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Electric Field-Assisted Ion Exchange of Borosilicate Glass Tubes

Ali Talimian and Vincenzo M. Sglavo

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Abstract

In this work, DC electric field-assisted ion exchange was carried out to enhance the sodium-potassium inter-diffusion and improve the mechanical performance of borosilicate glass. Electric fields with intensity varying between 100 V cm^{-1} and 3000 V cm^{-1} were applied in both direct and inverted polarizations. Four point bending test and the Vickers indentation method were used to characterize the mechanical properties. Energy dispersion x-ray spectroscopy was carried out to determine the potassium concentration within the surface layers of the samples.

The analysis of the potassium concentration profile near the surface shows that the external electric field governs the ion exchange process and it is possible to send potassium ions down to a depth of 45 μm in only 5 min. By plotting the electrical current versus time, it is revealed that the process stops after a certain saturation time. Vickers indentation measurements show that the compressive residual stress in the samples treated under electrical field is 3 times higher than that obtained by conventional chemical tempering. The bending strength of samples prepared by reversing the field direction is higher than that measured in specimens treated only on one side due to the symmetrical distribution of the stress on both sides.

Keywords: Field-assisted ion exchange, Borosilicate glass, Mechanical properties

1. Introduction

During the ion exchange process on glass, some ions in the materials are replaced by new ions from the liquid that can modify the physical and chemical properties locally [1-3]. The ion

exchange process has been widely used to change the reflective index in a selected area of glass for producing waveguide devices [4, 5]. Starting about 50 years ago, ion exchange has been employed also to improve the mechanical properties of silicate glass [1].

Surface defects are responsible for the limited glass resistance and its large scatter [6]. The creation of a compressive stress layer in the surface of the material can limit the formation or propagation of flaws and improve the mechanical properties; thermal and chemical tempering of glass are two main methods for producing a compressive stress in the glass surface. The thermal method is widely used to make windows and other transparent flat structural components [2, 7].

The ion exchange or chemical strengthening of glass was almost abandoned for many years because of the high processing cost and long-duration process. In recent years, this method has been reconsidered because of the possibility of mechanical treatment after strengthening, the applicability to complicated shape and limited thickness components, and the absence of optical distortion [8].

The ion exchange process is typically carried out by immersing the components made of a glass containing lithium or sodium in molten potassium nitride salt. The process can be carried out at a temperature between the melting point of the salt and the transforming temperature of the glass and takes times in excess to 4 h, depending on the required depth for the compressive stress layer. After finishing the process, the samples are removed from the bath and the salt on the surface is simply washed out by water [2, 9].

The ion exchange process can be considered as an inter-diffusion reaction between the mobile ions in glass and the cations in the molten salt while the other glass components are considered as an immobile matrix of negative groups [10-13]. An external electric field can be the source of an extra driving force for the inter-diffusion of the mobile ions. This process is known as electric field-assisted ion exchange (EF-IOX) and it has been used especially for manufacturing waveguides [4, 5, 14, 15]. Three different procedures have been proposed. In the first one, a thin metal film as a source for ions is applied on the glass surface and the application of an electric field induces the oxidation/reduction at the interface with glass that generates cations that move into the glass on the anode side, creating the chemical concentration profile [5, 16, 17]. Alternatively, a molten salt can be used as the ion source at only the anode side of the sample, the cations at the anode side penetrates into the glass under the field [5]. In the last approach, the sample acts as a wall, separates two molten salt baths and each bath is connected to an electrode; by applying the electric field the cations in the salt start moving in the direction of the electric field [4, 5, 14].

By considering the ions flow and the electrical charge neutrality balance, different mathematical modelling have been proposed for the ion diffusion during the exchange process [18]. For a large enough field, the concentration of exchanged ions, at distance x from the surface and at time t, can be defined as:

$$C(x,t) = \frac{C_0}{2} erfc\left(\frac{x - \mu E t}{2\sqrt{Dt}} \right)$$

(1)

where C_0 is the surface concentration of the ions, E the applied electric field, μ the ion mobility, and D the inter-diffusion coefficient [8]. Thermal diffusion does not play an active role and the migration of ions is governed by the electric field, only. Consequently, a step-like profile is generated in a short period of time for the ions concentration [9]. The long range migration of cations in the glass allow to produce a deeper compressive layer [18, 19].

Field-assisted ion exchange has been limitedly studied with the aim of improving the mechanical properties during the 1970s [20]. The main problem was the unbalanced residual stress that caused the deformation of the samples.

In this work, we performed electric field-assisted ion exchange on commercial borosilicate glass tubes, thus avoiding the problems associated with the deformation of the samples. The aim was to analyze the possibility of using an external field for speeding up the ion exchange process and obtaining improved mechanical properties.

2. Experimental procedure

Borosilicate test tubes from commercial sources, Fiolax clear, Schott, were used in this study. The glass transition temperature was measured by the differential scanning calorimeter (DSC) (DSC2010, TA Instruments, USA) method [21]. The chemical composition and the physical properties of the glass are shown in Table 1 [22]. The tubes having nominal thickness and outer diameter of 0.5 mm and 11.8 mm, respectively, were cut in 100 mm long samples. The limited thickness of the tubes allows thermal equilibrium between the sample and the salt bath during the process.

Chemical composition (wt%)					Physical properties	
SiO_2	B_2O_3	Al_2O_3	Na_2O	CaO	Density (g/cm³)	Glass transition temperature (°C)
75	10.5	5	7	1.5	2.34	582

Table 1. The chemical composition and the physical properties glass tubes used for ion exchange

The samples were ultrasonically cleaned in distilled water for 5 min, washed with acetone and air dried. They were treated in a modified lab furnace schematically reported in Figure 1. One sample at a time was treated but current and applied voltage were constantly monitored and controlled during the process to guarantee a similar procedure for all samples. The applied electric field varied between 100 to 3000 V cm^{-1} and the current density was limited to 4, 8, and 16 mA cm^{-2}. The samples were kept over the bath for 20 min before the process as a preheating step; then, they were filled with molten salt and immersed in the bath kept constant at 400±2°C. After applying the electric field. The tube was immediately emptied from the molten salt and held for 20 min over the bath. At the end of each cycle the samples were ultrasonically washed with distilled water. Ten samples were also treated by conventional ion exchange in a commercial lab furnace, Lema TC 20 A, Italy, for comparison, by holding 4 h at the identical temperature. Potassium nitrate salt (>99.5% pure) from commercial source was used.
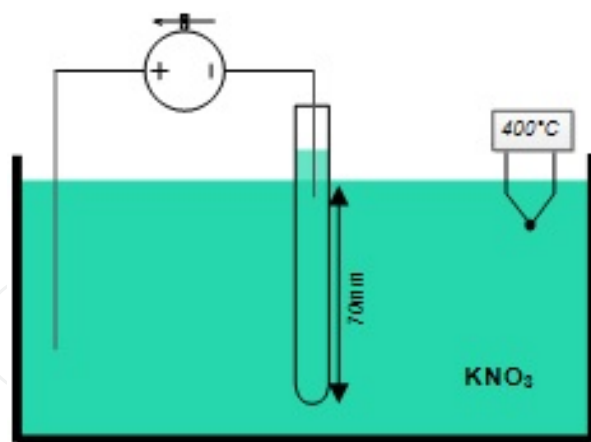
Figure 1. Schematic experimental setup used for field-assisted ion exchange

A four-point bending test was carried out to determine the mechanical strength, using inner (L1) and outer (L2) span equal to 10.3 and 40 mm, respectively. The test was carried out in lab air (temperature≈20°C, relative humidity ≈40%) with a constant loading rate of 1.1 MPa/s. The failure stress was calculated as:

$$S_b = \frac{4F_{max}r_2a}{\pi\left(r_2^4 - r_1^4\right)}$$

(2)

where a is (L2-L1)/2, r_1 and r_2 the internal and the external radius of the tube, F_{max} the maximum load.

The presence of residual stresses on the surface layers was estimated by Vickers indentation method. The residual stress, σ_r, approximated as constant on the surface layers can be calculated as: [23]

$$\sigma_r = \frac{K_c}{\sqrt{\pi\Omega c}}\left(1 - \chi_r\frac{P^*}{K_c c^{3/2}}\right)$$

(3)

P^* being the indentation load, c the crack length, K_c the fracture toughness, χ_r and Ω two geometrical constants depending on the indenter and the crack shape, respectively.

The potassium penetration profile was measured on the fracture surface of test tube fragments. The fragments were fixed on an aluminum disk with an adhesive conducting tape and coated with Au-Pd alloy. The microscopic observation was carried out by a scanning electron microscope (SEM) (JSM 5500, Jeol, Japan). A clean path was chosen for analyzing the potassium Kα on a certain length, around 70 μm long, by using energy dispersion x-ray spectroscopy

(EDXS) (EDS2000, IXRF System, USA) probe. The surface chemical composition of the glass before and after the treatment was also determined by EDXS.

3. Results and discussion

Figure 2 shows how the current density changes as a function of time during the EF-IOX tests. The current density limit was fixed at 20–25 A m^{-2} depending on the immersion depth of the test tube in the molten salt. For the samples subjected to fields with intensity lower than 500 V cm^{-1}, the current density shows similar trend, steadily decreasing with process time; for more intense electrical fields the current reaches a saturation limit, corresponding to the imposed current density limit, and rapidly decreases. During the process, it is thought that small sodium ions with high mobility are replaced by larger less mobile potassium ions, this determine an overall decrease in the ions movement and, consequently, a reduction of the current density.

The evolution of current density with time under different fields (500 to 3000 V cm^{-1}) in the condition of current limit = 16 mA cm^{-2} is plotted in Figure 3. All curves have a similar shape: the maximum current density is recorded at the initial application of the field and it is proportional to the applied field intensity. After 400 s, the current density decreases to 10% of the initial one.
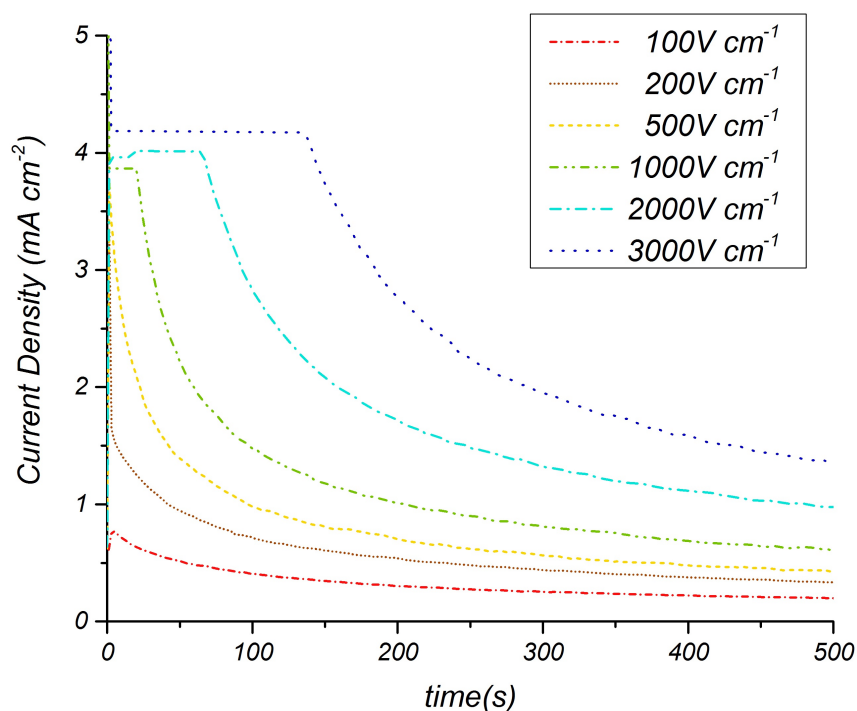

Figure 2. Current density vs. time for different fields (a constant current density limit was set at ≈ 4 mA cm^{-2})
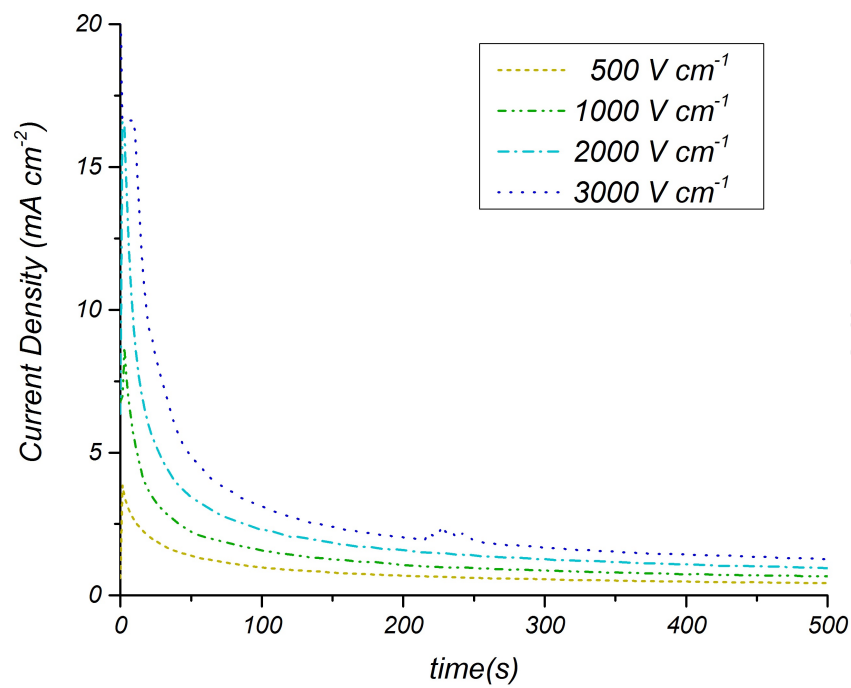
Figure 3. Current density vs. time for samples treated under different fields with current density limit of 16 mA cm^{-2}

The molar ratio between alkaline oxides ($K_2O/(Na_2O + K_2O)$) as measured by EDXS is chosen as an indicative parameter of the surface chemical composition variation. The values for samples treated under fields of 500 and 2000 V cm^{-1} and current limit of 16 mA cm^{-2} are summarized in Table 2: It is clear that sodium ions are completely replaced by potassium in the outer surface, cathode side, while in the inner surface, anode side, sodium is detected.

By applying the electric field, potassium ions are moved into the glass in the direction of the field. Highly mobile sodium ions move faster in the glass than potassium ions and can reach the other side of the glass; as a result, one side of the glass is saturated with potassium and the other one has high amount of sodium. Some limited thermal ion exchange can occur during the process on the anode side and sodium ions are replaced by potassium.

Treatment conditions	Alkali Ratio
As-received	0
500 V cm^{-1} - Inner surface	0.7
500 V cm^{-1} - Outer surface	1
2000 V cm^{-1} - Inner surface	0.7
2000 V cm^{-1} - Outer surface	1

Table 2. $K_2O/(Na_2O + K_2O)$ molar ratio of test tubes after the field-assisted ion exchange

The area beneath the current density versus time curves represents the amount of ions moved through the unit area of the sample during the process. According to Eq. 1, the exchanged layer has a constant concentration of potassium ions and the following equation was proposed to calculated the thickness of the exchanged layer, Δ, in soda-lime silicate glass [24]:

$$\Delta(t_2, t_1) = \frac{Q(t_2, t_1)}{FC_0} = \frac{\int_{t_1}^{t_2} J dt}{FC_0} \tag{4}$$

F being Faraday's constant, 96458.34 C mol^{-1}, C_0 the concentration of mobile ions in the base glass (i.e., the sodium concentration in the base glass = 2.64×10^{-3} mol cm^{-3}), and J the current density. By using Eq. 4, the depth of ion exchange varies between 8 to 120 μm depending on the intensity of the applied field. The depth of the exchanged layer is constant when the current density changes. Figure 4 shows how the current density varies with time for samples subjected to a field with intensity of 2000 V cm^{-1} and different current limits. By applying a current density limit, it assumes a constant value for a certain time and then decreases. After 200 s, all samples have similar behavior. The duration of the constant current step for the sample treated under a current limit of 8 mA cm^{-2} is longer; this makes the area underneath the curves and the amount of ions moved into the glass equal to the samples treated under current limit of 8 or 16 mA cm^{-2} and the amount of exchanged ions is the same for all samples after enough long time. Conversely, it is reported that the amount of exchanged ions depends on both the intensity of the electric field and the applied current limit for soda-lime silicate glass [24].
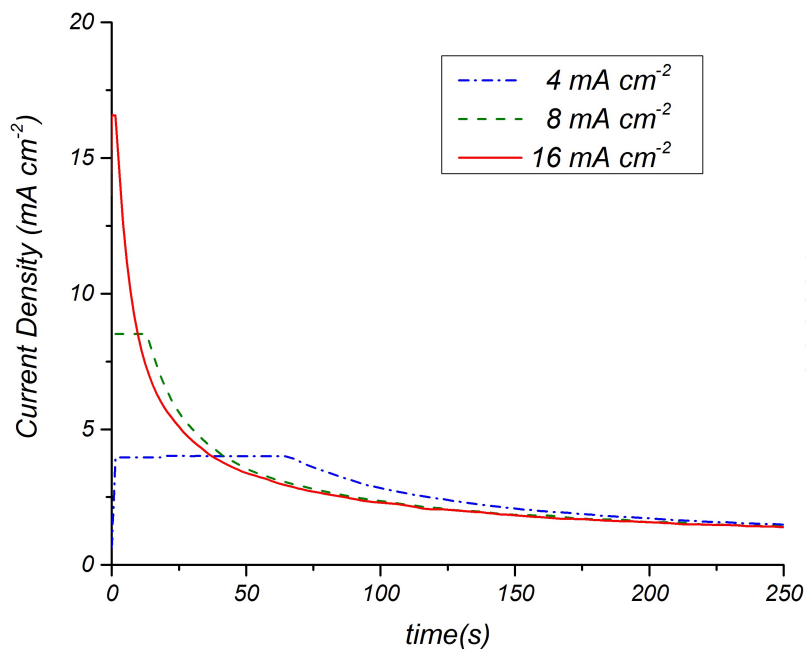

Figure 4. Current density vs. time for samples treated under field with intensity of 2000 V cm^{-1} and different current density

The potassium concentration profile near the surface of the samples subjected to the EF-IOX for 10 min are shown in Figure 5. In the outer surface a step in the concentration profile occurs for all conditions and the potassium penetration depth increases with the field intensity. The penetration depth is lower than that estimated by Eq. 4, according to mass balance and charge neutrality. During the process a local electric charge can be formed in the sample due to different mobility of sodium and potassium ions and, consequently, a local field is formed. Such local field can neutralize the external applied filed and prevent further exchange.
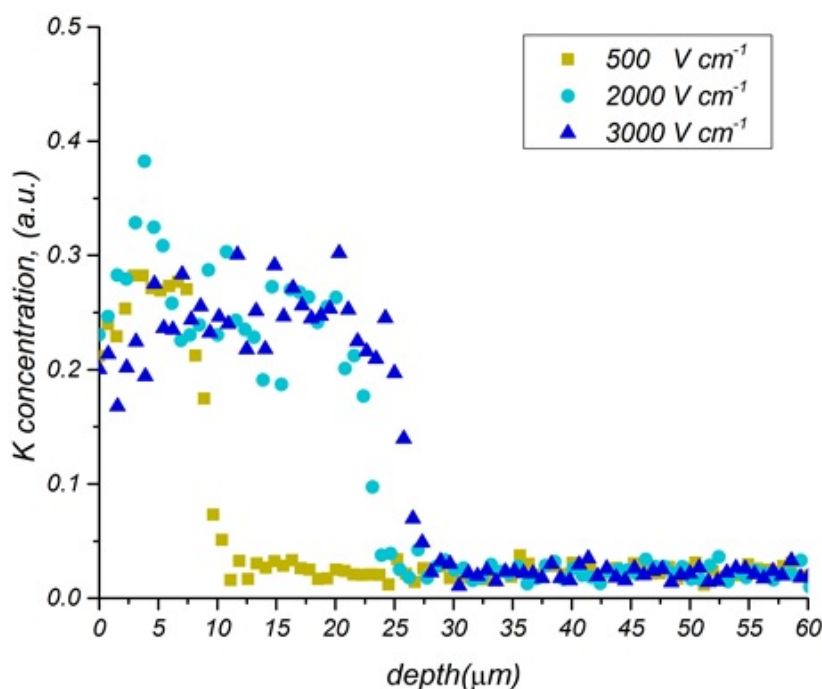

Figure 5. Potassium concentration profile in the external surface (cathode side) of tubes treated under different fields

Figure 6 shows the potassium concentration profile of glass tubes near the inner surface. Differently from Figure 5, similar profiles are recorded for different applied electrical fields and these resemble typical diffusion profiles obtained by conventional ion exchange process [7]. Probably, thermal ion exchange can be responsible for the observed diffusion concentration profile; nevertheless, more studies are required to reveal possible causes of such phenomenon.

All glass tubes subjected to the double (direct and inverse) field polarization—the initial one being out-to-in (Figure 7)—showed several surface cracks as in Figure 8; the cracks are on the inner surface and in some cases they reach the external one. Conversely, the samples treated first under a field with in-to-out polarization possess a structure similar to those subjected to conventional ion exchange. One possible reason for the formation of the observed cracks can be related to differential deformations between inner and outer surface upon the double ion exchange process. When potassium ions move into the outer surface of the tube first, the exchanged layer expands and compressive stress is formed due to the difference between the specific volume of the surface layer and the base glass. By exchanging the ions in the inner
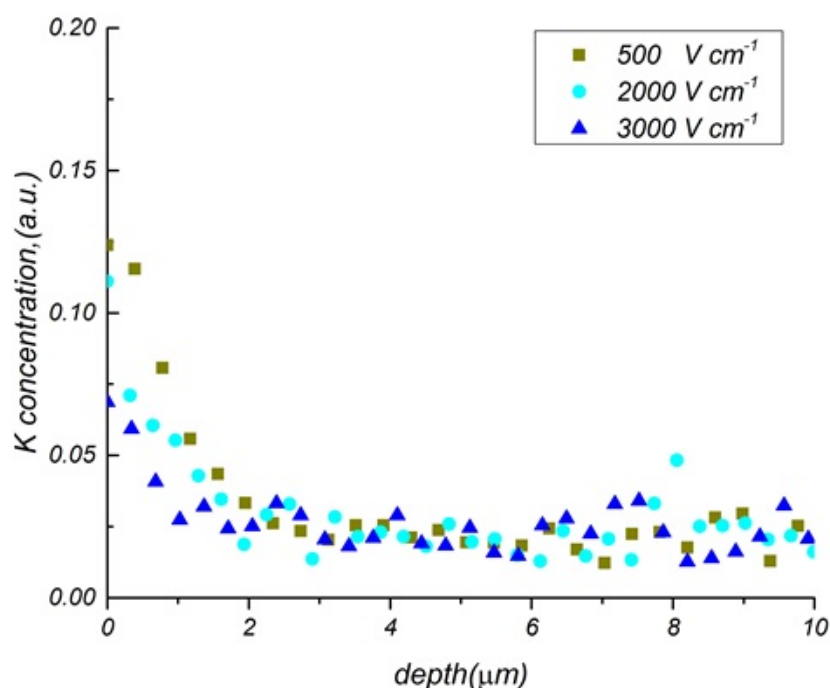
Figure 6. Potassium concentration profile in the internal surface (anode side) of tubes treated under different fields

surface during the second step, the expansion of the internal surface due to the geometry of the tube produces extra stresses in the interface of the exchanged layer and base glass. Conversely, by treating the inner surface first, the outer surface goes into tension because of the inner expansion and some cracks can be formed.

Figure 9 shows the bending strength of samples treated by different methods. The samples treated under the field on only one side are stronger than the as-received tubes but slightly weaker than the specimens subjected to conventional ion exchange processes. After the double-field polarization process, the strength increases further although the scatter becomes much larger.

Optical microscopy photographs of typical indentations on treated samples are reported in Figure 10. If the indentation load is 40 N no cracks are generated; conversely, at 50 N well-developed cracks are generated; therefore, a threshold load for crack formation can be pointed out for the strengthened samples, which is much higher than that for as-received glass, estimated equal to about 4 N. The effect of the compressive residual stress is absolutely clear.

The residual stress is built up by local replacement of small ions by larger ions during the ion exchange process; in the samples treated under the electric filed one should expect that the compressive stress is substantially built up only on one surface of the glass tube, it being balanced by tensile stresses in the remaining of the thickness [24]. The residual stress can be calculated by Eq. (3) from the measurement of the indentation crack length [25] and the results are shown in Table 3. The residual stress built up by the electric field-assisted process is significantly higher than that obtained in conventionally treated samples; the stress intensity increases further after the double-reversed electrical field treatment. Stress build up by
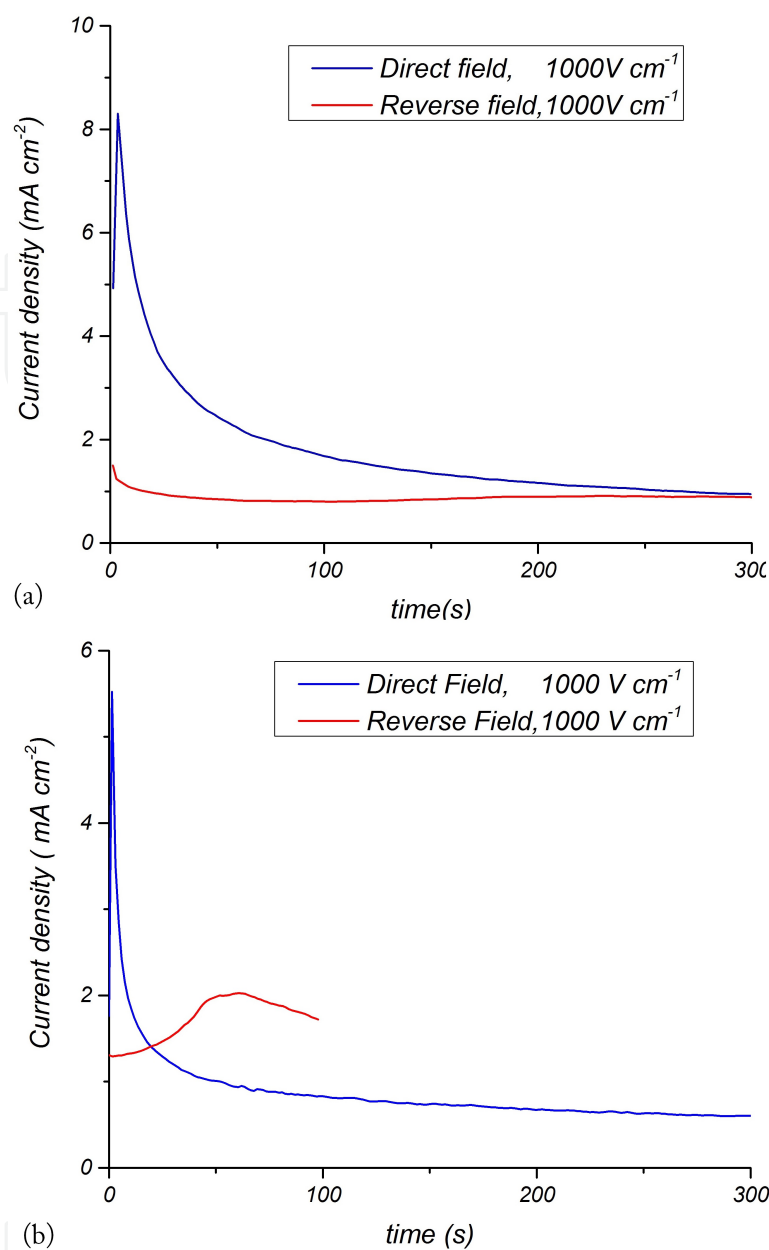
Figure 7. Current density vs. time for samples treated under direct and inverse electric field. The initial field polarization is (a) outside to inside, (b) inside to outside

exchanging ions is considered based on the volume change of glass during the process; the steep change of the potassium concentration profile produces higher residual stress compared to the gradual change in the thermally induced exchanged glass.

Treatment Condition	Conventionally-IOX	EF-IOX	Double & reversed EF-IOX
Residual stress (MPa)	26	49	91

Table 3. Calculated residual stress in the glass tubes treated by conventional ion exchange and EF-IOX
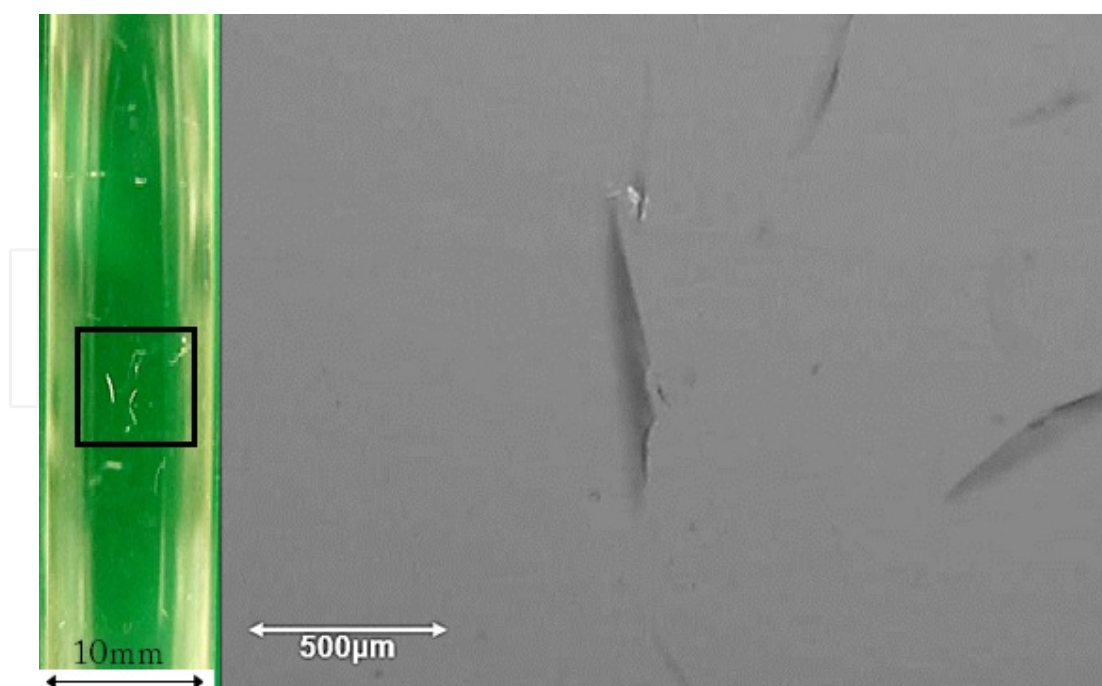
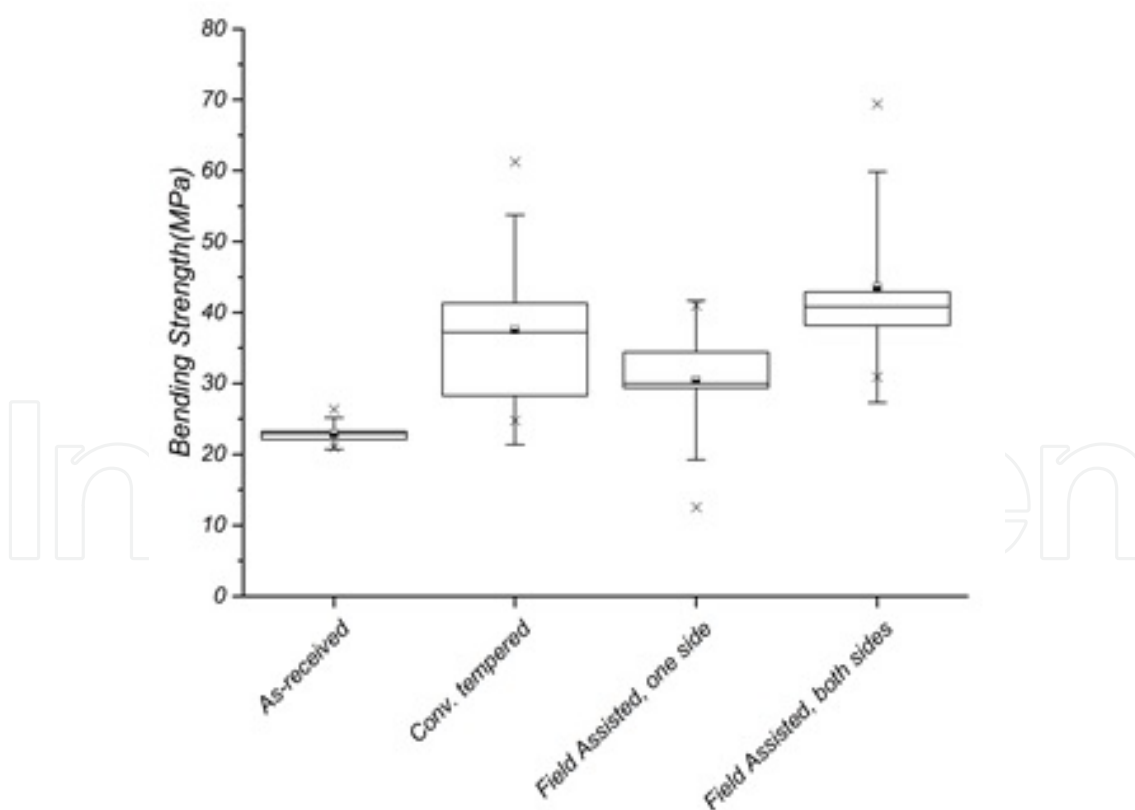**Figure 8.** Crack formation in the glass tube during the EF-IOX with "out-to-in" electrical field polarization

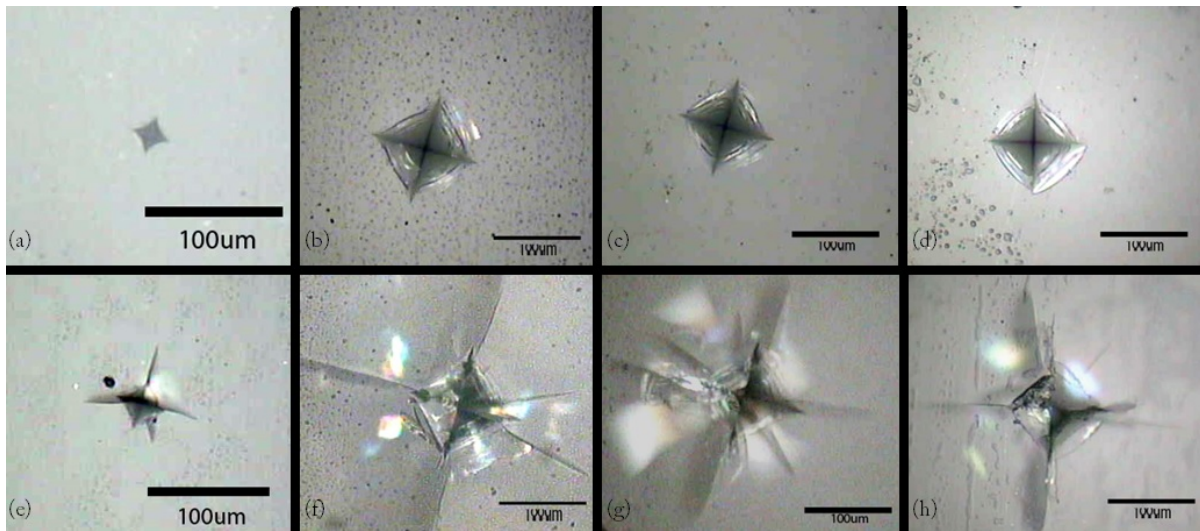**Figure 9.** Four-point bending strength of glass tubes

Figure 10. Vickers indentations on as-received samples subjected to (a) 3 N, (e) 5 N and samples subjected to 40 N indentation load, (b) ion exchanged (IOX), (c) EF-IOX, one side, (d) EF-IOX both sides, and 50 N indentation load, (f) ion exchange, (g) electric field-assisted ion exchange(EF-IOX), one side, and (h) EF-IOX both

4. Conclusions

Ion exchanged strengthening of borosilicate glass tubes was carried out under an electric field by using relatively short treatment times. The depth of the exchanged layer increases with the field intensity. Reversing the field polarization can modify the residual stress; moreover, the sequence of applying the fields with different polarizations is important to avoid the formation of cracks on the glass surface. Bending strength of samples treated by the double-reversed field is higher compared to those subjected to EF-IOX on one side or to conventional ion exchange.

Additional studies are required to find the effect of different parameters, such as salt and glass composition, treatment time and temperature, field intensity and other thermodynamic and electric factors on the assisted ion exchange process. The structural changes during the electric field should also be investigated. Nevertheless, the preliminary results obtained in the present work point out that electric field-assisted ion exchange can be employed for improving the mechanical properties by relatively short duration treatments.

Author details

Ali Talimian[*] and Vincenzo M. Sglavo

*Address all correspondence to: ali.talimian@unitn.it

Department of Industrial Engineering, University of Trento, Trento, Italy

References

[1] Varshneya AK. Chemical strengthening of glass: Lessons learned and yet to be learned. International Journal of Applied Glass Science. 2010;1(2):131-142. DOI: 0.1111/j.2041-1294.2010.00010.x.

[2] Karlsson S, Jonson B. The technology of chemical glass strengthening a review. Glass Technology.2010;51(2):41–54. ISBN: 0017-1050.

[3] Varshneya AK. The physics of chemical strengthening of glass: Room for a new view. Journal of Non-crystalline Solids. 2010;356(44-49): 2289–2294. DOI: 10.1016/j.jnoncrysol.2010.05.010

[4] Findakly T. Glass waveguides by ion exchange: A review. Optical Engineering. 1985; 24(2): 24-250.

[5] Tervonen A, West B, Honkanen S. Ion-exchanged glass waveguide technology: A review. Optical Engineering. 2011;50(7):711071-15.

[6] Varshneya AK. Fundamentals of Inorganic Glasses: Society of Glass Technology; 2006. 682 p. ISBN: 978-0-08-057150-8.

[7] René G. Ion exchange for glass strengthening. Materials Science and Engineering: B. 2008;149(2):159-165. DOI: 10.1016/j.mseb.2007.11.029.

[8] Mazzoldi P, Carturan S, Quaranta A, Sada... C. Ion exchange process: History, evolution and applications. Riv Nuovo Cimento. 2013;36(9):397-460. DOI: 10.1393/ncr/i2013-10092-1.

[9] Green DJ. Recent Developments in Chemically Strengthened Glasses. 64th Conference on Glass Problems: Ceramic Engineering and Science Proceedings, John Wiley & Sons, Inc.; 2008. p. 253–66. DOI: 10.1002/9780470294857.ch20v

[10] Liangbao J, Xintao G, Xiaoyu L, Lei L, Guanli Z, Yue Y. Different K+–Na+ inter-diffusion kinetics between the air side and tin side of an ion-exchanged float aluminosilicate glass. Applied Surface Science. 2013;265: 889–894. DOI: 10.1016/j.apsusc.2012.11.143.

[11] Morten MS, Qiuju Z, John CM, Marcel P, Steen M, Yuanzheng Y. Sodium diffusion in boroaluminosilicate glasses. Journal of Non-crystalline Solids. 2011;357(22-23): 3744–3750. DOI: 10.1016/j.jnoncrysol.2011.07.008

[12] Reiner K. On the mobility of alkaline earth ions in mixed alkali alkaline earth silicate glasses. Journal of Non-crystalline Solids. 2003;328(1-3): 157–163.DOI: 10.1016/S0022-3093(03)00474-5.

[13] Roling B, Ingram M. Mixed alkaline–earth effects in ion conducting glasses. Journal of Non-crystalline Solids. 2000;265(1–2):113–119. DOI: 10.1016/S0022-3093(99)00899-6.

[14] Ramaswamy RV, Srivastava R. Ion-exchanged glass waveguides: A review. Journal of Lightwave Technology. 1988;6(6):984–1002. DOI: 10.1109/50.4090.

[15] Hiroyuki Y, Takeshi K. Migration of two ions during electrolysis of glass waveguide. Journal of Applied Physics. 1985;58(5): 1739-1743.DOI: 10.1063/1.336022.

[16] Liu K, Pun EYB. K+-Na+ ion-exchanged waveguides in Er3+-Yb3+ codoped phosphate glasses using field-assisted annealing. Applied Optics. 2004;43(15):3179–3184. DOI: 10.1364/AO.43.003179.

[17] Tervonen A. A general model for fabrication processes of channel waveguides by ion exchange. Journal of Applied Physics. 1990;67(6):2746–2752. DOI: 10.1063/1.345440

[18] Abou-El-Leil M, Cooper AR. Analysis of field-assisted binary ion exchange. Journal of the American Ceramic Society. 1979;62(7–8):390–395. DOI: 10.1111/j. 1151-2916.1979.tb19086.x.

[19] Sviridov SI, Eliseeva NP. Field-assisted diffusion of potassium ions in sodium silicate glass. Glass Physics and Chemistry. 2006;32(6):604–11. DOI: 10.1134/ S1087659606060022.

[20] Urnes S. Na-K exchange in silicate glasses. Journal of the American Ceramic Society. 1973;56(10):514–517. DOI: 10.1111/j.1151-2916.1973.tb12400.x.

[21] International A. Standard Test Method for Assignment of the Glass Transition Temperatures by Differential Scanning Calorimetry. Calorimetry and Mass Loss. West Conshohocken, PA, 2014.

[22] Martienssen W, Warlimont H. Handbook of Condensed Matter and Materials Data. Springer; 2005. ISBN: 9783540304371.

[23] Marshall DB, Lawn BR. Residual stress effects in sharp contact cracking. Journal of Materials Science. 1979;14(8):2001–12. DOI: 10.1007/BF00551043.

[24] Abou-El-Leil M, Cooper AR. Fracture of soda-lime glass tubes by field-assisted ion exchange. Journal of the American Ceramic Society. 1978;61(3–4):131–136. DOI: 10.1111/j.1151-2916.1978.tb09255.x.

[25] Chuchai A, Kenneth JA, John JM, Jr. Residual stress in glass: Indentation crack and fractography approaches. Dental Materials. 2009;25(11):1453–8. DOI: 10.1016/j.dental. 2009.07.001.