, is shown in **Fig. FR-04**.

Fig. FR-04: Electrical contacting and temperature monitoring setup for testing the defogging function of fully assembled electrochromic lenses. The Ag ink or epoxy traces are used along the perimeter. The yellow Kapton tape pieces hold the thermocouples.



2.4.4 Assembly and Testing of Fully Functional (Electrochromic + Defogging) Spectacles and Goggles

This assembly was carried out as in our electrochromics-only prior work, with the major differences being in the presence of the additional, defog-function conductive coating on the inside of the lens (cf. **Fig. FR-01**) and proper methodology for separately electrical contacting the defog coating and electrochromic coating (cf. **Fig. FR-04**). Assembled spectacles and goggles are shown in **Fig. FR-05**.

As part of this work, we also studied **humidity sensors** to be used to *automatically detect fogging and activate the defogging function* of the spectacles and goggles. The humidity sensors finally selected, all extremely inexpensive (<\$3 in bulk purchase quantities), included the following: **(1)** TE Connectivity Inc. Model No. HTU21D, 4 μ s response time. <http://www.digikey.com/product-detail/en/HPP845E031R1/223-1590-1-ND/5416091> **(2)** Silicon Labs Inc. Model SI7007, 6 s response time. <http://www.digikey.com/product-detail/en/SI7007-A20-IM1/336-3127-ND/5050332>. A modification of the Microcontroller circuit was also carried out that incorporated input from the humidity sensor and automated defogging control. However, it was determined that, for this Phase I proof-of-concept, a *manual* defog switch would suffice. Thus, the prototypes in **Fig. FR-05** show manual rather than automated defogging control.

2.4.5 Driver Electronics for Defogging Function

As part of the work to demonstrate a final prototype complete with a refined Microcontroller capable of both the electrochromic and defog functions, driver electronics were arrived at refined, at our vendor, Zeta Electronic Design, Inc., Hooksett, NH.

2.4.6 CAD Design of Refined, Finalized Fully Functional (Electrochromic + Defogging) Spectacles

A CAD design was arrived at incorporating the final, refined features of the fully functional (electrochromic + defogging) spectacles, to be used as a prototype for manufacturing in potential future, Phase II work. This was done at our vendor, Tri-Power Design, Denville, NJ.

2.4.7 Design of Semi-Automated or Automated Manufacture for Future Pilot Plant

This was one of the objectives of the Phase I work. The automation design included further refinement and automation of our existing, semi-automated deposition ("electroplating") tanks, used for electrochemical polymerization of the active electrochromic Conducting Polymers onto the ITO/Mylar substrates.

2.5 RESULTS AND DISCUSSION

2.5.1 Best Conductive Coatings for Defogging Based on the Preliminary Temperature-Rise-Only Tests

The ITO/Mylar conductive coatings as identified in Section 2.4.1 above were screened using the temperature-rise-only methodology as identified in Section 2.4.2, above. Based on this, **the three best films identified for further, defogging studies were: LR-15; LR-30; and C3132**. Some (by no means all), salient results are summarized in Fig. FR-06 below.

Table FR-02:

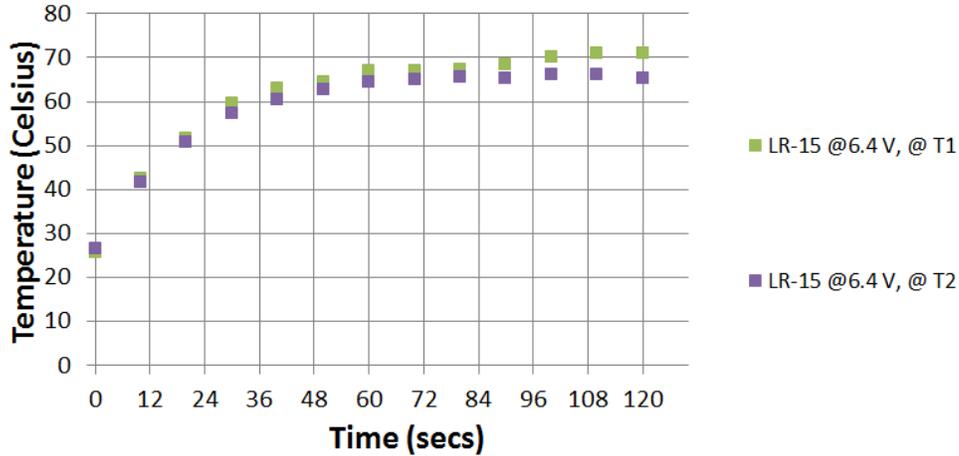
Defog times, and final temperatures at these defog times (starting temperature 25 °C in all cases) for the best defog conductive coating, designated LR-15.

Film LR-15 @ 7.6 V			Film LR-15 @ 7.4 V	
Trial#	ACTUAL (practical) defog time, seconds	Temp on film at defog time (°C) (starting temperature 25 °C in all cases)	ACTUAL (practical) defog time, seconds	Temp on film at defog time (°C) (starting temperature 25 °C in all cases)
1	5	31	7	30
2	6	32	8	31
3	6	31	8	31
4	6	32	6	30
5			5	29
6			6	31
7			6	31
8			6	30
Mean:	5.75 s	31.5 °C	6.5 s	30.4 °C

Figs. FR-05 (cont. overleaf):

A selection of salient results for temperature-rise-only testing of defog capability of conductive coatings. On the basis of these tests, the best conductive films identified for further, defogging tests were: **LR-15; LR-30; and C3132.** (For positions T1 and T2, see **Fig. FR-02.**)

Time vs temperature for film LR-15 at 6.4 V and two positions (T1&T2) on film



Time vs temperature for film LR-30 at two positions (T1&T2) on film

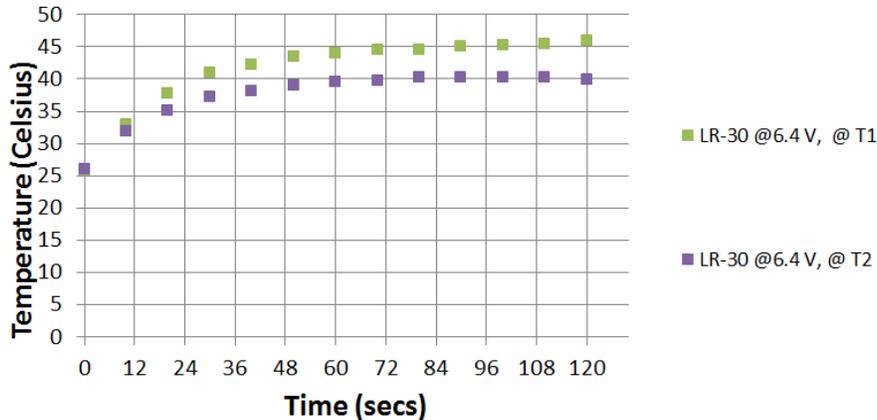
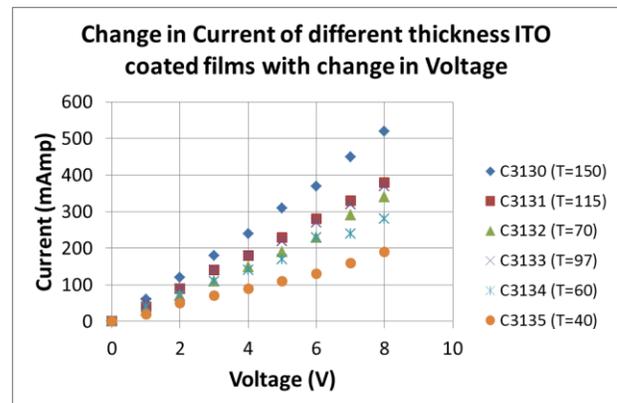
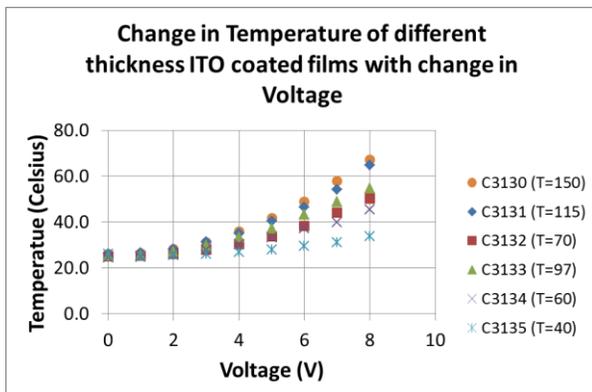
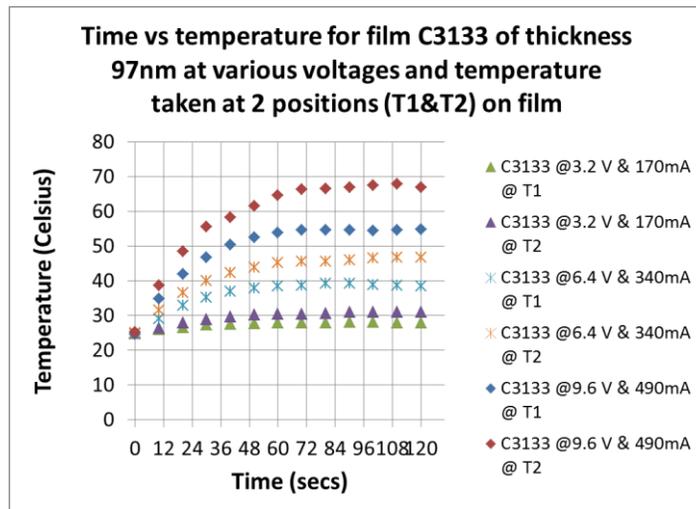
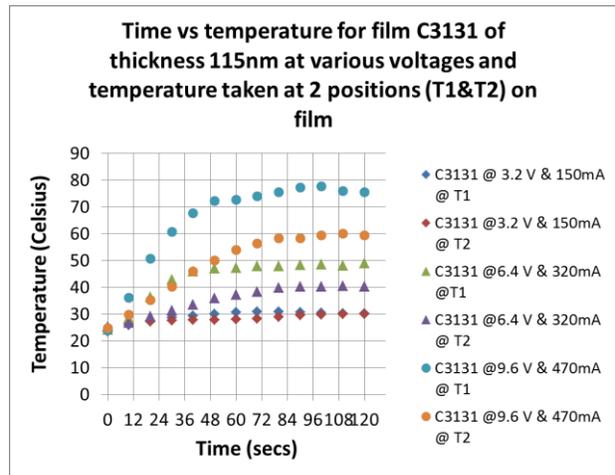
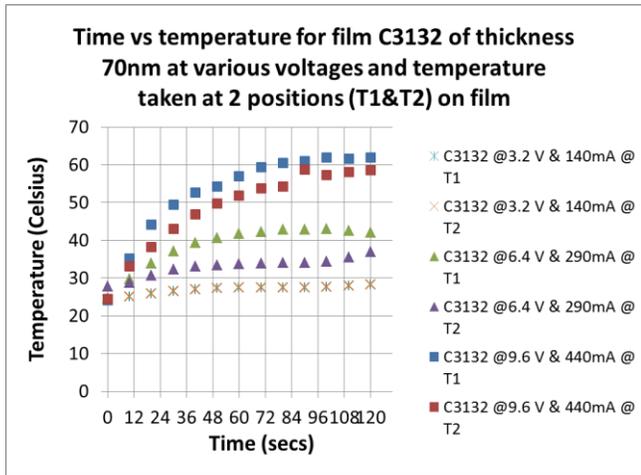


Fig. FR-05, cont.:



2.5.2 Results of Actual Defog Tests on Combined (Electrochromic + Defog)-Function Lenses

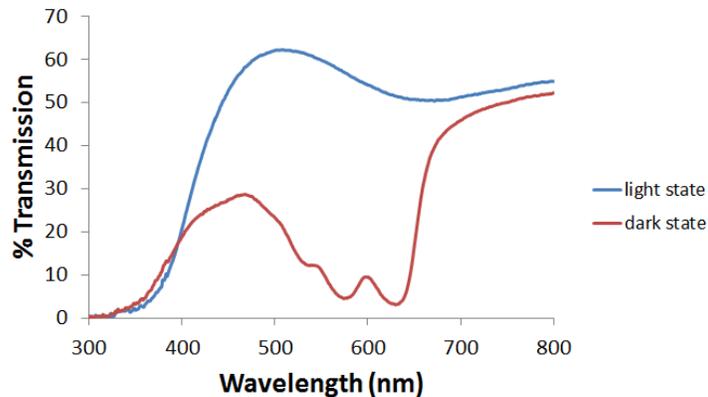
The methodology used for this work has been described in Section 2.4.2 above. The *electrochromic* function of these (electrochromic + defog)-function lenses is shown in **Figs. FR-06**. *Defogging time* results are summarized in **Table FR-03**. It is again clear from these results that **the best defog coatings were those designated LR-15 and LR-30**.

Figs. FR-06:

Electrochromic function of the combined (electrochromic + antifog) lenses tested. **Clockwise from top left:** Dark state of lens; light state; UV-Vis-NIR spectrum of light and dark states.



Combined (Electrochromic+ Defog)-Function Lens, #EC S4A032AD, Light/Dark States



Battery lifetime and full-day defogging use: For illustrative purposes, a typical LR-15-coating-based electrochromic lens yielded a defog time of about 7 seconds. The starting and ending battery voltages using the Tenergy 250 mAh battery at the beginning and end of the test were 7.2 and 7.1 V, showing little battery drain. Two of these 250 mAh batterie (identical to the battery used for our electrochromic-only sunglasses) were able to last a full day's (8 hours) expected defogging use before requiring recharging. The typical current flow during the few seconds required for defogging was 800 mA, but currents as high as 1.22 A were observed in some cases.

Table FR-03:

Summary of **defogging time** results for combined (electrochromic + defog)-function **lenses**. It is again clear from these results that **the best defog coatings were those designated LR-15 and LR-30**. (**Practical defog time is that for see-through defogging (no fogging observable to the naked eye. Total defog time is that where no traces of condensation are observable on the lens with 5X magnifying glass. The Practical defog time was generally found to be about 0.4 X the Total defog time.)

(Electrochromic+ Defog) Lens#	Conductive coating used	Avg. time to reach 35°C	%T at 575nm Light/Dark (L/D)
S4A025AD	LR-30	20 secs	53.5/6.5
S4A025BD	LR-15	8 secs	52.0/7.6

Lens# S4A029AD (with LR-30 coating), Run#	Practical** Defog Time (s)	Total** Defog Time (s)
1	5	14
2	6	15
3	5	14
4	5	14
5	6	15
6	5	14
7	6	15
Mean	5.43	14.4

Lens# S4A032AD (with LR-15 coating), Run#	Practical** Defog Time (s)	Total** Defog Time (s)
1	3	8
2	3	8
3	3	8
4	3	8
5	4	9
Mean	3.2	8.2

2.5.3 Results of Testing of Fully Functional (Electrochromic + Defogging) Spectacles and Goggles

Figs. FR-05 and FR-06 below show the fully-functional spectacles (sunglasses) and goggles, respectively.

Fig. FR-05: Fully-functional (with electrochromic + defog function) **spectacles** (sunglasses), assembled and tested for combined defog and electrochromic function in this work. **Clockwise from top left.** Top view with scale; unfogged spectacles; same after fogging; same, showing the manual On/Off switch; opened housing in side-arm of frame showing Microcontroller; opened housing in side-arm of frame showing Li battery.



Fig. FR-06: Fully-functional (with electrochromic + defog function) **goggles** assembled and tested for combined defog and electrochromic function in this work. **Clockwise from top left.** Front View; back view showing photosensor at lower right; side view showing Defog On/Off switch.

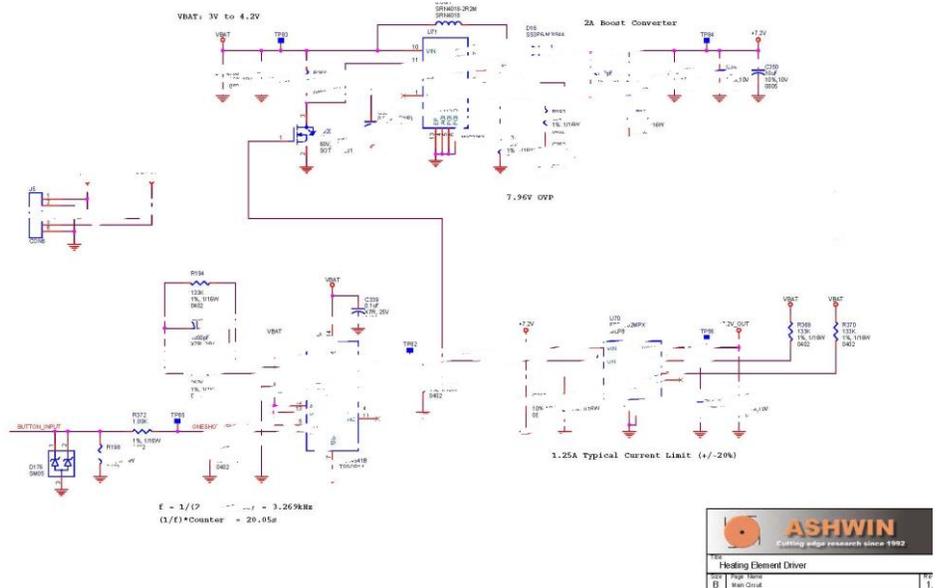


The fully assembled sunglasses and goggles having the combined (electrochromic + defogging) function gave defog times that were approximately 20% slower than those of the lenses alone. This was ascribed to the fact that the sunglasses' frames provided added mass which served as a heat sink for the heating effect used for defogging. As compared to a (mean) switching time of **3.2 seconds** obtained for (electrochromic + defogging) lenses fabricated with the LR-15 anti-fogging coating (cf. **Table FR-03** above), the defogging time for the fully functional **spectacles** was observed to be about **4 seconds**, and for the fully functional **goggles** was observed to be about **6 seconds**.

2.5.4 Modification (Electronic Driver) to Existing Microcontroller for Combined (Electrochromic + Defogging) Function

Our existing Microcontroller, used to control our electrochromic sunglasses developed in our prior work and having no defogging function, was modified so as to accommodate the Driver for the combined electrochromic + defog function. This was done at our vendor/subcontractor, Zeta Electronic Design Inc., Hooksett, NH. The driver circuit portion is shown in **Fig. FR-07**, obviously partially redacted for proprietary reasons.

Fig. FR-07: Modification of our existing Microcontroller, used to control the electrochromic sunglasses developed in our prior work and having no defogging function, so as to accommodate the Driver for the combined electrochromic + defog function. For proprietary reasons, the circuit diagram is partially redacted.



2.5.5 Humidity Sensor Evaluation

Several (six) different humidity sensors were evaluated for use in automated defogging (i.e. no wearer input, vs. the Phase I final prototype's On/Off switch for activating defogging), in potential Phase II work. As noted in the METHODOLOGY Section above, two sensors were down-selected for further testing from these, each very inexpensive: (1) TE Connectivity Inc. Model No. HTU21D, 4 μ s response time. <http://www.digikey.com/product-detail/en/HPP845E031R1/223-1590-1-ND/5416091> (2) Silicon Labs Inc. Model SI7007, 6 s response time. <http://www.digikey.com/product-detail/en/SI7007-A20-IM1/336-3127-ND/5050332>. (A modification of the Microcontroller circuit was also carried out that incorporated input from the humidity sensor and automated defogging control- see above.)

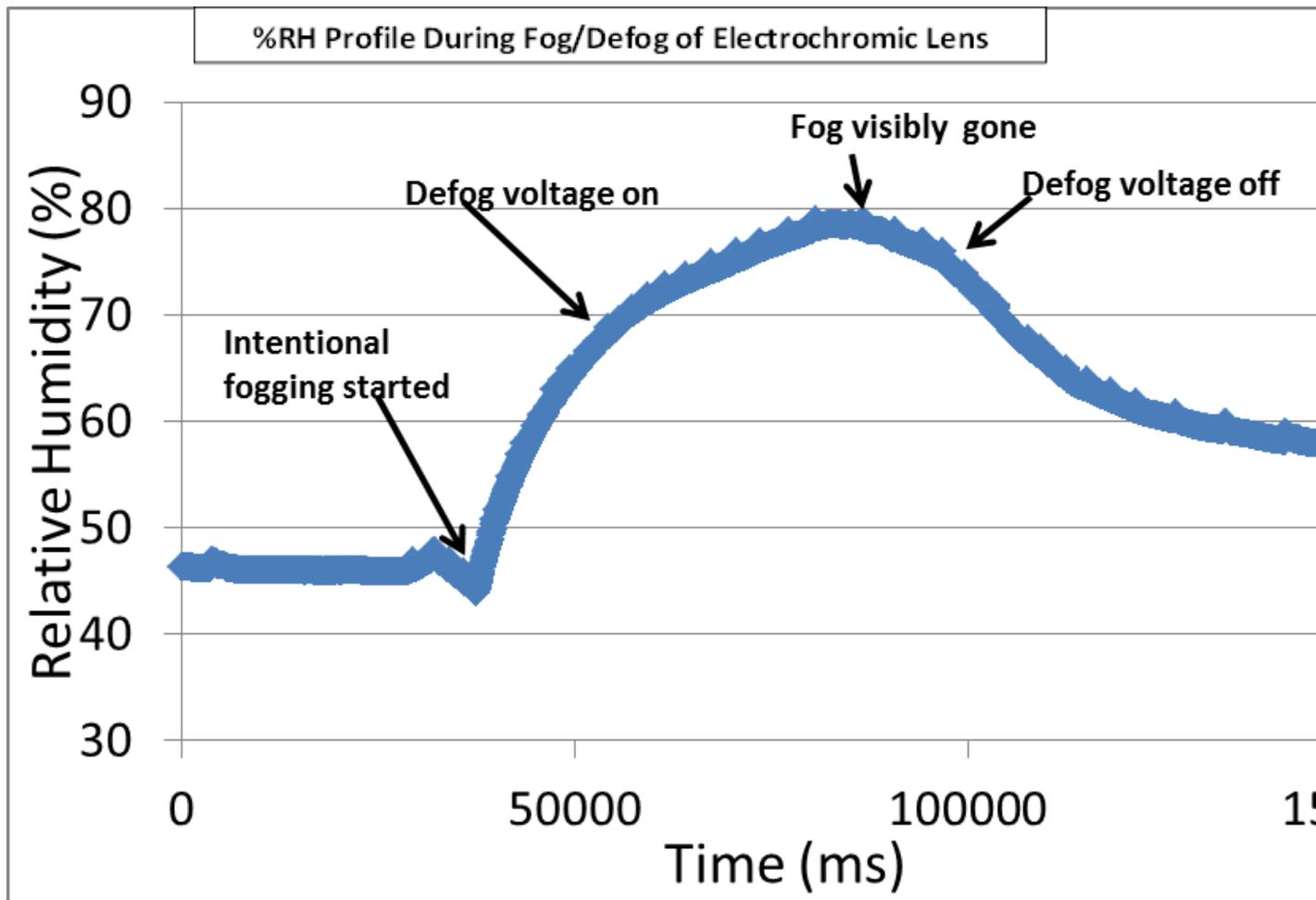
Finished, fully-functional sunglass (spectacle) prototypes were incorporated with the first humidity sensor from the above list to determine if the sensor was sensitive enough to detect thin fog layer at the surface of the lens. This was simply done by attachment, using Kapton tape, of the sensor to the lens, before and

after fogging. Before fogging, the humidity on the lens observed to be was close to that of the room, about 45%. However, once the glasses were intentionally fogged (see procedure above) and the sensor attached thereto, the humidity jumped immediately up to about 79%. Then, over time in air and with the defogging voltage turned on, the fog dissipated and the humidity dropped back down to about 49%.

Fig. FR-08 below displays the relative humidity over time as fogging and defogging occurred. It is clearly seen that humidity is stable around 45% until glasses are intentionally fogged, at which point an immediate jump in humidity to a peak of about 79% occurs. Then, once the defog voltage is turned on, the fog quickly clears, and the relative humidity begins to drop slowly back down to about 49% (not shown in graph). **From these data, it is clear that the humidity sensor is more than adequate in detecting the thin fog layer that forms on the lens inner surface.**

Thus, based on the above results, it is strongly recommended that, in potential Phase II work, an automated defog function with a humidity sensor in the control loop be implemented, in place of the simple On/Off switch implemented in the Phase I prototype.

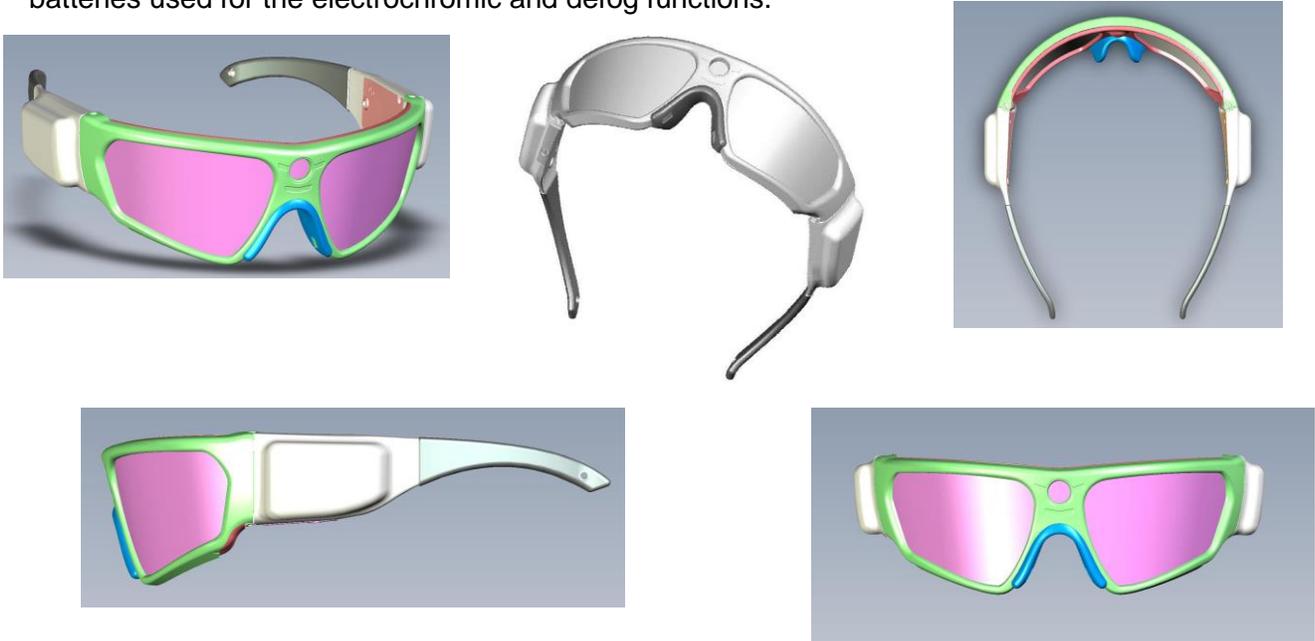
Fig. FR-08:



2.5.6 CAD Design of Fully Functional Spectacles (Sunglasses) Having Combined (Electrochromic + Defogging) Function

The design arrived at by our vendor, Tri-Power Design, Denville, NJ, is summarized in **Fig. FR-09**.

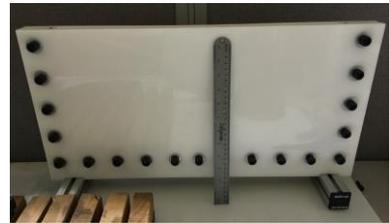
Fig. FR-09: Summary of CAD design of fully functional spectacles (sunglasses) having combined (electrochromic + defogging) function, as arrived at by our vendor, Tri-Power Design, Denville, NJ. Various views are shown. The "bulges" on the side-arms (temples) are to accommodate the separate batteries used for the electrochromic and defog functions.



2.5.7 Automation and Semi-Automation of Manufacture for Manufacture of Final Product.

The *additional* equipment fabricated and/or purchased for this is shown in **Fig. FR-10**.

Fig. FR-10: *Additional* equipment (besides equipment we already had from our prior work) fabricated and/or purchased for automation and semi-automation of manufacture for manufacture of final product. **Clockwise from top left:** Deposition ("electroplating") tanks for electrochemical polymerization of active conducting polymer, front and side views; this has pneumatic fluid fill/empty and auto-shut, and is 4X the size of the tank from our original work prior to this project, allowing for production of four lenses per deposition. Semi-automated "dip" (wash) tank for cleaning the electrochromic films after polymerization, again front and side views. Both custom produced for us based on our design, at Tri-Power Design. Automated machine for perimeter-laydown of conductive perimeter for the lenses, as also the gel electrolyte. This machine was procured from Fisnar, Inc.



2.6 SUMMARY OF RESULTS AND CONCLUSIONS

- All objectives of the original Phase I project eminently achieved, and in many cases exceeded.
- Fully functional, automated (photosensor-activated), Personal Protective Eyewear (PPE) with combined (electrochromic + defogging) function prototypes developed, fabricated and tested. Eyewear was in the form of spectacles (sunglasses) as well as goggles.
- These showed defogging times of **5 to 6 seconds**.
- Stand-alone lenses having (electrochromic + defogging) function showed even faster defog times of about 4 seconds.
- These prototypes used two types of conductive films, down-selected from seven evaluated in detail.
- Existing Microcontroller for this firm's current electrochromic sunglasses modified to accommodate electronics for driver for driving the defog function.
- Several humidity sensors evaluated for automated function of the defog capability based on internal/external humidity parameters, and two down-selected for further testing and implementation in potential Phase II work. Meanwhile, simple On/Off operation of the defog function demonstrated in the Phase I prototypes.
- Refined CAD design completed for the fully functional, automated (photosensor-activated), PPE spectacles with combined (electrochromic + defogging) function, to be used for pilot-plant manufacture in potential Phase II work.
- Semi-automated and automated instrumentation designed and developed for the key electrochemical polymerization ("electroplating") and processing steps for medium-scale manufacture of the PPE. Thus, pathway for semi-automated mass production of the (electrochromic + antifog) PPE clearly demonstrated.
- Clear pathway demonstrated for potential Phase II work that *would lead directly to a semi-automated, demonstration pilot plant for inexpensive manufacture of 1,000 PPE pieces per month (12,000 per year) with estimated cost of < \$60 per PPE piece. These PPE pieces would have excellent (electrochromic + defog) functionality and would defog within about 5 seconds. Both electrochromic and defog functionalities would be fully automated, requiring no wearer input whatsoever.* Such potential Phase II work would thus be strongly recommended.

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2.8 INCLUSION ENROLLMENT TABLE

N/A. No human subjects.

2.9 PUBLICATIONS

N/A. No publications or patents.

2.10 INCLUSION OF CHILDREN

N/A. No human subjects.

2.11 MATERIALS AVAILABLE FOR OTHER INVESTIGATORS

N/A. None.