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# Study of the degradation of Nafion modified membranes

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## INTRODUCTION

The development of new proton exchange membranes for PEM technology in fuel cells and electrolysers with increased durability is paramount to system´s lifetime and scalability. In this work, new modified Nafion membranes are proposed with increased resilience to chemical degradation by $H_2O_2$ /$Fe^{2+}$, mimicking ex-situ radical attack to membrane structure.

## EXPERIMENTAL

Membranes were prepared by casting Nafion®/DMAc solutions with 1.0 wt% of **BP1** and **BP2** dopants (Fig. 1a). Activation treatment is described elsewhere [1,2]. Characterization, before and after degradation tests, was done by ATR-FTIR spectroscopy (Perkin Elmer spectrometer) and SEM (Philips XL30 FEG). Their proton conductivity was also evaluated by electrochemical impedance spectroscopy, EIS (Solartron 1250 FRA), using a BekkTech conductivity cell under temperature and relative humidity (RH) control. Oxidation stability of membranes was assessed by Fenton´s test (3% $H_2O_2$ /4 ppm $Fe^{2+}$), at 80 °C for 112 h, through gravimetry measurements and fluoride ion release (ion selective electrode, ISE Sentek).

## RESULTS AND DISCUSSION

Morphological analysis by SEM revealed the formation of a heterogeneous surface for all membranes. The new modified membranes with **BP1** and **BP2** dopants (Fig. 1a) showed a weight loss of up to 3% at 112 h compared to the loss of near 18% of the Nafion membrane, at 80 °C. These results were corroborated with the measurements of fluoride ion loss. An increased release of fluoride ions vs exposure time is observed. The new membranes doped with **BP1** and **BP2** showed similar loss of the fluoride ion with values up to 14 mg e 12 mg per g of polymer at 112 h, respectively, vs. a higher loss observed for Nafion, with values of 88 mg per g of polymer, in the same experimental conditions (Fig. 1b and 1c). All membranes showed a large decrease to their proton conductivity down to 36 $mScm^{-1}$, obtained at 60 °C and 80% RH, nearly a third of the proton conductivity observed in similar conditions before their oxidative degradation. The new modified membranes showed higher proton conductivity than the Nafion membrane.

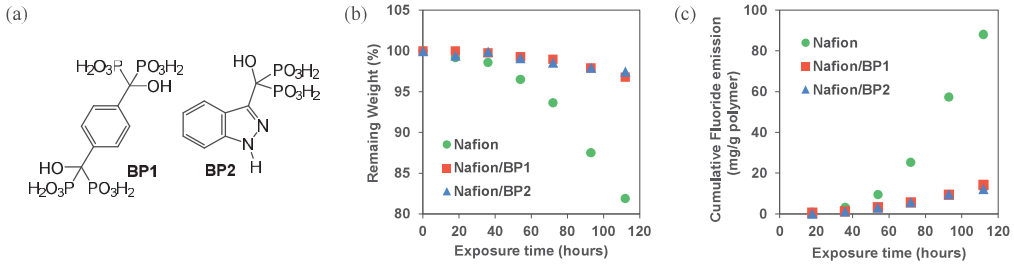


Fig. 1. Structure of BPs used as dopants (a); % remaining weight (b) and cumulative fluoride emissions (c) of membranes at 80 °C vs. exposure time.

## CONCLUSION

Prepared new modified membranes, with **BP1** and **BP2** used as dopants, exhibited a lesser degree of degradation regarding weight loss and released fluoride, and maintain a higher proton conductivity than Nafion in $H_2O_2$ /$Fe^{2+}$ environment.

## REFERENCES

[1] F.C. Teixeira, A.I. de Sá, A.P.S. Teixeira, C.M. Rangel, *Appl. Surf. Sci.*, 487, 889-897 (2019).
[2] F.C. Teixeira, A.I. de Sá, A.P.S. Teixeira, C.M. Rangel, *New J. Chem.*, 43, 15249-15257 (2019).

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