IA GRANJA: Revista de Ciencias de la Vida

pISSN:1390-3799; eISSN:1390-8596

http://doi.org/10.17163/lgr.n29.2019.02





0

INTERACTION OF POLYVINYLIDENE FLUORIDE (PVDF)-BASED BINDERS WITH STRONGLY ALKALINE SOLUTIONS

INTERACCIÓN DE AGLUTINANTES DE FLUORURO DE POLIVINILIDENO (PVDF) CON SOLUCIONES FUERTEMENTE ALCALINAS

Leonard Pagliaro¹[®] y Daniel A. Lowy^{*2}[®]

¹ Research Scientist, FlexEl, LLC, College Park, MD 20740, USA

² Northern Virginia Community College, Department of Science and Engineering, Alexandria Campus, Alexandria, VA 22311, USA

*Corresponding author: daniellowy@gmail.com

Article received on January 6th, 2019. Accepted, after review, on February 13th, 2019. Published on March 1st, 2019.

Resumen

Se propone una metodología para evaluar los fenómenos degradantes de aglutinantes en los medios alcalinos, información que debe de ser de gran ayuda para los expertos en el campo de la investigación y desarrollo de baterías, ya que se podría evaluar la estabilidad esperada de los aglutinantes fluorados antes de ser probados en células galvánica ensambladas. Por esto, se ahorra tiempo, esfuerzo y se agiliza el trabajo. Mientras que el poli (tetrafluoroetileno), PTFE, ha demostrado ser químicamente inerte, este plantea un desafío tecnológico severo, siendo difícil de procesar debido a su fibrilación. Los aglutinantes alternos son poli (1, 1-difluoroetileno), PVDF, y sus copolímeros, conocidos bajo el nombre comercial de Kynar(R), que son significativamente más fáciles de usar. Sin embargo, cuando se mantiene en contacto con soluciones fuertemente alcalinas, la estabilidad química de Kynars se ve comprometida. Estos pueden someterse a reacciones de eliminación con la liberación de iones de fluoruro y la formación de enlaces dobles. Estos enlaces π pueden degradarse aún más por oxidación, en contacto con oxidantes incorporados en el cátodo. Estos procesos químicos no deseados pueden inhibir las propiedades aglutinantes y, en última instancia, pueden reducir la vida útil de las células galvánica, agotando el rendimiento de la batería. En este rol, se investigó la descomposición de la aglutinación de PVDF en medios alcalinos siguiendo dos pasos: (i) los aglutinantes puros fueron probados exponiéndolos a 32 wt % solución acuosa de KOH, a 60°C, temperatura que acelera los procesos degradantes, y (ii) se investigaron los aglutinantes incorporados en la pasta cátodo en condiciones similares. La degradación del aglutinante se evaluó determinando la concentración de iones de fluoruro liberados, monitoreando el cambio de color y la formación de precipitados y grabando e interpretando los espectros FT-IR.

Palabras clave: Kynar, polivinílico (1,1- difluoretileno), PVDF, PTFE, deshidrohalogenación, aglutinante del cátodo,

células galvánicas.

LA GRANJA: *Revista de Ciencias de la Vida* 29(1) 2019:18-32. © 2019, Universidad Politécnica Salesiana, Ecuador.

Abstract

A careful methodology to monitor binder degrading phenomena in alkaline media is proposed, which should assist experts in field of battery research and development, as it can evaluate the expected stability of fluorinated binders, prior to being tested in assembled galvanic cells. By this, it saves time, effort, and expedites work. While poly(tetrafluoroethylene), PTFE, has proven chemically inert, it poses a severe technological challenge, being difficult to process due to its fibrillation. Alternate binders are poly(1,1-difluoroethylene), PVDF, and its copolymers, known under the trade name of Kynar®, which are significantly easier to use. Nevertheless, when kept in contact with strongly alkaline solutions, the chemical stability of Kynars is compromised. They may undergo elimination reactions with the release of fluoride ions and the formation of double bonds. These π bonds may further degrade by oxidation, in contact with oxidizers incorporated in the cathode. Such undesired chemical processes may inhibit the binding properties and, ultimately, may reduce shelf life of galvanic cells, depleting battery performance. In this paper PVDF binder decomposition in alkaline media was investigated in two steps: (i) pure binders were tested by exposing them to 32 wt % aqueous KOH solution, at 60°*C*, a temperature that accelerates degrading processes, and next (ii) binders incorporated in cathode paste were investigated under similar conditions. Binder degrading was evaluated by determining the concentration of released fluoride ions, monitoring color change and precipitate formation and recording and interpreting FT-IR spectra.

Keywords: Kynar, poly(1,1-difluoroethylene), PVDF, PTFE, dehydrohalogenation, cathode binder, galvanic cells.

Suggested citation:Pagliaro, L. and Lowy, D.A. (2019). Interaction of Polyvinylidene fluoride (PVDF)-
Based Binders with Strongly Alkaline Solutions. La Granja: Revista de Ciencias de la
Vida. Vol. 29(1):18-32. http://doi.org/10.17163/lgr.n29.2019.02.

Orcid IDs:

Leonard Pagliaro: https://orcid.org/0000-0002-3969-2636 Daniel A. Lowy: https://orcid.org/0000-0003-2210-6757

1 Introduction

Poly(tetrafluoroethylene), PTFE, is a material with unique properties, chemically inert in strongly acidic or alkaline media, and in contact with organic solvents. Also, it possesses excellent heat and cold resistance, flame retardance, non-tackiness, and is a good electrical insulator. PTFE poses, however, severe technological challenges, as it is difficult to be processed due to its fibrillation. It is identified as a polymer which shows essential microstructure formation during cold processing, such as paste extrusion (Patil et al., 2008; Mitsoulis and Hatzikiriakos, 2009). Given that paste making is a mandatory step in the manufacturing of galvanic cells, in battery industry one prefers other binders which are more cost-effective and easier to handle, and by this increases throughput and reduces processing downtime (Vora and Gingras, 2012b,a). Widely used alternate binders are poly(1,1-difluoroethylene) or poly(vinylidene fluoride), PVDF, and its copolymers, known under the trade name of Kynar® (Arkema Technical Polymers, 2018).

Poly(vinylidene fluoride), PVDF, is considered one of the most chemically and mechanically resistant polymers available commercially (Grasselli and Betz, 2005). Therefore, PVDF is a very popular material for membrane fabrication, such separators having wide use in various industrial applications. Among the important properties of PVDF that enable membrane formation is its natural hydrophobicity, thermal stability, and chemical inertness in alkaline media (Liu et al., 2011). Owing to these properties, PVDF serves as one of the most common binders in battery manufacturing. Nevertheless, a detrimental interaction of PVDF and cathode materials was revealed for Li-ion batteries. It was demonstrated that the contact of PVDF with LiCoO₂ depletes the stability of the active mass. Particularly at elevated temperatures, the formation of surface oxide (Co_3O_4) and dissolution of Co ions is accelerated at contact points between the active mass and the binder (Markevich et al., 2005). More recently, similar phenomena have been documented for $Li - O_2$ batteries, where PVDF, a commonly used cathode binder degrades in the presence of reduced oxygen species during $Li - O_2$ discharge,

when impurities are present (Papp et al., 2017).

When used in alkaline batteries, strongly basic conditions can decline the mechanical and thermal stability of PVDF films, and can cause surface degradation and structural modifications. As early as in 1984, Dias and McCarthy demonstrated that when virgin PVDF is exposed to strong alkaline solutions, the polymer surface can be modified (Dias and McCarthy, 1984). It was also shown that the dehydrofluorination proceeding on the polymer surface is temperature dependent (Shoichet and McCarthy, 1991). When PVDF films are exposed to alkaline media, the films are damaged by the formation of pores in the texture of the polymer. Several chemical etching studies have been conducted with 9-10 mol L^{-1} or 20 wt. % sodium hydroxide solution, in the temperature range from 55 to $85^{\circ}C$ (Grasselli and Betz, 2005; Komaki et al., 1996; Hashim et al., 2011). While alkaline etch at $55 - 65^{\circ}C$ yields cylindrical pores, at 85°C conical-shaped track-etched pores are produced (Grasselli and Betz, 2005). Even dilute KOH solutions (≤ 0.2 M) were shown to generate a large number of pores in the polymer texture by an etching process (Samsure et al., 2016). The presence of an oxidizing agent in the alkaline solution amplifies the etching of PVDF (Grasselli and Betz, 2005). In an investigation of the cycling performance of Fe(III) oxide electrodes, four binder materials were compared to be used in alkaline solution. It was found that PTFE offers better cycling properties than PVDF (Kitamura et al., 2012).

Dehydrohalogenation of PVDF is a known phenomenon and has been used as a synthetic method for introducing double bonds into the polymer chain, which eventually served for grafting other polymers onto it. To enable elimination, tetramethylammonium hydroxide was used as the base ($K_b = 4,2$) (Yan et al., 2016; Zhang, 2015), which is close to 4 orders of magnitude weaker than the KOH utilized in the work reported here. These chemical etching studies suggest that exposing PVDF to alkaline solutions deteriorates its mechanical and thermal stability. Further, high alkali concentrations and temperatures would cause additional degrading of PVDF.



Decay of PVDF in strongly alkaline solution likely occurs by the loss of HF from the fluorinated hydrocarbon chains, via elimination reaction (Equation 1). Fluoride ions are released and double bonds formed. This reaction may proceed further to form additional double bonds (Equation 2). The outcome is an unsaturated chain, containing a conjugated system, which absorbs light in the visible/UV range.

Over the time, a darkening of the polymer can be noticed (Danks et al., 2002, 2003; Hinksman et al., 2000). The unsaturated carbon chains may further degrade by oxidation in contact with the cathodeactive materials, *NiOOH* (Guiader and Bernard, 2018), *MnO*₂ (Biswal et al., 2015), or *RuO*₂ (Peckerar et al., 2011b,a) which serve as the oxidizer. A possible schematic of the oxidation process is shown in Equation 3, where [*O*] represents the oxidizing agent.

All these undesirable chemical processes may deplete the binding properties and, ultimately, may reduce shelf life of the galvanic cells. With the aim of evaluating the possible use of PVDF in alkaline battery system, its degrading was evaluated. One used a methodology specifically designed for the investigation of PVDF binder decomposition in alkaline media. Released F- ion concentration (expressed in ppm), color change, formation of precipitate, and reflectance FT-IR spectra.

2 Materials and Methods

2.1 Chemicals and Materials

Fluorinated PVDF-based binders were purchased or received as a gift from Arkema, Inc. (King of Prussia, Pennsylvania, USA). Poly(tetrafluoroethylene), PTFE, was purchased from DuPont, in the form of 60wt.% suspension in water. Listed in Table 1 are trade names, chemical names, CAS numbers, and compositions of the binders, reported by the manufacturer. All binders were used as received. Aqueous alkaline solutions were prepared by dissolving KOH pellets ($\geq 85\%$, Sigma-Aldrich) in de-ionized water $(18, 2M\Omega \cdot cm,$ Super-Q[®] Plus Water Purification System, EMD Millipore). For fluoride probe calibration were used 1000. ppm Ion-Selective Standard Solution, Fluoride (Cole-Parmer), while 100. ppm, 10.0 ppm, and 1.00 ppm F^- standard solutions were prepared inhouse by serial dilution of the 1000. ppm standard with de-ionized water. The ionic strength adjuster was TISAB 1 (Total Ionic Strength Adjuster Buffer, #EW-27502-69, Fluoride ISE Double junction solution kit, Cole-Parmer).

Trade Name	Chemical Name	CAS Number	Composition/ Physical State
Kynar Flex [®]	Poly(1,1-difluoroethylene)-co-	Copolymer #0011 17 0	Monomer ratio
Kynar Ultraflex RC-10,204	Poly(1,1-difluoroethylene)-co- hexafluoropropylene (PVDF-HFP)	Copolymer PVDF: #24937 – 79 – 9 HFP: #116 – 15 – 4	35 – 55wt. % copolymer in water / Suspension
Kynar [®] 32 Latex PVDF	Poly(1,1-difluoroethylene) homopolymer (PVDF) + $C_7 - C_{13}$ perfluorocarboxylic acid, ammonium salt (PFAA)	Hompolymer with additive PVDF: #24937 – 79 – 9 PFAA: #72968 – 38 – 8	99wt.% PVDF & <1wt.% PFAA, in aq. / Suspension
PTFE TE3859	Poly(tetrafluoroethylene), PTFE Polyethylene glycol trimethylnonyl ether (Tergitol [®] TMN)*	PTFA: #9002 - 84 - 0 Tergitol: #60828 - 78 - 6	45-65wt.% polymer, 1-10wt.% Tergitol in 25-50wt.% water / Suspension

Table 1. Physical properties of PVDF-based and PTFE binders.

* Tergitol TMN serves as a surfactant for maintaining PTFE in aqueous suspension.

2.2 Methods

2.2.1 Samples Used for Fluoride Measurement

Experiments were performed with weighed amounts of 4 binders (received either as solids or aqueous dispersions), which were exposed to aqueous 32*wt*. % KOH solution (pH > 14), at 60°C, for increasing durations. The release of F^- ions was monitored over the time by means of a fluoride combination electrode (for details see Section 2.2.4 below). Later, galvanic half-cells were built using 4 different cathode pastes, containing the binders listed in Table 1. Each cathode paste was confined to a current collector, then wound with a battery separator, and immersed in aqueous 32wt. % KOH solution. This approach mimics the real-life use of binders in galvanic cells. A sulfonated olefin film, Freudenberg FV-4304, served as the separator (Freudenberg Performance Materials, LP, Durham, North Carolina). Each roll was tied with tear-resistant CU-RAPROX PTFE Floss Tape (Code DF820, Curaden AG, Kriens, Switzerland), and then, these wound cathodes were immersed in 32wt.% aqueous KOH solution individually, in a separate polypropylene vial for timed durations.

2.2.2 Sample Preparation

Sample preparation involved three steps: (i) the precipitated part of the binder was filtered off, (ii) sample was cooled in ice bath, for avoiding possible damage caused by the heat released over neutralization, in the next step; (iii) sample was buffered to pH 5.5-6.5 via neutralization with glacial acetic acid. According to our protocol, 14.7 g of glacial acetic acid buffering agent was added to 22.4 g filtered solution, such that the sample was adjusted to pH 6.5 \pm 0.2, which is the ideal range for fluoride ion determination.

2.2.3 Preventing Interference in the Response of F– Selective Probe

Caution was taken for not contaminating the samples with any interfering anions, including halides (Cl^-, Br^-, I^-) , nitrate, sulfate, etc. To prevent sample contamination, the use of glass containers was avoided over the entire sample preparation process (described in Section 2.2.4). All samples were diluted, as needed, in volumetric flasks made of polypropylene (Corning PP Plastic Volumetric Flasks, 100 mL, ± 0.20 mL at $20^{\circ}C$), and all F^- ion concentration measurements were conducted in polypropylene beakers (Cole-Parmer Tri-Corner Beaker, PP, 100 mL).

2.2.4 Potentiometric Monitoring Fluoride Concentration

Next, the F^- concentration in the filtered buffered samples was determined by using a Fluoride Ion Combination Epoxy Electrode (Cat. No. 27504-14, Cole-Parmer), with a measurement range from 1.0 mol L^{-1} to 1.0 μ mol L^{-1} , attached to a Model Orion Star A211 pH/mV meter (Thermo Scientific). Measurements were carried out at pH ~ 6.5.

LA GRANJA: *Revista de Ciencias de la Vida* 29(1) 2019:18-32. ©2019, Universidad Politécnica Salesiana, Ecuador.

On each day of measurements, the F^- -selective probe was calibrated with 4 standard solutions. The calibration curve of the probe was linear over 3 orders of magnitude of F^- concentration (1-1000 ppm), with a slightly over-Nernstian slope of $62,1mV/(F^-$ concentration decade), and close to theoretical correlation coefficient of $R^2 = 0.9998$. The probe was re-calibrated by 4-point calibration every day. In addition, prior to each measurement, the slope of F^- -selective electrode was checked again via 2-point calibration, with two standard solutions containing 10 and 100 ppm F^- , respectively. The ionic strength of each solution was adjusted to constant value, by adding TISAB 1 (Total Ionic Strength Adjuster Buffer, #EW – 27502 – 69, Fluoride ISE Double junction solution kit, Cole-Parmer). This operation is imposed by the need for high and constant ionic strength relative to the sensed F^- ion concentration, so that the activity coefficient, γ , is constant; then, fluoride activity becomes directly proportional to fluoride concentration.

Given that the two consecutive calibration standards encompass a concentration decade, the difference of the recorded potential in mV corresponds to the slope of the probe (mV/decade).

2.2.5 Color Change of Binders

Color change of binders as a function of exposure time to the alkaline solution was monitored in the clear solution, after removing the solids by gravity filtration. Photographs were taken periodically and compared visually to assess color changes. The formation of precipitates was also recorder when it occurred.

2.2.6 FT-IR spectra

We recorded FT-IR spectra of the PVDF polymers prior and after having been exposed to concentrated hydroxide solution. After exposure, the solid was collected by gravity filtration, rinsed 7 times with DIW for removing any trace of KOH, and then dried in air, at room temperature for 48*h*. FT-IR spectra of polymer samples were recorded in reflectance mode; as controls one used samples of the identical polymer that had not been exposed to alkaline media. Spectra were recorded on a Model Nexus 870 FT-IR ESP instrument, manufactured by Thermo Nicolet, in the spectral range from 4000 to $400 \, cm^{-1}$. As shown in the Appendix, all spectra were recorded as absorbance vs. wavelength.

3 Analysis and Results

One important detail of the implemented methodology was to operate the F^- -selective probe in slightly acidic solution, imposed by the manufacturer's instructions. (Cole-Parmer Company Fluoride Ion Electrodes, 2018). As described, our sample solutions were all strongly basic (pH > 14). Therefore, prior to any potentiometric measurement, sample preparation was needed, according to the methodology described in Section 2.2.2. A schematic of the sample preparation and analytical procedure is displayed in Figure 1.



Figure 1. Schematic of the sample preparation and the analytical procedure.

The physical state of one binder was solid, while the other 3 were received in the form of aqueous suspensions (see Table 1). The mass of each binder sample taken for these tests was calculated such that it contained ca. 1 g solid material. Therefore, the measured F^- ion concentration (expressed in ppm), liberated from the binder sample, parallels the mass loss of binder (in mass %), caused by F^- ion release. PTFE binder immersed in the same strongly alkaline solution served as the control experiment.

Curves in Figure 2 illustrate the release F^- ions from each binder over the time. Loosing fluoride de-

LA GRANJA: *Revista de Ciencias de la Vida* 29(1) 2019:18-32. ©2019, Universidad Politécnica Salesiana, Ecuador. pletes the binding properties and, therefore, corresponds to the degrading of the binder. Data points for PTFE are close to 0 ppm of released F^- ; therefore, they are aligned along the x axis, and cannot be seen on the graph. Out of the pure binders exposed to 32wt.% KOH solution, Kynar Ultra Flex degrades

at the fastest pace; given that it is a suspension, the fluorinated polymer contained in the binder has the largest contact area with the electrolyte. By contrast, Kynar Flex, which is solid, exhibits a much slower degrading (see green triangles in Figure 2).



Figure 2. Fluoride ion release over 2 days from 4 different fluorinated binders upon being immersed in 32wt.% KOH solution, and kept at $60^{\circ}C$; the greater the F^{-} concentration (in ppm) measured over 48 h the greater the extent of binder degrading. The PTFE control released negligible concentrations of F^{-} (see red circles at the bottom of the graph).

Next, the real-life environment of the binder was mimicked, which was encountered in alkaline battery research and development. Each binder was blended into the cathode paste, and then the paste was applied onto the current collector. The binder content of each cathode paste expressed as *wt*.% of solid polymer, is listed in Table 2. Cathode samples were weighed and wound with the sulfonated polymer.

yolefin separator (Freudenberg FV-4304). The obtained rolls were tied with PTFE floss tape, and immersed in 32wt. % KOH solution, each roll in a separate plastic vial. Then, all vials were placed in an environmental chamber, and maintained at $60^{\circ}C$. Again, the control experiment was the degrading rate of PTFE binder. Results of fluoride release monitoring are shown in Figure 3.

Binder	Solid content of the Binder in the cathode	Dried in Air	Annealed
Kynar Flex	2.44 wt.%	N/A	$150^{\circ}C$, 15 min
Kynar Ultra Flex	3.36 wt. %	60° <i>C</i> , 1 h	95°C, 15 min
PVDF Latex-32	4.24 wt.%	60° <i>C</i> , 1 h	150°C, 15 min
PTFE	0.988 wt. %	60° <i>C</i> , 1 h	N/A

For the investigated cathode half-cells, it was found that in 1 week at 60°, Kynar Ultra Flex binder degraded at the highest rate, followed by PVDF Latex-32 and Kynar Flex. Control experiment with PTFE showed degrading to a negligible extent. Color change (darkening of the sample solution) or precipitate formation (caused by the shedding of the cathode active material from the current collector) parallels the degrading assessed by the increase of fluoride concentration. FT-IR spectra reveal disappearing C - F bonds as a result of PVDF degrading, which caused the increase of carbon chain unsaturation.



Figure 3. Degrading of binders from half cells over the time when exposed to 32wt.% KOH solution. Tests were performed on binders incorporated in half cells, and the F^- concentration (in ppm) was monitored over 1 week. The PTFE control released negligible concentrations of F^- (see red circles at the bottom of the graph).

4 Discussion and Conclusions

Fluoride release from different binders shows a similar trend for the free binders (not incorporated in cathode paste, displayed in Figure 2), and for binders present in half-cells (Figure 3). Fluoride loss from the binders rises in the order shown below, which also corresponds to the extent of the chemical degrading of the binders:

 $PTFE \ll Kynar Flex < PVDF Latex-32 \ll Kynar Ultra Flex$

In Figures 4 and 5 the visual proof of binder degrading was displayed:

- Over the time Latex-32 exhibits a color change (darkening of the solution), Figure 4.
- PTFE does not show any sign of degrading (either color change or precipitate formation), Figure 5.

Lastly, in Figure 6 one compares cathodes made with Kynar Ultra Flex (the most stable of the investigated Kynar binders) and cathodes prepared with PTFE (control). Pictures were taken after 168 h of exposure to KOH 32wt.% solution (serving as typical electrolyte in alkaline cells). Pictures reveal more shedding of the cathode made Kynar Ultra Flex than with PTFE.



Figure 4. Photograph showing the color change of 32*wt*. % KOH solution and precipitate formed over the time for PVDF Latex-32; darkening corresponds to the increasing number of double bonds on the carbon chains, because of fluoride loss; precipitate consists of particles shedding from the cathode and settled to the bottom of the vial.



Figure 5. Photograph showing the color change of 32*wt*. % KOH solution and precipitate formed over time for PTFE, used as the control; the strongly alkaline solution stays tear-clear and there is no noticeable precipitate.

The appendix contains overlaid FT-IR spectra; each binder was analyzed after being exposed to 32wt.% KOH solution, and then overlaid with the spectrum of the initial, untreated binder. Spectral band assignments are based on Robinson (1974) and other literature resources (Bhullar, 2014; Smith, 2011; Stuart, 2004; Ningrum and Kusumawati, 2016; Perusich, 2000). Except for PTFE, each binder exhibits a change in its C - F bonds, namely, the absorption of this bond gets the more or the less depleted, demonstrating that part of the C - F bonds are cleaved by the strongly alkaline electrolyte. Spectra in Figure 1A reveal significant change in the composition of the binder. Over immersion in concentrated alkaline solution, the $> CF_2$ stretching absorption band almost disappears, while additional absorption bands show up in the $1575 - 1660 \, cm^{-1}$

region, which can be assigned to the formation of -C = C - double bonds. Some of these π bonds may undergo addition reactions of water molecules, and form carbonyl groups, which absorb at $1700 \, cm^{-1}$ (see shoulder in Figure A.1). A conjugated double bond system (-C = C - C = C - C = C -) accounts for the orange-brown color assessed for several of the binder solutions (see Figure 5). Precipitate formation corresponds to shedding of the cathode-active materials from the nickel foam. The extent of the chemical degrading of binders increases in the order:

 $\mbox{PTFE} \ll \mbox{Kynar Flex} < \mbox{PVDF Latex-32} \ll \mbox{Kynar Ultra Flex}$

It is believed that the methodology reported here will allow for monitoring the fluoride release from any fluorine-containing binder when present in full cells. Therefore, such investigations should

LA GRANJA: *Revista de Ciencias de la Vida* 29(1) 2019:18-32. ©2019, Universidad Politécnica Salesiana, Ecuador. convey to the experts in the field valuable information on the expected stability of binders, prior to being tested in assembled galvanic cells, saving ti-

me and effort, and expediting battery research and development.



Figure 6. More shedding of the cathode exposed to the action of 32*wt*.% KOH solution (the electrolyte in alkaline batteries) can be noticed for Kynar Ultra Flex than for PTFE (in each photograph the top picture is the Ni foam, while the bottom is the separator).

Acknowledgements

Authors are grateful to Dr. Jean-François Audebert, CEO and President of FlexEl, LLC, for valuable discussions and his permanent encouragement to carry out this study and disseminate its results. Ms. Mahsa Dornajafi is acknowledged for providing technical assistance, which allowed to significantly expedite the work reported here.

References

- Arkema Technical Polymers (2018). Materials database. Online: https://bit.ly/2SfO0ti.
- Bhullar, S. K. ; Bedeloglu, A. . M. B. G. (2014). Characterization and auxetic effect of polytetrafluo-

roethylene tubular structure. *International journal of Advanced Science and Engineering*, 1(2):8–13. Oline:/urlhttps://bit.ly/2GB4sTu.

- Biswal, A., Tripathy, B., Subbaiah, T., Meyrick, D., and Minakshi, M. (2015). Electrodeposition of manganese dioxide: effect of quaternary amines. *Journal of Solid State Electrochemistry*, 17(5):1349– 1356. Online:/urlhttps://bit.ly/2BKIHOj.
- Cole-Parmer Company Fluoride Ion Electrodes (2018). *Instruction Manual*. Cole-Parmer Company. Online:https://bit.ly/2EnZB5V.
- Danks, T. N., Slade, R. C. T., and Varcoe, J. R. (2003). Alkaline anion-exchange radiation-grafted membranes for possible electrochemical application in fuel cells. *Journal of Materials Chemistry*, 13(4):712– 721. Online:/urlhttps://bit.ly/2GRYOfb.

LA GRANJA: *Revista de Ciencias de la Vida* 29(1) 2019:18-32. © 2019, Universidad Politécnica Salesiana, Ecuador.

- Danks, T. N., Slade, R. T., and Varcoe, J. R. (2002). Comparison of PVDF-and FEP-based radiationgrafted alkaline anion-exchange membranes for use in low temperature portable dmfcs. *Journal of Materials Chemistry*, 12(12):3371–3373. Online:/urlhttps://rsc.li/2XcNakX.
- Dias, A. J. and McCarthy, T. J. (1984). Synthesis of a two-dimensional array of orgroups: surface-selective ganic functional poly (vinvlidene modification of fluori-Macromolecules, 17(12):2529-2531. Onlide). ne:/urlhttps://bit.ly/2X8DEiC.
- Grasselli, M. and Betz, N. (2005). Making porous membranes by chemical etching of heavyion tracks in β-pvdf films. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 236(1-4):501–507. Online:/urlhttps://bit.ly/2NgrH5M.
- Guiader, O. and Bernard, P. (2018). Understanding of $Ni(OH)_2/NiOOH$ irreversible phase transformations: Ni_2O_3H impact on alkaline batteries. *Journal of The Electrochemical Society*, 165(2):A396– A406. Online:/url.
- Hashim, N. A., Liu, Y., and Li, K. (2011). Preparation of PVDF hollow fiber membranes using *SiO*₂ particles: the effect of acid and alkali treatment on the membrane performances. *Industrial & Engineering Chemistry Research*, 50(5):3035–3040. Online:/urlhttps://bit.ly/2EiVNCM.
- Hinksman, P., Isaac, D. H., and Morrissey, P. (2000). Environmental stress cracking of poly (vinylidene fluoride) and welds in alkaline solutions. *Polymer Degradation and Stability*, 68(2):299–305. Online:/urlhttps://bit.ly/2VaAh9d.
- Kitamura, H., Zhao, L., Hang, B. T., Okada, S., and Yamaki, J.-i. (2012). Effect of binder materials on cycling performance of *Fe*₂*O*₃ electrodes in alkaline solution. *Journal of Power Sources*, 208:391–396. Online:/urlhttps://bit.ly/2SNrnle.
- Komaki, Y., Ishikawa, N., Morishita, N., and Takamura, S. (1996). Radicals in heavy ion-irradiated polyvinylidene fluoride. *Radiation Measurements*, 26(1):123–129. Online:/https://bit.ly/2T3vnx3.
- Liu, F., Hashim, A. N., Liu, Y., Abed, M. R., and Li, K. (2011). Progress in the production and modification of pvdf membra-

nes. *Journal of membrane science*, 375(1-2. Online:/urlhttps://bit.ly/2SdM3Oa):1–27.

- Markevich, E., Salitra, G., and Aurbach, D. (2005). Influence of the pvdf binder on the stability of *licoo*₂ electrodes. *Electro-chemistry communications*, 7(12):1298–1304. Online:/urlhttps://bit.ly/2GRNM9G.
- Mitsoulis, E. and Hatzikiriakos, S. G. (2009). Steady flow simulations of compressible PTFE paste extrusion under severe wall slip. *Journal of Non-Newtonian Fluid Mechanics*, 157(1-2):26–33. Online:/urlhttps://bit.ly/2DVviCh.
- Ningrum, R. D. C. and Kusumawati, N. (2016). Development and characterization of Polysulfone/Polyvinylidene Flouride blend membrane induced by delayed liquid-liquid demixing. *International Journal on Advanced Science, Engineering and Information Technology*, 6(5):716–722. Online:/urlhttps://bit.ly/2NfBdX9.
- Papp, J. K., Forster, J. D., Burke, C. M., Kim, H. W., Luntz, A. C., Shelby, R. M., Urban, J. J., and McCloskey, B. D. (2017). Poly (vinylidene fluoride)(pvdf) binder degradation in *li* – *o*₂ batteries: a consideration for the characterization of lithium superoxide. *The journal of physical chemistry letters*, 8(6):1169–1174. Online:/https://bit.ly/2T6Q9vZ.
- Patil, P. D., Ochoa, I., Feng, J. J., and Hatzikiriakos, S. G. (2008). Viscoelastic flow simulation of polytetrafluoroethylene (PTFE) paste extrusion. *Journal of Non-Newtonian Fluid Mechanics*, 153(1):25– 33. Online:https://bit.ly/2Xf7bHF.
- Peckerar, M., Dilli, Z., Dornajafi, M., Goldsman, N., Ngu, Y., Proctor, R. B., Krupsaw, B. J., and Lowy, D. A. (2011a). A novel high energy density flexible galvanic cell. *Energy* & Environmental Science, 4(5):1807–1812. Online:/urlhttps://rsc.li/2EmhEto.
- Peckerar, M., Dornajafi, M., Dilli, Z., Goldsman, N., Ngu, Y., Boerger, B., Van Wyck, N., Gravelin, J., Grenon, B., Proctor, R. B., et al. (2011b). Fabrication of flexible ultracapacitor/galvanic cell hybrids using advanced nanoparticle coating technology. Journal of Vacuum Science & Technology B, Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena, 29(1):011008. Online:/urlhttps://bit.ly/2BKnPFM.

LA GRANJA: *Revista de Ciencias de la Vida* 29(1) 2019:18-32. ©2019, Universidad Politécnica Salesiana, Ecuador.

- Perkin-Elmer (2018). Polymer Identification Using Mid Infrared Spectroscopy. Perkin-Elmer.
- Perusich, S. A. (2000). Fourier transform infrared spectroscopy of perfluorocarboxylate polymers. *Macromolecules*, 33(9):3431–3440. Online:/urlhttps://bit.ly/2GS712Q.
- Robinson, J. W. (1974). Handbook of Spectroscopy: Volume I. CRC press.
- Samsure, N. A., Hashim, N. A., Sulaiman, N. M. N., and Chee, C. Y. (2016). Alkaline etching treatment of PVDF membrane for water filtration. *RSC Advances*, 6(26):22153–22160. Online:/urlhttps://rsc.li/2tvUQRJ.
- Shoichet, M. S. and McCarthy, T. J. (1991). Convenient syntheses of carboxylic acid functionalized fluoropolymer surfaces. *Macromolecules*, 24:982– 986. Online:/urlhttps://bit.ly/2ScTt3Z.
- Smith, B. C. (2011). Fundamentals of Fourier transform infrared spectroscopy. CRC press.
- Stuart, B. H. (2004). *Infrared Spectroscopy: Fundamentals and Applications*. John Wiley & Sons, Ltd., Chichester (West Sussex, England), 1st edition.
- Vora, V. and Gingras, J. (2012a). Pvdf fluoropolymer process aids: For best-in-class performance,. *Modern Plastics & Polymers*, september:71–72.
- Vora, V. and Gingras, J. (2012b). Pvdf fluoropolymer process aids: Increasing throughput, reducing downtime. *Modern Plastics & Polymers.*, january:190–192.
- Yan, K.-b., Guo, G.-b., Liu, J.-y., Huang, Q., and Zhang, J.-h. (2016). Preparation and characterization of oil/water separation membranes via grafting methyl methacrylate onto Poly (vinylidene fluoride. *Acta Polymerica Sinica*, (5):659–666.
- Zhang, Jia-Han ; Guo, G.-B. A. S.-L. H. Y. Z. D. Y. K.-B. (2015). Synthesis and properties of proton exchange membranes via single-step grafting psbma onto pvdf modified by TMAH. Acta Physico-Chimica Sinica, 31(10):1905–1913. Online:/urlhttps://bit.ly/2TW9BIT.

Appendix

A FT-IR Studies on initial and degraded binders

For enabling easier overview, each IR band has been marked with the molecular vibration to which it corresponds. Spectra reveal significant change in the composition of the binder. Over KOH treatment the > CF_2 stretching absorption band almost disappears, while additional absorption bands show up in the 1575 – 1660 cm^{-1} region, which correspond to the presence of conjugated double bonds. Some of these may add a water molecule, and form carbonyl groups, which absorb at 1700 cm^{-1} (see shoulder in Figure 1A.).



Figure 1. A. Overlay of IR spectra for Kynar Ultraflex: blue – initial binder, red – after 48 h exposure to 32wt. % KOH solution, at $60^{\circ}C$.



Figure 2. A. Overlay of IR spectra for Kynar Kynar Flex: blue – initial binder, red – after 48 h exposure to 32*wt*. % KOH solution, at 60°*C*. No relevant change in polymer structure can be assessed (peak heights differ because of the amount of sample).



Figure 3. A. Overlay of IR spectra for PVDF Latex-32: blue – initial binder, red – after 48 h exposure to 32*wt*. % KOH solution. As for Kynar Kynar Flex (Figure 2), the absorption band of conjugated double bonds show up after exposing the binder to alkaline electrolyte for 1 week, at 60°*C*. Nevertheless, the change in polymer structure does not appear to be dramatic.

LA GRANJA: *Revista de Ciencias de la Vida* 29(1) 2019:18-32. © 2019, Universidad Politécnica Salesiana, Ecuador.



Figure 4. A. The figure shows in red the FT-IR spectra for PTFE after 96 h exposure to 32wt. % KOH solution.



Figure 5. A. The figure shows in black the library spectrum of PTFE (Perkin-Elmer, 2018). There insignificant differences between the two spectra, demonstrating that PTFE does not undergo chemical degrading.