CA membranes as habit modifiers for the growth of whiskers of inorganic salts

N. YELLIN*
Department of Solid State Physics, Soreq Nuclear Research Centre, Yavne, Israel
N. ZELINGHER
Department of Mechanical Engineering, Ben-Gurion University, Be'er-Sheva, Israel
L. BEN-DOR
Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem, Israel

Many water-soluble inorganic salts grow as whiskers by means of cellulose–acetate (CA) membranes. This habit modification is independent of salt structure and properties and is due to the porosity of the support matrix of the membrane.

1. Introduction

Research concerning the growth of whiskers, their characterization and application is not abundant. Of the studies reported on growth from solution, most deal with alkali halides in aqueous solutions (see e.g. [1]) with some using porous media such as porcelain or cellophane [2, 3]. The state of the art in all studies leaves a lot to be desired. Whiskers of various materials could play a greater role for different applications provided they were more easily available (see e.g. [4]).

Celluluse–acetate (CA) membranes are well known for their use in ultra-filtration and desalination by reverse osmosis process [5, 6]. In this pressure-driven process, the transport of the solution is across the asymmetric membrane: a thin, dense skin ($< 0.5\,\mu$m) which is supported by a porous matrix ($\approx 100\,\mu$m). The skin is the salt-rejecting medium. Zelingher [7] was the first to point out the existence of a vector mass transport along the membrane, resulting in whisker growth. The transport of the solution occurs via the porous support layer, with the whiskers growing almost exclusively on its exposed surface [8, 9]. In the present work, whiskers of various inorganic salts were grown from aqueous solutions by means of CA membranes. An explanation of the habit modification of the crystals by the membrane is suggested.

2. Experimental details

The experimental details concerning the casting of the tubular CA membranes and the procedure for the growth of whiskers have been described previously [9]. All membranes used were freshly prepared and unannealed. The growth solutions were prepared from analytical grade dried salts in deionized water. Whisker growth was carried out at room temperature (23 to 28° C).

The composition and morphology of the whiskers were determined by X-ray diffraction, optical and scanning electron microscopy.

3. Results

A large number of soluble inorganic salts having various structures and different properties such as oxidation states, chemical bonding, hydration energies, mobilities and interaction with water, were studied. Table I lists all the salts from which whiskers were easily grown, and Fig. 1 shows a typical example of whisker growth. Whisker morphology was obtained

TABLE I Whiskers grown by means of CA membrane from aqueous solutions

Compound	Whisker composition (XRD)	Compound	Whisker composition (XRD)
1. KCl	KCl	13. K_2CrO_4	K_2CrO_4
2. $NaCl$	$NaCl$	14. $K_2Cr_2O_7$	$K_2Cr_2O_7$
3. KBr	KBr	15. K_2SO_4	K_2SO_4
4. $NaNO_3$	$NaNO_3$	16. Na_2SO_4	Na_2SO_4
5. KNO_3	KNO_3	17. $CuSO_4$	$CuSO_4 \cdot 5H_2O$
6. CH_3COONa	$CH_3COOH \cdot 3H_2O$	18. $NaNO_2$	$NaNO_2$
7. NH_4Cl	NH_4Cl	19. $Na_2C_4H_4O_6$	$Na_2C_4H_4O_6 \cdot 2H_2O$
8. $(NH_4)_2(COO)_2$	$(NH_4)_2(COO)_2$	20. $NaKC_4H_4O_6$	$NaKC_4H_4O_6 \cdot 4H_2O$
9. $BaCl_2$	$BaCl_2 \cdot 2H_2O$	21. Li_2SO_4	$Li_2SO_4 \cdot H_2O$
10. $[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_6]Cl_3$	22. $(NH_4)_2SO_4$	$(NH_4)_2SO_4$
11. $K_3[Fe(CN)_6]$	$K_3[Fe(CN)_6]$	23. $NiSO_4$	$NiSO_4 \cdot 6H_2O$
12. $CoCl_2$	$CoCl_2 \cdot 2H_2O$	24. $RbCl$	$RbCl$

*On sabbatical leave at the Hebrew University, Jerusalem, Israel.

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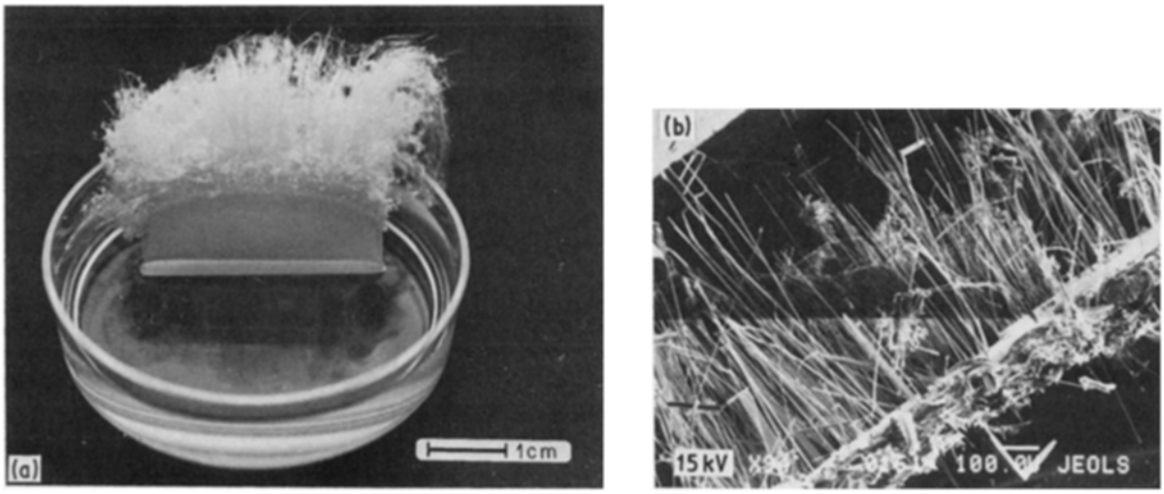

Figure 1 Whisker growth of NaCl. (a) Optical photograph of whiskers and membrane in the growth dish; (b) scanning electron micrograph of membrane and whiskers.

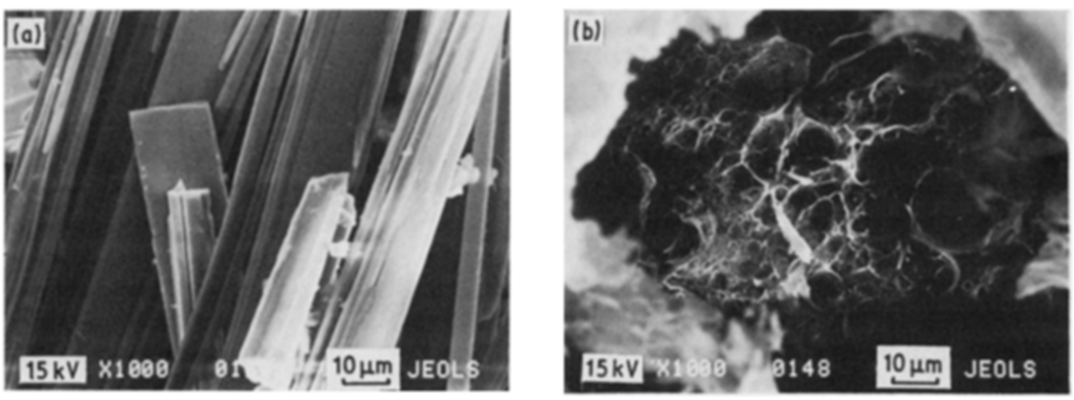

Figure 2 SEM micrographs of (a) K_2CrO_4 whiskers; (b) the porous support matrix; note the dimensions of the whiskers and pores.

exclusively (Table I) in spite of the differences in material properties, indicating that the membrane acts as a habit modifier.

The whiskers which were all single crystals grew to a length of several centimetres depending on growth time. Experiments of long duration (≈ 10 days) yielded easily whiskers up to 20 cm long. It seems that even longer whiskers can be obtained, prodivided feed solution is continuously added to the system. Typical dimensions of cross sections of whiskers were several micrometres or less (Fig. 2a), similar in size to the pore diameter of the support matrix (Fig. 2b). Note the honeycomb structure of the matrix. This similarity suggests that the pore structure modifies the crystal morphology. Whiskers were observed growing either separately or in inseparable sheaves (Fig. 3). The crystallographic axis of each whisker in a given sheaf was parallel to that of the others: e.g. a sheaf of Rochelle salt changed the plane of the polarized light as a single crystal. The whiskers were not hollow and growth was found to proceed from the bottom. Growth could be achieved from saturated as well as nonconcentrated solutions.

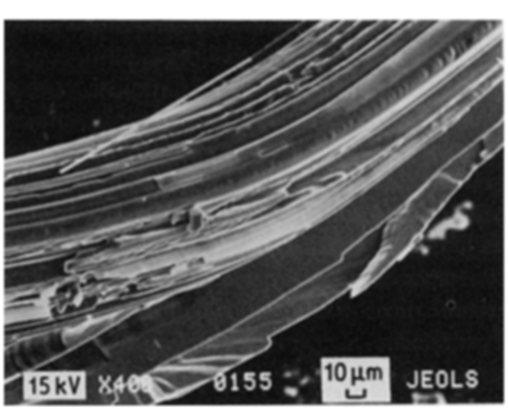

Figure 3 Sheaf of NaCl whiskers, note the flexibility of the whiskers.

Deliquescent salts, which do not crystallize out from aqueous solution, accumulate in the top part of the membrane exposed to the atmosphere in the form of sweat-like droplets. These droplets are saturated solutions of the salts [8]. This family of compounds includes, among others, LiCl, $MgCl_2$, $CaCl_2$ or halides of transition metals such as Ni^{2+} or Cd^{2+}. In the case of basic or acidic solutions or organic solvents (alcohol, acetone, ethylacetate, etc.) the properties of the membrane are altered and no whiskers can be grown.

Typical examples of whisker "roots" are shown in Fig. 4. Although it seems as if the whiskers grow from within the support matrix, not even one case of a whisker penetrating through the membrane could be detected by SEM, when carefully examining cross sections of various samples; instead, the whiskers seem to nucleate at the membrane surface.

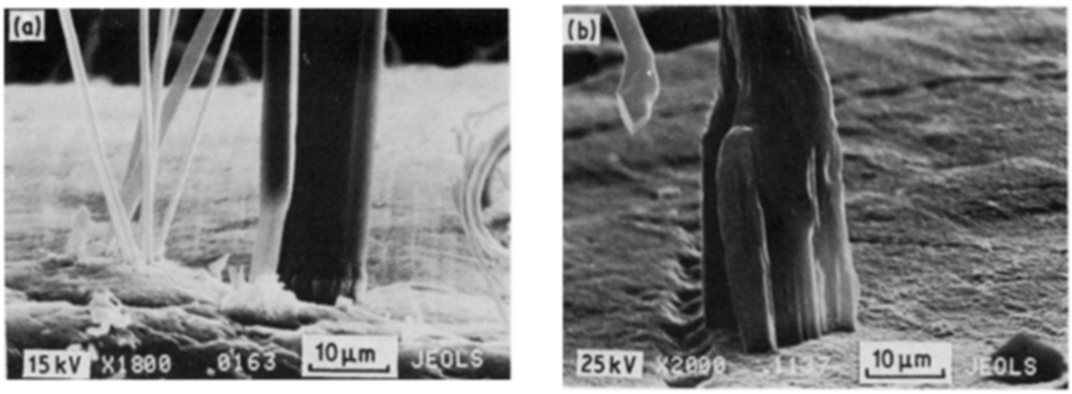

Figure 4 Scanning electron micrographs of whiskers "roots". (a) NaCl; (b) $Co(NH_3)_6Cl_3$.

4. Discussion

A membrane half submerged in solution loses water from its exposed surface evaporation. The lost water is replaced by water flowing along the porous support matrix of the membrane, as solution. This flow is affected by interactions between the hydrated ions and the acetate groups, as confirmed by the different transport rates along the membrane of the various salts [8, 9]. While the water is continuously evaporating from the surface of the exposed membrane, the solute accumulates and a concentration gradient is built up, its direction being opposed to the direction of flow. The solution at the exposed surface reaches saturation first, and solute nucleates at the pore exit. Nucleation occurs in the support matrix surface since the ions are rejected from the skin layer [5, 6]. The continuous supply of solute through the pores promotes crystal growth from that side of the nuclei which faces the solution. Thus, the pore serves as a mould and a whisker is formed. This model explains the experimental findings that all salts examined showed whisker morphology with very similar characteristics and with dimensions similar to that of the pore diameter.

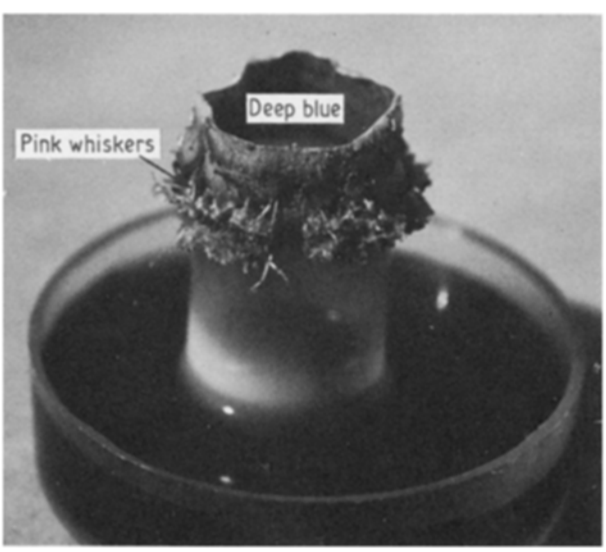

Figure 5 Pink $CoCl_2 \cdot 2H_2O$ whiskers growing on top of the "blue" membrane.

Several salts (Table I) grow whiskers having a hydrated salt composition. It was not clear whether this composition is due to water coming from the solution or absorbed from the atmosphere. In the case of $CoCl_2$, Fig. 5 shows the deep blue colour characteristic of tetrahedral Co^{2+} (see e.g. [10]) indicating deficiency of water in the membrane, while pink octahedral hydrated Co^{2+} whiskers grow on the outside. The acetate groups of the membrane could serve as potential ligands for the tetrahedral Co^{2+} when water molecules are limited in number. It seems that this is the case also for the other hydrated salts such as $CuSO_4 \cdot 5H_2O$ or for deliquescent salts such as $CaCl_2$: the droplets of the saturated solution are formed by absorption of water from the atmosphere.

It is assumed that the model outlined above is general, suggesting that other porous media similar in properties to the porous support matrix of the CA membranes should serve as habit modifiers for whisker growth. Studies using other porous media are in progress. Preliminary results obtained with porous glass are very promising.

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Received 25 February
and accepted 20 March 1985